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Synthetic strategies to nanostructured photocatalysts for CO₂ reduction to solar fuels and chemicals

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Artificial photosynthesis represents one of the great scientific challenges of the 21st century, offering the possibility of clean energy through water photolysis and renewable chemicals through CO₂ utilisation as a sustainable feedstock. Catalysis will undoubtedly play a key role in delivering technologies able to meet these goals, mediating solar energy via excited generate charge carriers to selectively activate molecular bonds under ambient conditions. This review describes recent synthetic approaches adopted to engineer nanostructured photocatalytic materials for efficient light harnessing, charge separation and the photoreduction of CO₂ to higher hydrocarbons such as methane, methanol and even olefins.

1. Introduction

The use of sunlight to split water as a source of electrons that can be stored in chemical bonds for the production of primary energy carriers and molecular building blocks underpins the natural world. Humanity remains highly dependent upon such elegant photosynthetic processes, developed through natural evolutionary selection, for the sustainable growth of biomass, which literally feeds our planet. However, recent technological

breakthroughs offer a glimpse of a mid-term future in which anthropogenic systems will enable artificial photosynthesis with efficiencies surpassing that of plants, to deliver solar fuels and chemicals.^{1,2} Arguments for the development and global deployment of artificial photosynthesis technology to reduce anthropogenic CO₂ emissions from their historic high,^{3,4} increase fuel security,⁵ and support a sustainable global economy and ecosystem have been recently expounded,^{6,7} and new mechanisms for enhancing the policy and governance profile in the context of energy sustainability sought.

Solar fuels include H₂ (from the reduction of H⁺ derived from water photolysis) or carbon-based fuels (derived from the photoreduction of CO₂) such as methane, methanol or CO, and

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associated higher hydrocarbons *via* subsequent well-established industrial thermal chemistry. Artificial photosynthesis may be considered to span the genetic engineering of plant or algal crops to tailor their lignocellulosic or lipid constituents for biofuels production, synthetic biology to combine incorporate cyanobacterial proteins into chloroplasts and hence improve the rate of CO₂ fixation,⁸ and the use of nanotechnology *via* inorganic or molecular systems to produce photo-electro-chemical devices.^{9–12} In contrast to a number of competing renewable energy technologies, such as wind, tidal and photo-voltaics, wherein electricity is the end product, and hence a dependency exists upon concomitant advances in storage and smart grid capabilities, the trapping of solar energy within chemical bonds provides immediate access to (potentially high) energy density carriers for transportation fuels. Water photo-oxidation for H₂ production has been reviewed extensively elsewhere;^{13–15} hence this review focuses on photocatalytic CO₂ reduction.

The potential of CO₂ as a chemical feedstock *via* chemical and biochemical,¹⁶ electrocatalytic^{17,18} and photocatalytic transformations has been widely recognised, with methane¹⁹ and methanol^{20–23} obvious targets to replace fossil fuels in stationary power generation and transportation. Another key area in which CO₂ sequestration may have a profound impact is as a carbon source for renewable polymers and plastics and solvent.^{24–26} In the context of polymers, the thermochemical incorporation of CO₂ into polycarbonates/carbamates is well-established; however, its direct photoreduction to light (C₁–C₃) olefins represents a greater challenge. Olefins and their polymers are the single largest chemical commodity in the world, with annual global ethene and propene production capacity in 2012 around 156 and 80 Mt respectively.^{25,27} These olefins are currently obtained from non-renewable fossil fuels:²⁸ commercial ethene and propene manufacture involves steam or catalytic cracking of naphtha, gasoil and condensates to hydrocarbon mixtures followed by distillation. Cracking crude

oil to produce ethene or propene is thermodynamically unfavourable ($\Delta G \approx +100 \text{ kJ mol}^{-1}$), requiring high temperatures (>600 °C) to overcome the huge activation barriers to C–C cleavage (280 kJ mol^{−1} for kerosene conversion²⁹). Hence steam cracking is the most energy-consuming process in chemistry, accounting for 8% of the sector's primary energy use and annual CO₂ emissions of 180–200 Mt.²⁸

1.1. Brief history and fundamental principles of photocatalytic materials for CO₂ reduction

Renewable solar energy, harnessed *via* innovative catalysts and reactors, has the potential to photoreduce linear CO₂ molecules by breaking the C=O bonds to form C–H bonds and then to yield products, such as methane, methanol or light olefins (*e.g.* CO₂ + 2H₂O ↔ CH₃OH + 3/2O₂; CO₂ + 2H₂O ↔ CH₄ + 2O₂; and 2CO₂ + 2H₂O ↔ C₂H₄ + 3O₂), thereby creating new chemical supply chains free of current dependencies on oil, coal and natural gas and offering an economical and potentially environmentally-benign CO₂ utilisation process (Fig. 1).³⁰

Great challenges lie in the robust chemical state of carbon atoms in CO₂, which requires not only the participation of incident protons but also effective excited electrons, and thus additional reductive agents can offer better opportunities to facilitate the activation of CO₂. In this regard, H₂O is preferred as a reducing agent because it simultaneously takes advantage of water oxidation and CO₂ fixation compared with other sacrificing reductive agents such as amines, H₂, and S^{2−}. Hence, the harvesting of input energy by means of photocatalytic materials from incident light plays a pivotal role in achieving these processes. The first study on the photocatalytic CO₂ reduction was reported by Halmann in 1978, employing a Hg lamp and single crystal, p-type GaP cathode within an electro-chemical cell through which CO₂ was bubbled to yield formic acid, formaldehyde and methanol.³¹ A year later, Inoue and co-workers reported the photoelectrocatalytic reduction of CO₂ to formic acid, formaldehyde, methanol and methane, over a variety of semiconductors including TiO₂, ZnO, CdS, GaP, SiC, and WO₃.³²

These pioneering studies were followed by the development of visible-light driven photocatalysts and production of more



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addresses the rational design of nanoengineered materials for clean catalytic technologies, notably sustainable chemical synthesis and energy production, and the development of *in situ* methods providing molecular insight into surface reactions, for which he was awarded the 2012 Beilby Medal and Prize by the Royal Society of Chemistry.

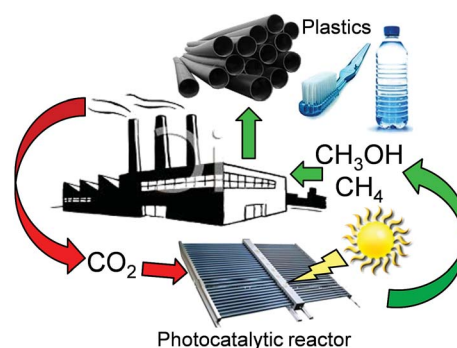


Fig. 1 Schematic of a carbon zero route to solar fuels and renewable olefins through the photocatalytic reduction of CO₂.



functionalised organic moieties, *e.g.* CO₂ photoreduction *via* colloidal CdS aqueous solutions to glyoxylic and acetic acids.³³

Moreover, large-scale photocatalytic CO₂ reduction to solar fuels or chemicals requires intensified processing and carefully engineered robust (and hence likely heterogeneous) catalysts with high accessibility, able to activate small molecules at ambient conditions.³⁴ This challenge can only be met through novel nanotechnologies, which permit the construction of tailored materials whose structure (and function) can be precisely tuned.^{35–37} A practical photocatalytic chemical reactor requires appropriately selected coupled redox reactions, and the ability to efficiently harness light capable of driving the requisite electron-transfer chemistry.³⁸ The former favours water as a green chemical reductant (mimicking natural photosynthesis), while the latter requires active catalysts either able to absorb solar energy directly or coupled to sensitisers which help gather and focus energy onto the active sites.

The optical properties of potential solid photocatalysts are dictated by the rate-limiting oxidation and reduction steps that must occur at the surface of their nanostructures:³⁹ 2H₂O → O₂ + 4H⁺ + 4e[−]; CO₂ + e[−] → CO₂^{•−} (*E*_{redox}^o = +1.64 V and −1.90 V, respectively, on the basis of NHE (normal hydrogen electrode) at pH = 7). Such values impose a minimum for the photoexcitation energy of electrons needed to reduce CO₂, whereas few pure materials are photoresponsive to these wavelengths and catalytically active towards CO₂ and water conversion, even though visible light can create sufficiently excited electrons. These insurmountable limitations necessitate the development of new photocatalytic materials particularly with specially-nanostructured antennas to harvest both UV and visible light efficiently and to initiate the chemical reactions effectively.

1.2. Strengths and challenges of nanostructured photocatalysts

Nanoscale materials often exhibit unique physicochemical which diverge widely from their bulk counterparts. Such nanomaterials, commonly synthesised in the form of nanoparticles (NPs), nanofibres (NFs) and nanotubes (NTs), in addition to more exotic topologies such as nanobelts and nanoflowers, afford high surface areas, tunable architectures and distinct electronic surface states. In particular, photocatalytic nanostructures can offer high densities of photoactive surface sites and thin-walled structures/ultrathin films able to facilitate rapid interfacial charge carrier transport to adsorbates.^{35,40} For many years, CO₂ reduction has centred around titania-based photocatalysts, which are only able to utilise a fraction of the solar spectrum (~2%, mainly as UVA),^{41–45} and require exploitation of quantum effects or doping to reduce their intrinsic band gaps,⁴⁶ sometimes in combination with inorganic or organic supramolecular (biomimetic) sensitisers.⁴⁷ Significant advances in artificial photosynthesis have been achieved through such photocatalytic nanoarchitectures,^{37,48} *e.g.* the discovery of 'self-repairing' Co_xPO₄ catalysts producing O₂ akin to the natural Mn catalyst in photosystem II,⁴⁹ corrosion resistant TiO₂ nanocomposites able to split water⁵⁰ or reduce CO₂ with H₂O to yield CH₄ and olefins,^{40,51} and the use of metal

oxynitrides⁵² and polymeric nitrides⁵³ for efficient water splitting under visible light. Solar CH₄ production from CO₂ has seen dramatic improvements in recent years, with TiO₂ NTs delivering 17.5 nanomoles h^{−1} cm^{−2} mW^{−1} of hydrocarbons from 1 bar CO₂ under sunlight, with a quantum efficiency of 0.74%,⁴⁰ defined throughout this review as:

$$\eta = \frac{\sum_i M_i n_i}{P_m}$$

where *M_i* is the mols of product *i*, *n_i* is the number of electrons attending the production of product *i*, and *P_m* is mols of incident photons.^{54,55} Cu-doped titania coatings deposited on a monolithic substrate have even been reported able to deliver 117 nanomoles h^{−1} cm^{−2} mW^{−1} of methane.⁵⁶ In addition to maximising the quantum efficiency, productivity and selectivity towards hydrocarbons, the stability of semiconductor photocatalysts under reaction conditions (notably resistance to photocorrosion^{57,58}) and routes to their incorporation into reactor designs which facilitate efficient light absorption and mass transport,^{59–61} are also key considerations.

Significant developments in molecular nanocatalysts for photochemical CO₂ reduction have been achieved and reviewed;^{38,62,63} nevertheless, improvements in the mechanical strength, physicochemical stability and photocatalytic efficiency of such materials remain necessary to meet the engineering requirements for large-scale applications. Molecular band structures control incident light absorption, electron-hole pair generation and charge carrier migration. Similarly, energy band engineering of semiconductor photocatalysts to impede the recombination of photo-excited electron-hole pairs and enhance light absorption is of paramount importance.^{64–66} A further challenge is the optimisation of CO₂ and H₂O adsorption over photocatalyst surfaces, which is poorly understood to date,^{67,68} and requires a thorough knowledge of the atomic structure of the photocatalyst interface. Advanced inorganic synthetic methods afford precise manipulation of exposed crystal facets, morphologies, structural periodicity, and hierarchical pore networks,^{69–71} in addition to the co-assembly of sensitisers or co-catalysts and promoters. Meeting these challenges will also necessitate continued advances in our fundamental understanding of photocatalytic reaction and deactivation mechanisms. This review discusses progress in the design of nanostructured solid materials CO₂ to solar fuels and chemicals, with a particular focus on new synthetic routes to inorganic photocatalysts possessing well-defined physicochemical properties and the elucidation of associated structure-function relations. Materials chemistry approaches to porous and layered semiconductor architectures, and hybrid photoactive nanomaterials (*e.g.* plasmonic nanostructures) are also highlighted, and the most active and selective systems benchmarked.

1.3. Mechanistic complications in CO₂ photoreduction

Before considering the vast array of nanomaterials employed in for CO₂ photoreduction, we consider briefly some of the particular analytical challenges in evaluating photoactivity and



product formation. Carbon-containing precursors and/or solvents are employed in the synthesis of most heterogeneous photocatalysts, and few studies quantify the carbon content of the resulting as-prepared materials. Such carbonaceous residues can either decompose directly upon subsequent irradiation,⁶⁸ or react with photoexcited molecular species generated from CO₂ or water,⁷² to liberate carbon-containing liquid/gas phase products. Discriminating whether such products originate *solely* from desired CO₂ conversion and/or carbon residues is not possible by conventional chromatographic methods, and rarely accorded the attention deserved.

Yui and co-workers reported that organic adsorbates such as acetic acid present over commercial, untreated P25 TiO₂ were responsible for CH₄ evolution as a major product during CO₂ photoreduction.⁶⁸ A photo-Kolbe decarboxylation mechanism was proposed that accounted for the observed methane solely in terms of acetic acid reduction: $\text{CH}_3\text{COOH} + \text{H}^+ \rightarrow \text{CH}_3^\cdot + \text{CO}_2 + \text{H}^+$; $\text{CH}_3^\cdot + \text{CH}_3\text{COOH} \rightarrow \text{CH}_2\text{COOH}^\cdot + \text{CH}_4$. Pre-calcination and washing of the TiO₂ suppressed methane production, with CO the dominant products; convincing evidence for the Kolbe mechanism hypothesised. Isotopic-labelling using ¹³CO₂ over an organic-free 2 wt% Pd/TiO₂ catalyst revealed the co-production of ¹³CH₄ (unequivocally through direct photoreduction) and some ¹²CH₄ likely originating from the CO₃²⁻ species on the parent titania. In a complementary investigation, Yang *et al.* explored the mechanism of ¹³CO₂ photoreduction in H₂O over Cu(I)/TiO₂ by means of *in situ* DRIFT spectroscopy.⁷² ¹²CO was identified from its 2115 cm⁻¹ Cu(I)-CO signature as the primary product of reaction between photocatalytically activated adsorbed water and carbonaceous residues on the as-prepared photocatalyst surface. The residual surface carbon reflects the use of a titanium(IV) butoxide precursor and polyethylene glycol structure-directing agent, with (an unquantified amount of) carbon persisting even after the resulting sol-gel was calcined at 500 °C for 5 h. Prolonged UV irradiation of the fresh catalyst under moist air to remove carbon contaminants significantly lowered the yield of reactively-formed CO, although some ¹³CO was observed, evidencing true CO₂ photoreduction. These studies highlight the importance of eliminating organic (and carbonate) surface residues from photocatalysts prior to CO₂ photoreduction tests, *via e.g.* high temperature calcination, solvent washing and/or pre-exposure to UV light in the absence of CO₂. Yang and co-workers also recommended that an additional control experiment be undertaken to ensure no carbon-containing products are formed in the absence of CO₂ but presence of H₂O. To date very few studies have acted upon this sound recommendation.

The overwhelming majority of CO₂ photoreduction employs water as the electron (net hydrogen) source, and should therefore be accompanied by oxygen co-generation. Selective reduction to CO should proceed according to: $\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 + 2\text{O}_2$ (combining $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$ and $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 + \text{O}_2$), for which the molar ratio of (H₂ + CO) : O₂ should be 2 : 1. However, very few studies report such oxygen evolution, let alone endeavour to quantify it and thereby demonstrate that water is the sole electron donor. In the case of ZrO₂ in aqueous NaHCO₃,⁷³ KTaO₃ (ref. 74) and Ag doped ALa₄Ti₄O₁₅ (A = Ca, Sr,

and Ba) perovskites,⁷⁵ the co-evolution of CO, H₂ and O₂ is reported with the predicted 2 : 1 stoichiometry; albeit isotopic labelling experiments with ¹³CO₂ also revealed the formation of trace ¹²CO over for KTaO₃ due to either ¹²CO₂ from reactor purging or organic residues within the photoreactor. Isotope labelling, a full complement of control experiments, and careful analysis of evolved oxygen are thus critical to accurately quantify CO₂ photoreduction and understand underlying reaction pathways.

2. Developments in nanostructured materials

2.1. Crystallinity and the role of engineered surface defects

The catalytic behaviour of photocatalysts is intrinsically linked to their surface electronic/optical properties and adsorption behaviour, all of which can (in principle) be systematically tuned through crystal structure engineering; the nature, dimensions, uniformity and termination of crystalline phases strongly influence their resultant photocatalytic efficiency.⁷⁶ For instance, monoclinic sheet-like BiVO₄ significantly outperformed tetragonal rod-like BiVO₄ counterparts in the rate of CO₂ photoreduction to C₂H₅OH (accompanied by O₂ evolution), under both UV and visible light illumination in the presence of water.⁷⁷ These monoclinic and tetragonal phases were obtained by introducing CTAB (cetyltrimethyl ammonium bromide) or PEG (polyethylene glycol), respectively, during BiVO₄ synthesis. The superior photoactivity of the monoclinic BiVO₄ was attributed to the more asymmetric local environment of the Bi³⁺ ions relative to those within the tetragonal phase. Accordingly, the Bi³⁺ ions exhibit stronger lone pair character in the monoclinic phase and are hence drive to form Bi-O bonds with CO₂ bound as the carbonate, and consequential transfer of photogenerated electrons from the V 3d bands into the chemisorbed CO₃²⁻. It is worth noting that these two phases exhibited different UV-Vis absorbances, with the band gaps of monoclinic and tetragonal BiVO₄ around 2.24 eV and 2.56 eV respectively. More recently, Li *et al.* demonstrated that cubic NaNbO₃ was more effective than orthorhombic NaNbO₃ for CO₂ photoreduction.⁷⁸ The cubic NaNbO₃ (c-NaNbO₃), which is normally only stable at *T* > 813 K, was successfully prepared through a furfural alcohol derived polymerisation-oxidation (FAPO) method in the presence of P123 as a surfactant stabiliser. The more common orthorhombic NaNbO₃ (o-NaNbO₃) phase was prepared through a polymerised complex (PC) method. While c-NaNbO₃ comprised predominantly cuboid morphologies, a mixture of irregular and cuboid particles was obtained for o-NaNbO₃. Both crystal phases exhibited a comparable crystallite size (c-NaNbO₃ = 18.5 nm *versus* o-NaNbO₃ = 23.1 nm) and surface area (c-NaNbO₃ = 28.6 m² g⁻¹ *versus* o-NaNbO₃ = 26.4 m² g⁻¹), however, the band gap of c-NaNbO₃ (3.29 eV) was smaller than that of o-NaNbO₃ (3.45 eV). Under UV irradiation (300 W Xe arc lamp) in the presence of a Pt co-catalyst and water vapour, c-NaNbO₃ generated almost double the amount of CH₄ (0.486 μmol h⁻¹) than that obtained from o-NaNbO₃ (0.245 μmol h⁻¹) in a gaseous, closed circulation system pressurised with 80 kPa CO₂. Density functional



theory (DFT) calculations ascribed this variation in photocatalytic performance to differences in conduction band (CB) energies, reflecting different octahedral ligand fields. Accordingly, electron excitation and transfer was more efficient over the high symmetry *c*-NaNbO₃ phase than *o*-NaNbO₃. In addition to CO (0.082 $\mu\text{mol h}^{-1}$) and H₂ (0.71 $\mu\text{mol h}^{-1}$), trace amounts of C₂H₄, C₂H₆ and C₃H₈ were detected during CO₂ photocatalysis over the *c*-NaNbO₃.

Numerous preparative routes have been developed to nano-materials with controllable crystal facets such as pH regulation of the synthetic media, or post-synthesis treatments. Truong *et al.* selectively prepared anatase (pH 2, only 3% rutile), rutile (pH 6, only 6% of anatase) and a bi-crystalline anatase(73%)-brookite(27%) composite at pH 10.⁷⁹ Under UV (500 W Xe lamp) or visible light irradiation (NaNO₂ solution as a UV cut-off filter), and in the presence of a NaHCO₃ solution, these materials were able to photoreduce CO₂ to CH₃OH, whereby the photoactivity followed the order anatase-brookite composite > rutile > anatase > commercial P25. Liu *et al.* also successfully prepared three different nanostructures of TiO₂ polymorphs including anatase (TiA) NPs, rutile (TiR) nanoellipses and brookite (TiB) nanorods for CO₂ photoreduction,⁸⁰ by subjecting the as-synthesised titania to heat treatment under a He environment at 220 °C for 1.5 h to induce surface defects, such as oxygen vacancies (V_O) and Ti³⁺ ions on these TiO₂ polymorphs. Illumination by a 150 W solar simulator in the presence of CO₂/water vapour revealed the untreated TiO₂ polymorphs as active for CO₂ photoreduction to CO and a small amount of CH₄ under continuous-flow (2.0 mL min⁻¹). Product yields decreased in the order TiA > TiB > TiR. As depicted in Fig. 2, He-treated materials TiA(He) and TiB(He) significantly outperformed their untreated counterparts, with TiB(He) exhibiting the highest photoactivity, followed by TiA(He); such annealing treatments had less impact upon the photoactivity of TiR wherein the activation barrier to surface oxygen vacancy creation was presumably higher.

In situ DRIFTS and DRUVS suggested that the relative V_O : Ti³⁺ concentration in TiA(He) was comparable to that of TiB(He), while the surface defect concentration on TiR(He) was negligible. The higher photoactivity of TiB(He) and TiA(He) was thus attributed to surface defects, with the energy of vacancy formation for TiB (He) of 5.52 eV lower than that for anatase (5.58 eV) and rutile (5.82 eV). CO₂ photoreduction over titania is clearly a strong function of the crystal structure and surface defect density; the latter postulated the active catalytic sites.

An increasing volume of research has established the influence of crystal facets upon photocatalysis; physical and chemical properties of single crystals are highly sensitive to crystallographic termination.^{76,81} Calculations have established that the average surface energies of low-index anatase facets decrease in the order 0.90 J m⁻² (001) > 0.53 J m⁻² (100) > 0.44 J m⁻² for (101).^{82,83} The highest energy (001) surface is expected to be the most reactive, and indeed experimental studies confirm that dissociative molecular adsorption of water and methanol occur readily on the (001) surface.^{84,85} Consequently, efforts to control the morphology of TiO₂ have focused on the synthesis of nanostructures preferentially exposing (001) facets or coexposing (001) and (101) facets⁸⁶ to enhance water splitting and dye

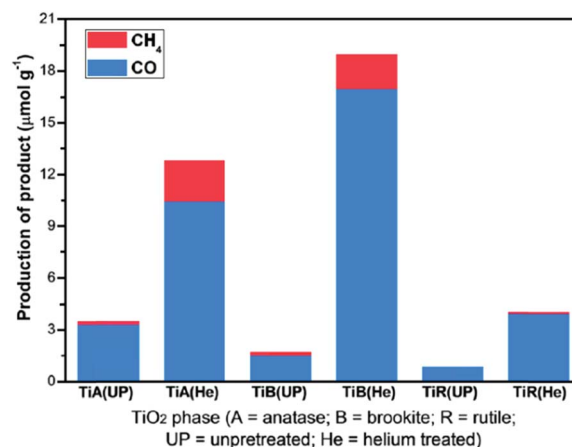


Fig. 2 CH₄ and CO productivity from untreated and He-treated TiO₂ polymorphs during 6 h illumination under 150 W solar simulator in the presence of CO₂/H₂O vapour, in a continuous-flow mode photo-reactor operating at a flow rate of 2 mL min⁻¹. Reprinted with permission from ref. 80. Copyright 2012 American Chemical Society.

degradation.^{87–90} However, other studies suggest that photoreduction and photooxidation activities follow the order (001) < (101) < (010),⁹¹ with the superior performance of the (010) facet attributed to a synergy between the surface atomic structure (dictating adsorption/reactivity) and electronic band structure (dictating the CB potential).

TiO₂ nanorods preferentially exposing (010) facets were therefore screened in CO₂ photoreduction.⁹¹ Such nanorods were synthesised by hydrothermal treatment of a H_{0.68}Ti_{1.83}O₃ precursor in the presence of Cs₂CO₃ as a pH mediator, and subsequent promotion by 1 wt% Pt. The resulting Pt-doped TiO₂ nanorods outperformed P25 in CO₂ photoreduction by water vapour to CH₄ under 300 W Xe lamp UV irradiation in a Teflon-lined steel chamber under 0.06 MPa CO₂. Enhanced activity was attributed to the unique properties of (010) facets which promote CO₂ adsorption,⁹² specifically their more negative conduction band potential. The same group prepared hollow anatase TiO₂ single crystals and mesocrystals, wherein both nanostructures were dominated by (101) facets.⁹³ These materials were successfully synthesised by hydrothermal treatment of a Ti(SO₄)₂, Na₃PO₄ and HF solution. Fig. 3A–D shows the resulting 400 nm diameter octahedral single crystals obtained using 500 mM HF; lowering the HF concentration to 400 mM yielded hollow crystals with less prominent octahedral shapes of ~160 nm (Fig. 3B and E). Fig. 3H reveals that these hollow crystals were single crystalline and principally (101) oriented, with a small proportion of higher-index (103) facets. Even lower HF concentrations favoured sphere-like hollow cages 150 nm diameter (Fig. 3C and F), each formed from ~35 nm octahedral crystals, which spontaneously self-organised during crystal growth to adopt a common crystallographic orientation, resulting in ‘single crystal-like’ mesocrystals with well-defined selected area electron diffraction (SAED) patterns. Under UV irradiation (300 W Xe lamp) and in the presence of a RuO₂ co-catalyst and water vapour, the hollow single crystal and mesocrystal materials titanias outperformed a non-porous



single crystal by a factor of 4–5 times in photoreducing CO_2 to CH_4 , attributed to their (i) higher surface areas ($35 \text{ m}^2 \text{ g}^{-1}$ and $42 \text{ m}^2 \text{ g}^{-1}$ respectively) relative to the solid crystal ($17 \text{ m}^2 \text{ g}^{-1}$) and (ii) shorter diffusion length of charge carriers and concomitant suppressed bulk recombination. Fig. 3J illustrates the different electronic band structures of the single crystal, hollow single crystal and hollow mesocrystal titanias, and more negative CB potential of the hollow mesocrystal.

Adsorbate-induced restructuring of highly reactive facets remains an intrinsic problem due to their high surface energies. In this regard, reagents such as HF and isopropanol have been employed as structure-directing agents to favour exposure of (001) facets over single-crystal anatase nanosheets.⁶⁰ Use of such capping agents is itself problematic since they must be removed by thermochemical treatment prior to photocatalytic application (*e.g.* solvent extraction or calcination) which in turn may induce surface restructuring/phase changes. Fabrication of stable and uniform nanostructures terminating in specific atomic rearrangements requires continued development.

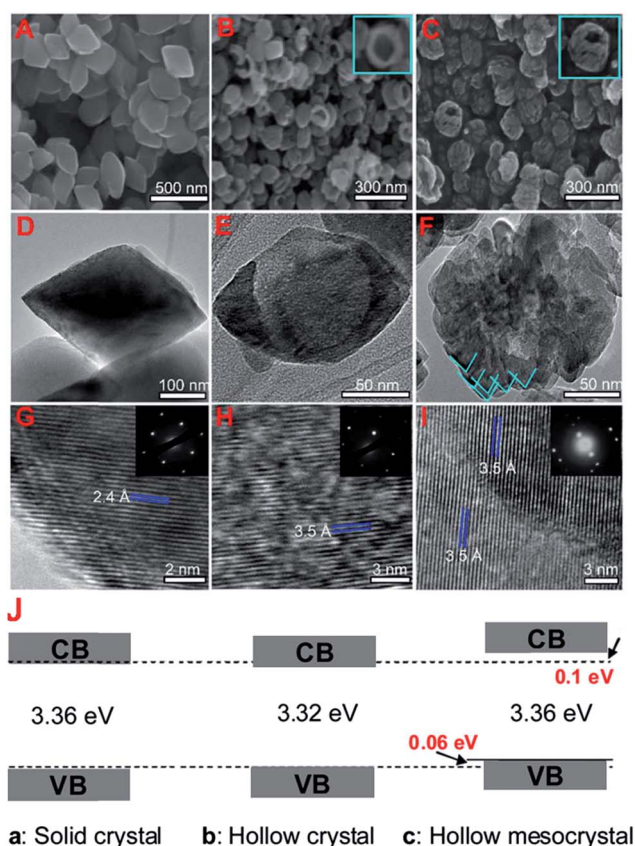


Fig. 3 SEM images (A)–(C), TEM images (D)–(F), HRTEM images (G)–(I) and (J) electronic band structures based on UV-Vis and valence band XPS spectra of single crystal solid anatase TiO_2 , single crystal hollow anatase TiO_2 , and hollow anatase TiO_2 mesocrystals. Insets in (B) and (C) highlight hollow cores in the single and mesocrystal particles, insets in (G)–(I) show SAED patterns for the solid single crystal, hollow single crystal and mesocrystal anatase TiO_2 . Reprinted with permission from ref. 93. Copyright 2012 American Chemical Society.

2.2. Nanostructured photocatalysts

2.2.1. Low dimension nanomaterials. One-dimensional nanomaterials are generally more attractive than their bulk and nanoparticle counterparts in photocatalysis, because they facilitate more efficient electron transport and exhibit higher surface area to bulk volume ratios.⁶⁵ Recent work has shown that Zn_2GeO_4 nanoribbons and nanorods photoreduce CO_2 more efficiently than Zn_2GeO_4 prepared through conventional reaction.^{96,97} As depicted in Fig. 4a, single crystalline Zn_2GeO_4 nanoribbons of around 7 nm in thickness, 20–50 nm width and hundreds of microns long, were successfully prepared by Liu *et al.* via a binary ethylenediamine/water solvent system during solvothermal treatment at 180°C .⁹⁴ The solvent system was proposed to regulate the velocity and direction of crystal growth through a solvent-coordination molecular-template mechanism. Nanoribbons were obtained due to preferential crystal growth along the [001] direction. Catalytic screening highlighted the improved photoactivity of the resulting nanoribbons over Zn_2GeO_4 produced *via* solid state reaction (SSR) in producing CH_4 under UV illumination (300 W Xe arc lamp) in a $\text{CO}_2/\text{H}_2\text{O}$ saturated glass reactor system. The better photocatalytic performance was attributed to (i) the higher surface area of the nanoribbons ($28 \text{ m}^2 \text{ g}^{-1}$ *versus* $1 \text{ m}^2 \text{ g}^{-1}$ for the SSR material) (ii) the high quality single crystalline nature of the nanoribbons, which reduced electron–hole pair recombination, and (iii) the improved electron transport properties of the nanoribbons owing to their ultra-longitudinal dimension, and (iv) the geometry of the nanoribbons that permits rapid charge carrier diffusion to the oxide surface for CO_2 reduction. Photoactivity of these Zn_2GeO_4 nanoribbons could be further promoted by co-catalysts such as Pt, RuO_2 or a combination thereof, and even coupling to metal–organic frameworks such as ZIF-8 to enhance their CO_2 adsorption capacity.⁹⁵

A similar synthesis was employed to prepare highly crystalline $\text{In}_2\text{Ge}_2\text{O}_7(\text{En})$ hybrid sub-nanowires, as shown in Fig. 4b, with diameters around 2–3 nm.⁹⁶ Although the nanowires outperformed a SSR prepared sample in CO_2 photoreduction by water vapour under UV illumination (300 W Xe arc lamp) within a gas-tight Pyrex glass reactor, CO was the only photoreduction product. A low temperature solution phase route, which does not require any surfactant, was reported for the preparation of single crystalline, hexagonal Zn_2GeO_4 nanorods for CO_2 photoreduction.⁹⁷ A mixed solution of Na_2GeO_3 and $\text{Zn}(\text{CH}_3\text{COO})_2$ was heated at 40 – 100°C to yield Zn_2GeO_4 nanorods with a regular, hexagonal prism geometry. As shown in Fig. 4c and d, nanorod dimensions were strongly dependent on synthesis temperature: nanorods around 400 nm long and 50 nm wide were obtained at 40°C , while nanorods 250 nm long and 150 nm wide formed at 100°C . Surprisingly, the prepared nanorods contained some blind holes due to the different crystal growth rate along the *c*-axis, as well as nanosteps in the surface of nanorods prepared at 100°C . The absorption band edge of nanorods was blue-shifted (4.68 eV and 4.65 eV for 40°C and 100°C syntheses respectively) relative to that of SSR-prepared material (4.5 eV) due to quantum size effects, restricting their use to hard UV applications. Under illumination, Zn_2GeO_4

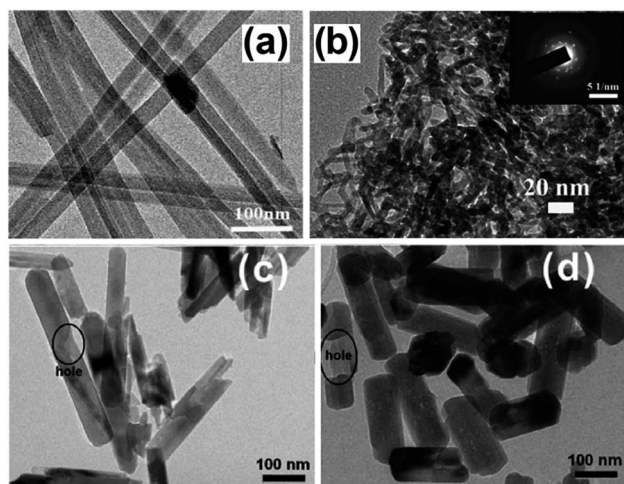


Fig. 4 TEM images of (a) Zn_2GeO_4 nanoribbons⁹⁴ and (b) $\text{In}_2\text{Ge}_2\text{O}_7$ sub-nanowires (inset: corresponding SAED pattern)⁹⁶ prepared by solvothermal treatment using a binary ethylenediamine/water solvent system, and Zn_2GeO_4 sub-nanowires prepared through solution phase route (c) at 40 °C and (d) 100 °C. Reproduced from ref. 97 with permission from The Royal Society of Chemistry.

nanorods outperformed those prepared by SSR towards photocatalytic H_2 generation and CO_2 reduction, with nanorods grown at 100 °C proving the most active for H_2 evolution owing to their greater crystallinity and the presence of surface nano-steps promoting charge separation. Conversely, the 40 °C synthesised nanorods exhibited better CO_2 photoreduction activity than their higher temperature analogues due to their higher surface area and CO_2 adsorption capacity.

Highly ordered one-dimensional TiO_2 NTs arrays have also been developed for photocatalytic applications.^{98–101} These nanotube arrays have increasingly gained popularity as they: (i) exhibit a relatively high interfacial surface area (because of their internal and external surfaces); (ii) promote efficient transport of electrons owing to the thin walls of NTs; (iii) efficiently retard electron-hole recombination (which can occur up to ten times slower than equivalent nanoparticle films); and (iv) demonstrate improved photon absorption efficiency attributed to strong light scattering within the nanotube arrays.^{98–103} The development of TiO_2 NTs arrays, including their synthesis and application, has been thoroughly reviewed by Rani *et al.*¹⁰³ spanning first generation (0.5 μm in length) to current 4th generation ($\sim 1000 \mu\text{m}$) technologies. Electrochemical anodisation is the preferred method for nanotube arrays synthesis since it enables the nanotube dimensions to be precisely tuned through varying synthetic parameters such as electrolyte composition and anodising time. Varghese *et al.* prepared N-doped TiO_2 NTs arrays with pore size and wall thickness of $95 \pm 13 \text{ nm}$ and $20 \pm 5 \text{ nm}$, respectively by anodising Ti foil in an NH_4F /water/ethylene glycol electrolyte at 55 V.⁴⁰ The resulting TiO_2 NTs arrays were then calcined and sputter coated with large, irregular patches of Pt, Cu or both metals, as co-catalysts, albeit little information was provided on the morphology and dispersion of these promoters, with the final material

containing between 0.4–0.75 at% N. Irradiation under natural sunlight and water vapour within a batch reactor, afforded CO_2 photoreduction to mainly H_2 , CH_4 and other alkanes (*i.e.* C_2H_6 , C_3H_8 , C_4H_{10} , C_5H_{12} and C_6H_{14}), with olefins and branched paraffins also formed as minor products. Higher NTs calcination temperatures improved the photocatalytic activity, attributed to their higher crystallinity. Platinum promoted arrays generated more H_2 (almost $200 \text{ ppm cm}^{-2} \text{ h}^{-1}$) than hydrocarbons, giving a total productivity of $273 \text{ ppm cm}^{-2} \text{ h}^{-1}$, whereas the copper promoted array exhibited superior hydrocarbon production ($\sim 104 \text{ ppm cm}^{-2} \text{ h}^{-1}$). Furthermore, the Cu- TiO_2 NTs arrays evolved five times more CO than Pt- TiO_2 arrays. Doubly promoted NTs arrays (Fig. 5) afforded a total hydrocarbon productivity of $111 \text{ ppm cm}^{-2} \text{ h}^{-1}$ without any detectable CO. It was concluded that Pt was more active for water reduction, while Cu was more efficient at reducing CO_2 , their combination resulting in a strong synergy and maximal CO_2 conversion to hydrocarbons, with one of the highest visible light quantum efficiencies of 0.74%.

The synthesis of two-dimensional WO_3 nanosheets using a solid-liquid, phase arc discharge method for CO_2 photoreduction was recently reported by Chen *et al.*¹⁰⁴ Crystal growth was proposed to occur *via* the formation of a large number of 4–5 nm WO_3 seeds. These nanocrystals fused together into two-dimensional nanosheets during aging, while maintained a thickness $< 5 \text{ nm}$, with preferential growth in the [100] and [010] directions. The resulting band gap of these nanosheets (2.79 eV) was larger than that of commercial WO_3 powder (2.63 eV) due to quantum size effects, with their CB potential estimated to be more negative than the reduction potential for CO_2/CH_4 conversion. Conversely, the CB position of commercial WO_3 appeared more positive than the CO_2/CH_4 redox potential, which should hence disfavour CO_2 reduction. Indeed, visible light illumination (300 W Xe arc lamp equipped with a 420 nm cut-off filter) of the as-prepared nanosheets showed that they outperformed the commercial WO_3 powder in photoreducing

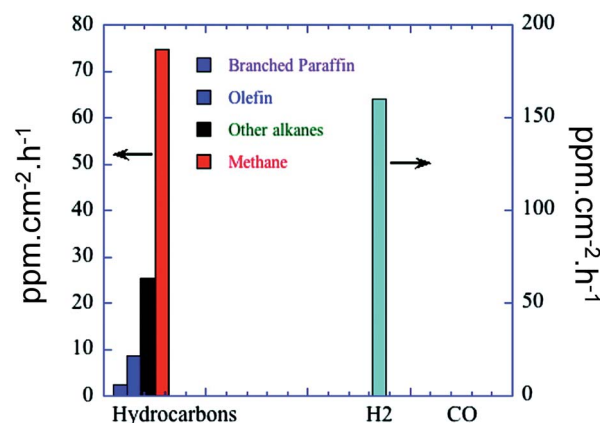


Fig. 5 Product formation of N-doped TiO_2 NTs arrays, calcined and sputtered coated with Pt and Cu. CO_2 photoreduction was conducted in a batch reactor under natural sunlight illumination in the presence of water vapour at 44 °C. Reprinted with permission from ref. 40. Copyright 2009 American Chemical Society.



CO₂ to CH₄ in a gas-tight system. Superior nanosheet photoactivity was therefore attributed to both their ultrathin geometry, expected to promote efficient charge carrier diffusion, and their more negative conduction potential. CO₂ adsorption can be enhanced through the use of alkali or alkaline earth basic oxides. Strontium promoted niobates prepared by conventional SSR have shown promise in CO₂ photoreduction by water vapour, but possess extremely low surface areas and are hence unsuitable for achieving high photoactivity. An alternative hydrothermal approach affords two-dimensional SrNb₂O₆ nanoplates around 12 nm thick and 5–300 nm across,¹⁰⁵ conferring a 20-fold increase in CO₂ adsorption capacity and quantum efficiency of 0.065% over 10 h, an order of magnitude higher than P25. In contrast to many studies, high selectivity to CO₂ reduction to CO and CH₄ *versus* competing H₂O reduction to H₂ was observed, alongside significant oxygen evolution. Transient photocurrent response measurements suggest that separation of photogenerated electron–hole pairs was rate-determining, with the nanoplate morphology facilitating charge-carrier diffusion to the surface and subsequent reaction with adsorbed CO₂ and water.

2.2.2. Porous structured photocatalysts. Mesoporous and hierarchical heterogeneous catalysts have proved superior to their non-porous analogues in a number of important chemical transformations, including catalytic cracking, selective oxidation, biomass valorisation and pollution abatement systems. Hence, it may be anticipated that porous semiconductor photocatalysts will likewise outperform their bulk counterparts. Such enhanced reactivity may reflect a combination of factors including the generally higher surface area of porous nanostructures, which in turn increases the number of active sites and thus photoconversion efficiency,^{79,106–109} and high aspect ratios which assists rapid transport of photoexcited carriers to the catalyst surface, thereby suppressing competing bulk recombination processes.^{107,109–111} Macropore incorporation into mesoporous architectures can confer additional benefits *via* increased light scattering and faster in-pore mass transport of sterically hindered reagents, finding particular application in the photodegradation of organic dyes.

Crystalline, porous structured Ga₂O₃ has been successfully synthesised by Park *et al.* employing a tetradecyl trimethyl ammonium bromide template.¹⁰⁷ Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) images (Fig. 6), revealed the co-existence of macropores and mesopores throughout the resulting mono-dispersed material. Subsequent photocatalytic screening showed that CO₂ conversion over this hierarchically porous Ga₂O₃ was much higher than that of reference Ga₂O₃ nanoparticles. Further investigations into CO₂ adsorption established that the porous Ga₂O₃ possessed a vastly superior CO₂ adsorption capacity, 300% higher than that of the bulk reference, accounting for its improved photoreduction of CO₂ to CH₄. Surfactant templating was also utilised to prepare mesoporous, micrometric ZnO spheres with the Pluronic P123 templating agent through hydrothermal treatment.¹¹² Individual ZnO spheres were composed of stacks of thin ZnO flakes, which created interparticle mesoporous voids. This mesoporous

architecture gave higher CO₂ conversion than the equivalent non-porous ZnO, and following Cu impregnation the mesoporous ZnO favored the selective production of CH₄ and CH₃OH. The utility of porous structures for CO₂ photoreduction to CH₄ has also been reported for titania,⁷⁹ albeit the surface area of the mesoporous TiO₂ decreased significantly upon subsequent nitridation to generate visible light active, N-doped TiO₂.

In recent years, a new synthetic protocol has been developed to create multicomponent, mesoporous photocatalysts for CO₂ reduction. Here an inorganic precursor is used to construct more thermally robust mesostructures.¹¹³ The synthetic route of Yan *et al.* to prepare mesoporous ZnGa₂O₄ is illustrated in Fig. 7A. A powdered NaGaO₂ starting material was synthesised through a solid-state route, which formed colloidal particles upon dispersion in water. Weak surface repulsion between the resulting nanoparticles enabled their subsequent flocculation to form a mesoporous framework, followed by Na⁺ and Zn²⁺ ion-exchange to yield a mesoporous ZnGa₂O₄ (visualised in Fig. 7B). The final material remained crystalline after the ion-exchange, obviating the need for hydrothermal treatment or high temperature calcination. The final ZnGa₂O₄ exhibited a mean pore diameter of 3.5 nm and surface area around 110 m² g^{−1}. Catalytic screening demonstrated that the mesoporous ZnGa₂O₄ was superior to ZnGa₂O₄ prepared through solid-state synthesis, with photogenerated CH₄ prevalent when a RuO₂ co-catalyst was employed. In common with many such studies there was no justification for the choice of co-catalyst, nor its mode of operation, which was simply presumed to improve separation of photogenerated electron–hole pairs. This synthetic procedure was further adapted to prepare a ZnAl₂O₄-modified, mesoporous ZnGaNO visible light photocatalyst¹¹¹ from a NaGa_{1−x}Al_xO₂ precursor to form an amorphous mesoporous colloid template by flocculation. Following ion-exchange with Zn²⁺, the resultant Zn(Ga_{1−x}Al_x)₂O₄ was hydrothermally treated to improve its crystallinity prior to nitridation; Al was claimed to enhance the thermal stability of the mesostructure. CO₂ photoreduction was negligible over the parent ZnGaNO (with or without ZnAl₂O₄ modification) without Pt doping to promote electron–hole separation. The superior performance of the ZnAl₂O₄ modified material was attributed to improved mass transport, increased basicity and hence CO₂ chemisorption, and narrowing of the band gap. Micro/mesoporous Zn₂GeO₄ and mesoporous zinc germanium oxynitride synthesised *via* the

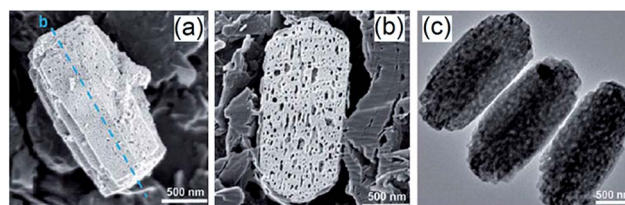


Fig. 6 FE-SEM images of (a) porous Ga₂O₃, (b) vertical cross-section of porous Ga₂O₃ fractured by ion beam and (c) TEM image of the porous Ga₂O₃. Reproduced from ref. 107 with permission from The Royal Society of Chemistry.



same method also evidenced superior CO₂ photoconversion compared to their solid state synthesised counterparts.^{106,114}

Regular mesopore voids can also be created through the self-assembly of nanoparticles wherein the mesopores are formed at the junction between nanoparticles. This approach was successfully employed by Wang *et al.* to prepare sub-micron TiO₂-SiO₂ mesoporous composites.¹⁰⁸ These materials were obtained by atomising TiO₂ and SiO₂ nanocolloidal solutions of 20–45 nm particles into micron-sized droplets at elevated temperature. Solvent evaporation drove colloidal self-assembly to yield the mesoporous TiO₂-SiO₂ composite imaged by FE-SEM image in Fig. 8a. Cu doped variants were also produced by introducing Cu(NO₃)₂ into the colloidal precursor solution. Higher synthesis temperatures promoted TiO₂ nanocrystal segregation at the composite surface (Fig. 8b). The porous SiO₂ matrix ensured that TiO₂ dispersed across the composite surfaces as ~20 nm crystals, rather than larger agglomerates. TiO₂-SiO₂ composites exhibited superior photoactivity to pure TiO₂ for CO₂ photoreduction to CO. Activity increased with processing temperature up to 1000 °C due to an increasing density of TiO₂ nanocrystals decorating the mesoporous framework, with a composite comprising 2 mol% TiO₂ and 0.01 mol% Cu giving the highest rate of CO₂ photoreduction. Mesoporous In(OH)₃ has also been prepared through a template-free hydrothermal treatment¹¹⁰ resulting in the self-assembly of crystalline In(OH)₃ nanocubes. The introduction of mesoporosity enhanced CO₂ photoreduction to CH₄ by 20-fold relative to conventional In(OH)₃ crystallites attributed to the higher surface area and CO₂ adsorption affinity of the mesoporous variant.

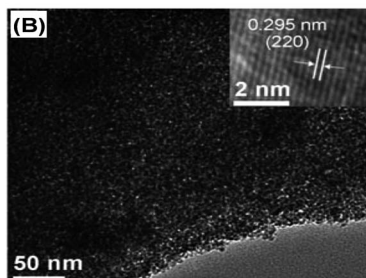
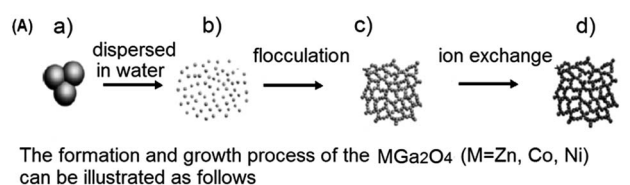


Fig. 7 (A) Schematic diagram showing the synthesis steps of preparing mesoporous ZnGa₂O₄ through mesoporous colloidal template and ion-exchange reaction and (B) TEM image of the resulting mesoporous ZnGa₂O₄ (inset: HR-TEM image of the crystal fringes). Reproduced with permission from ref. 113. Copyright 2010 Wiley.

Graphitic carbon nitride (C₃N₄), a metal-free polymeric semiconductor, has gained increasing popularity in photocatalysis for visible light application.^{113,115–118} Switching the precursor from melamine to melamine chloride followed by rapid heating afforded porous C₃N₄.¹¹⁹ Fig. 9 compares the platelet-like structure of melamine-derived C₃N₄ (g-C₃N₄) with the porous platelets obtained from the melamine chloride analogue, (p-g-C₃N₄) whose surface area was significantly higher (69 m² g^{−1} versus 1.7 m² g^{−1} for g-C₃N₄). Despite these textural differences the non-porous g-C₃N₄ outperformed the porous p-g-C₃N₄ during CO₂ the photoreduction to CO under visible light. This surprising result was attributed to the slightly broadened band gap and poorer crystallinity of p-g-C₃N₄, which may arise from a higher density of defects acting as electron-hole recombination centres. Porous C₃N₄ was also prepared by Mao *et al.* (denoted u-g-C₃N₄) from a urea precursor, which displayed superior CO₂ photoreduction activity relative to melamine-derived C₃N₄ (m-g-C₃N₄).¹²⁰ Akin to the findings of Dong and co-workers, porous u-g-C₃N₄ was less crystalline than the melamine analogue, with an order of magnitude higher surface area and slightly wider band gap. However, in this instance u-g-C₃N₄ exhibited superior photoactivity, presumably due to enhanced reactant adsorption and more efficient charge carrier separation. Under visible light, and in the presence of 1 M NaOH, u-g-C₃N₄ photoreduced CO₂ to a mixture of CH₃OH and C₂H₅OH, while m-g-C₃N₄ favoured C₂H₅OH with only trace methanol. Selective photocatalytic CO₂ reduction is hence achievable through tuning of material crystallinity and microstructure.

Table 1 shows that most mesoporous semiconductors possess modest surface area, however there is scope for enhancing these through their immobilisation onto higher area supports such as mesoporous silicas.^{121,122} Such high area templates, albeit inert, facilitate dispersion of photoactive phases, thereby increasing the surface active site density and hence photoconversion efficiency. Yang *et al.* reported that TiO₂ supported on SBA-15 exhibited superior photoactivity to P25 during CO₂ photoreduction to CH₃OH.¹²² The crystallite size of the dispersed TiO₂ increased with loading but remained smaller than that of commercial P25, however it is unclear how much titania was incorporated with the SBA-15 pore network *versus* external surface, and hence performance may have been sub-optimal. Further studies revealed that higher CH₃OH yields were achievable by Cu doping these TiO₂/SBA-15 catalysts. Li

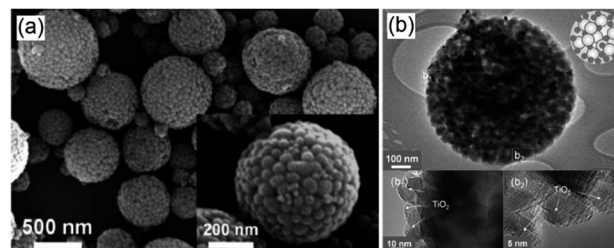


Fig. 8 (a) FE-SEM and (b) TEM and HR-TEM images of mesoporous TiO₂-SiO₂ composites prepared at 800 °C. Reproduced from ref. 108 with permission from The Royal Society of Chemistry.



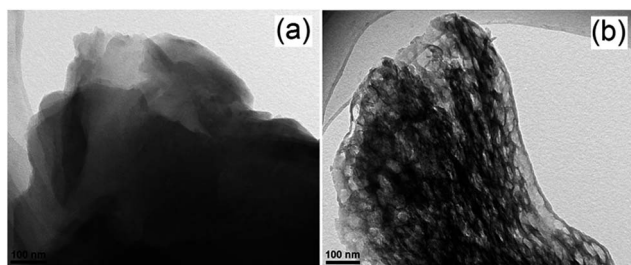


Fig. 9 TEM images of (a) non-porous g-C₃N₄, and (b) porous p-g-C₃N₄. Reproduced from ref. 119 with permission from The Royal Society of Chemistry.

et al. prepared TiO₂/mesoporous silica composites through a one-pot, sol-gel method.¹¹³ The resulting material was more active than pure TiO₂ in photoreducing CO₂ to CO and CH₄, with Cu addition favouring CH₄ production.

2.2.3. Layered structured photocatalysts. Improvements in charge carrier separation and charge transfer for various photocatalytic applications have been sought for many years through the development of layered semiconductors, such as lamellar titanates and niobates.^{124–127} Li *et al.* recently synthesised such layered materials for CO₂ photoreduction through the hydrothermal processing of KNb₃O₈ and HNb₃O₈.¹²⁸ In a typical synthesis, Nb₂O₅ powder in KOH solution was hydrothermally treated in the presence of a P123 Pluronic surfactant and the resulting precipitate was calcined to yield KNb₃O₈. Solid niobic acid, HNb₃O₈, was obtained through subsequent proton exchange of the KNb₃O₈ in nitric acid (KNb₃O₈ is isostructural with HNb₃O₈). As shown in Fig. 10a, HNb₃O₈ comprised two-dimensional Nb₃O₈[−] anion layers, constructed from edge-sharing NbO₆ octahedral units, with protons located in the interlayer spacing. Nanobelts of around 50 nm thickness were obtained during hydrothermal processing of KNb₃O₈, in contrast to the irregular micron size particles usually obtained from conventional SSR. Surface areas of the hydrothermal KNb₃O₈ and HNb₃O₈ materials of 29 m² g^{−1} and 39 m² g^{−1} respectively were higher than those prepared by SSR (2.7 m² g^{−1} and 6.5 m² g^{−1}) as a consequence of their layered

morphologies. CO₂ photoreduction by water vapour under UV illumination (350 Xe lamp) demonstrated enhanced performance of the layered niobates for CH₄ production within a sealed quartz tubular reactor, possibly due to more efficient charge carrier migration to the nanobelt surface compared with that of irregular particles. Methane productivity over HNb₃O₈ was twice that reported for KNb₃O₈, accredited to more effective water diffusion within the hydrophilic HNb₃O₈ interlayers as illustrated in Fig. 10b, and hence a ready supply of protons to drive CO₂ reduction over the solid acid. Hydrothermal synthesis of HNb₃O₈ thus afforded improved photoactivity due to both its thin nanobelt morphology and better water adsorption properties.

Expanded HNb₃O₈ interlayers were explored by Li *et al.* as a means to further boost photocatalysis through pillaring silica as a guest compound within the interlayer space.¹²⁹ A HNb₃O₈ precursor was first prepared by conventional SSR and subsequent proton exchange. HNb₃O interlayers were then expanded *via* *n*-dodecylamine, enabling access to tetraethyl orthosilicate. Calcination of the resulting material created a SiO₂-pillared HNb₃O₈ with XRD indicating that silica pillaring increased the interlayer spacing from 0.37 nm to 2.10 nm, facilitating their visualisation by TEM (Fig. 11). Pillaring also dramatically increased the niobic acid surface area from ~7 to 197 m² g^{−1}, while simultaneously lowering the band gap from 3.5 eV to 3.3 eV. Under UV irradiation (350 W Xe lamp) under water vapour,

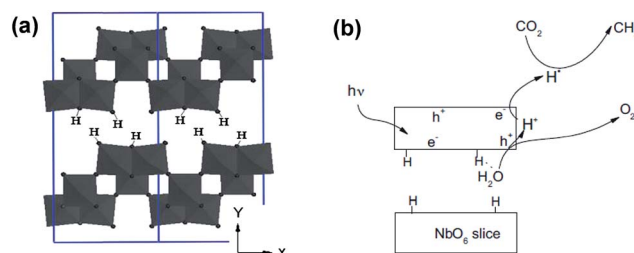


Fig. 10 Schematic depicting (a) the layered structure of HNb₃O₈, and (b) proposed mechanism of CO₂ photoreduction over HNb₃O₈. Reprinted from ref. 128, Copyright 2012, with permission from Elsevier.

Table 1 Textural properties of porous, structured photocatalysts and associated products of CO₂ photoreduction

Photocatalyst	Surface area/m ² g ^{−1}	Pore diameter/nm	Product
Ga ₂ O ₃ (ref. 107)	43	3.8, 5–30	CH ₄
1.5 wt% Cu/ZnO ¹¹²	22	31.2	CH ₃ OH, CH ₄ , CO, H ₂
0.12 wt% Pt/TiO ₂ (ref. 123)	147	7.8	CH ₄
0.84 at% N-TiO ₂ (ref. 123)	70	12.6	CH ₄ (Pt)
ZnGa ₂ O ₄ (ref. 113)	110	3.5	CH ₄
ZnAl ₂ O ₄ /ZnGaNO ¹¹¹	53	15.2	CH ₄
Zn ₂ GeO ₄ (ref. 114)	91	1.2–2, 2–12	CH ₄
ZnGeON ¹⁰⁶	36	—	CH ₄
TiO ₂ -SiO ₂ (ref. 108)	72	28.3	CO
In(OH) ₃ (ref. 110)	65	9.5	CH ₄
u-g-C ₃ N ₄ (ref. 120)	40	—	CH ₃ OH, C ₂ H ₅ OH
45 wt%TiO ₂ -SiO ₂ (ref. 122)	436	2–12	CH ₃ OH
0.5%Cu/TiO ₂ -SiO ₂ (ref. 113)	386	—	CO, CH ₄



and doping with 0.4 wt% Pt promoter, this SiO₂-pillared HNb₃O₈ proved superior to both the Nb₂O₅ precursor and non-pillared HNb₃O₈ layered structure for photoreducing CO₂ to CH₄ in a sealed quartz tubular reactor. Active sites of lamellar solid acids are considered to reside at the internal surfaces of interlayers.¹³⁰ Accordingly, Li and co-workers proposed that this enhanced photoactivity arose from increased active site accessibility within the HNb₃O₈ interlayers by CO₂ and H₂O. However, in common with many other studies, the simultaneous variation of physical and optical properties makes it hard to elucidate the principal origin of this enhancement. SiO₂-pillared HNb₃O₈ also outperformed the aforementioned HNb₃O₈ nanobelts. Additional investigations found that CH₄ production was lower over SiO₂-pillared KNb₃O₈ (prepared by cation exchange with K₂CO₃) than SiO₂-pillared HNb₃O₈, suggesting that water adsorption by the solid acid variant also played an important role in driving CH₄ formation.

Solid bases are well-established as CO₂ capture agents.^{67,131–133} Accordingly, layered double hydroxides (LDHs) composed of [M^{II}_{1-x}M^{III}_x(OH)₂]^{x+} cationic sheets with intercalated anions have been exploited for CO₂ photoreduction.^{134,135} These materials are attractive because of their strong and tunable basicity, and hence good CO₂ adsorption capacity. The semi-conducting nature, and hence photoabsorption properties, of LDHs can be tuned to some extent through careful selection of the intralayer M^{II} and M^{III} metal cations. Recent work from Sastre *et al.* showed that CO₂ photoreduction to CH₄ was enhanced by Zn/Ti or Zn/Ce LDHs,¹³⁵ presumably through increased CO₂ adsorption at the LDH surfaces facilitating subsequent photochemistry. Ahmed *et al.* prepared photoactive Zn²⁺/Ga³⁺ LDH catalysts.¹³⁴ Under UV irradiation (500 W Xe arc lamp), the resulting [Zn₃Ga(OH)₈]₂⁺(CO₃)₂²⁻·mH₂O solid base was active for reducing CO₂ into CO and CH₃OH as primary and secondary products respectively, employing a closed, circulating system pressurised with a mixture of 2.3 kPa CO₂ and 21.7 kPa H₂, *i.e.* highly reducing conditions wherein commercial application would require an independent photocatalytic or electrochemical hydrolysis process to supply hydrogen, or close proximity to a fossil fuel derived syn gas feed. Copper incorporation into the LDH to form a [Zn_{1.5}Cu_{1.5}Ga(OH)₈]₂⁺(CO₃)₂²⁻·mH₂O material improved selectivity towards CH₃OH threefold, rendering it the major product. Control experiments

in the absence of CO₂ suggested that at least some of the observed reactivity was associated with the conversion of CO₃²⁻ ions originating within the parent LDH, although this could not account for the total product yield. Replacing Ga³⁺ with Al³⁺ to create a [Zn₃Al(OH)₈]₂⁺(CO₃)₂²⁻·mH₂O LDH enhanced overall photoconversion efficiency, but favoured CO formation (even after Cu²⁺ incorporation). These layered catalysts were reported active for 20 h continuous CO₂ photoreduction, although methanol productivity declined over time. In an effort to boost selectivity towards methanol, the interlayer CO₃²⁻ anions were exchanged for [Cu(OH)₄]₂²⁻ anions, thereby creating a [Zn_{1.5}Cu_{1.5}Ga(OH)₈]₂⁺(CO₃)₂²⁻·mH₂O material¹³⁶ with a methanol yield almost three times that achievable over the carbonate counterparts. Copper was thus hypothesised as the active photocatalytic site, with the localisation of Cu sites within the interlayers facilitating their accessibility to CO₂, while the replacement of CO₃²⁻ with [Cu(OH)₄]₂²⁻ counterions significantly decreased the band gap of the resulting LDH while expanding the interlayer spacing, both factors likely contributing towards the enhanced photoactivity of the copper anion doped variant.

2.2.4. Hierarchical ordered photocatalysts. Three-dimensional, hierarchical photocatalysts with novel properties arising from their unique morphology have also been exploited to further optimise photocatalytic performance. Many studies have shown that such complex architectures, typically possessing high surface areas and diverse pore-interconnectivities, offer enhanced catalytic activity relative to their bulk, nanoparticulate or monomodal nanoporous counterparts.¹³⁷ The unique surface and textural characteristics of these superstructures can also increase photon absorption, leading to enhanced quantum efficiency.^{138–143} To date, semiconductors with diverse three-dimensional, hierarchical structures have been developed for harvesting solar energy, including ZnO nanowire forests,¹⁴³ Si/InGa core-shell nanowire arrays,¹⁴² TiO₂/ZnO/CuO forest-like architectures,¹⁴⁰ Bi₂O₃/Bi₂WO₆ microclews,¹⁴⁴ N-doped Bi₃NbO₇ peony-like architectures,¹⁴⁵ flower-like Ta₂O₅,¹⁴⁶ Bi₁₂TiO₂₀,¹⁴⁷ Bi₁₂TiO₂₀/TiO₂,¹⁴⁸ Nb₃O₇F,¹⁴⁹ Bi₂O₃,¹⁵⁰ and NiO-CdS architectures,¹⁵¹ CdS@ZnO and CdS@Al₂O₃ urchin-like heteroarrays,⁹¹ N-doped (BiO)₂CO₃ microspheres,¹⁴¹ Fe₃O₄/WO₃ core-shell structures,¹⁵² WO₃ hollow dendrites, spheres and dumbbells,¹⁵³ porous TiO₂ hollow microspheres,^{138,154} and γ-TaON urchin-like hollow spheres.¹³⁹ Such complex structures are generally created through the self-assembly of nanoscale building blocks, such as nanosheets and nanorods, *via* hydrothermal routes.^{91,141,144–152} In some instances, pore networks created within hierarchical networks not only increase the total surface area, but also serve to accelerate reactant/product diffusion to/from active centres.^{141,154} While relatively few studies have targeted the development of hierarchical structures for CO₂ photoreduction, a number of promising three-dimensional nanostructures have been created for solar fuels production.

Highly ordered, sheaf-like, hyperbranched Zn₂GeO₄ superstructures were prepared in the presence of ethylenediamine through a solvothermal method by Liu *et al.*¹⁵⁵ The FE-SEM image in Fig. 12a highlights 3–4 μm sheaf-like features which

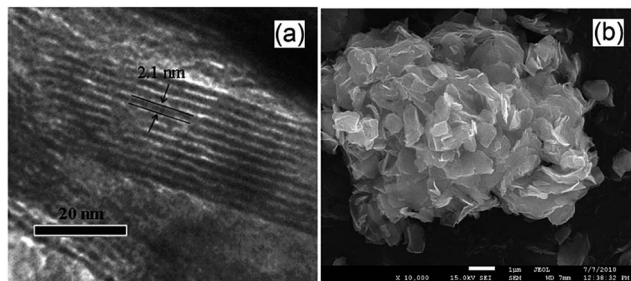


Fig. 11 (a) TEM and (b) SEM images of SiO₂-pillared HNb₃O₈. Reprinted with permission from ref. 129. Copyright 2009 American Chemical Society.



assembled from closely packed, well-aligned nanowires with fantails oriented toward the center and projecting radially outwards. This unique morphology was proposed to arise through a crystal-splitting growth mechanism, with the degree of splitting a function of reaction time, precursor concentration and solvent. In order to improve the visible light performance of the normally large band gap Zn_2GeO_4 , these as-prepared fusiform bundles were subject to nitridation at 700 °C, resulting in a yellowish zinc germanium oxynitride ($\text{Zn}_{1.7}\text{GeN}_{1.8}\text{O}$) photocatalyst. While the bundle morphology of the parent $\text{Zn}_{1.7}\text{GeN}_{1.8}\text{O}$ precursor was retained after this high temperature treatment, an added benefit was a concomitant significant increase in surface roughness (Fig. 12b), which doubled the $\text{Zn}_{1.7}\text{GeN}_{1.8}\text{O}$ surface area relative to the Zn_2GeO_4 parent. Under visible light illumination (300 W Xe arc lamp equipped with a 420 nm cut-off filter), and only upon promotion with Pt or RuO_2 co-catalysts, this hierarchically structured $\text{Zn}_{1.7}\text{GeN}_{1.8}\text{O}$ material showed good ambient pressure CO_2 photoreduction to CH_4 , albeit with an apparent quantum efficiency still only approaching 0.024%. It is noteworthy that the CH_4 yield reached saturated around 6 h, possibly due to reversible adsorption of reactive intermediates.

Hexagonal nanoplate-textured micro-octahedral Zn_2SnO_4 were synthesised through a hydrothermal treatment in the presence of L-tryptophan.¹⁵⁶ The resulting material comprised ordered and uniform micro-octahedra with edges of approximately 3 μm (Fig. 13a). At higher magnification, it is apparent that each micro-octahedron is densely packed with ~ 50 nm thin, hexagonal nanoplates Fig. 13b. These nanoplates are vertically arranged within octahedra such that they lie parallel to neighbouring edges. The octahedral geometry was proposed as a consequence of L-tryptophan impeding reaction along the [111] direction, favouring faster nucleation and growth in the [100] direction. The resulting hierarchical nanoplate/micro-octahedron morphology blue-shifted the Zn_2SnO_4 band gap from the bulk value of 3.67 eV to 3.87 eV, yet delivered exclusively CH_4 production at 20 ppm g^{-1} from CO_2 under UV irradiation within a gas-tight Pyrex glass cell, albeit for only 1 h in the absence of promoters. This far exceeded the photoactivity of bulk Zn_2SnO_4 (1.5 ppm g^{-1}), smooth Zn_2SnO_4 micro-octahedra (4.7 ppm g^{-1}) or Zn_2SnO_4 atactic particles (2.4 ppm g^{-1}) prepared without L-tryptophan. This rate enhancement was ascribed to such superstructures acting as light-scattering centres promoting photon harvesting, in combination with the nanoplate morphology promoting electron transport along

individual plates, and the open nanoplate-/micro-octahedron architecture which facilitated rapid molecular diffusion.

Hierarchical, hollow Bi_2WO_6 microspheres, which were constructed from crossed nanosheets prepared through an anion exchange method by Cheng *et al.*, successfully photo-reduced CO_2 to CH_3OH under visible light irradiation.¹⁵⁷ As depicted in Fig. 14, the synthesis involved anion exchange of BiOBr solid microspheres, prepared from $\text{Bi}(\text{NO}_3)_3$ and a $[\text{C}_{12}\text{Mim}]\text{Br}$ ionic liquid, with Na_2WO_6 under hydrothermal conditions at 160 °C. BiOBr and Bi_2WO_6 comprise crystalline layered structures consisting of alternating $(\text{Bi}_2\text{O}_2)^{2+}$ slabs separated by intercalating anion layers. Since the solubility of Bi_2WO_6 was lower than that of BiOBr , thin layers of Bi_2WO_6 formed at the BiOBr^- surfaces during the exchange process. Owing to the slower diffusion of WO_4^{2-} versus Br^- , a fast, continuous outflow of Br^- through the Bi_2WO_6 shell resulted in the formation of hollow cores over a prolonged period. These 2–5 μm diameter, hollow microspheres were themselves mesoporous, with a surface area far higher than that of Bi_2WO_6 prepared by a solid state route (Bi_2WO_6 SSR). Hollow Bi_2WO_6 microspheres generated around 25 times more CH_3OH from CO_2 photoreduction by water than Bi_2WO_6 SSR at under visible light (300 W Xe arc lamp equipped with a 420 nm cut-off filter). This performance was notably achieved without the aid of noble metal co-catalysts. As in the previous examples, this enhanced photocatalysis was attributed to the higher surface area and CO_2 adsorption affinity (eight times that of Bi_2WO_6 SSR) of the hierarchical structure.

An exciting biomimetic approach was recently adopted by Zhou *et al.* to prepare hierarchical, three-dimensional provskite titanates, ATiO_3 ($A = \text{Sr}, \text{Ca}, \text{Pb}$), for CO_2 photoreduction.¹⁵⁸ In an effort to move one-step closer to artificial photosynthesis, fresh Cherry Blossom green leaves were employed as a structure-directing agent to prepare inorganic photocatalysts *via* a modified sol-gel protocol; natural leaves possess high porosity, connectivity and surface areas, tailored to facilitate efficient gas diffusion, water transport and the harnessing of solar energy. The success of this synthesis was evidenced by the FE-SEM images in Fig. 15a and b, wherein the resulting SrTiO_3 exhibited a macroporous venation network characteristic of the parent leaves. Higher magnification TEM imaging revealed the network walls consisted of a

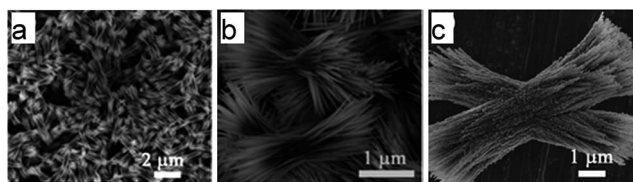


Fig. 12 FE-SEM images of (a and b) sheaf-like Zn_2GeO_4 superstructure solvothermally treated for 12 h, and (c) $\text{Zn}_{1.7}\text{GeN}_{1.8}\text{O}$ prepared through high temperature nitridation of Zn_2GeO_4 fusiform bundles. Reproduced from ref. 155 with permission from The Royal Society of Chemistry.

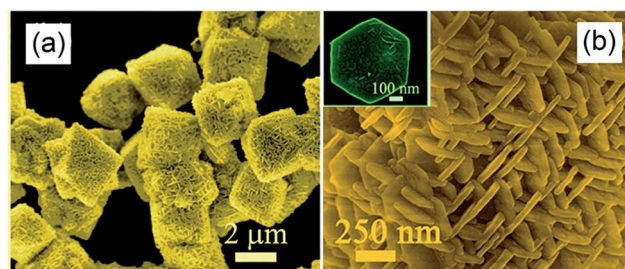


Fig. 13 FE-SEM images of the nanoplate/micro-octahedron Zn_2SnO_4 at (a) lower magnification and (b) at higher magnification. The inset of (b) shows an isolated hexagonal nanoplate. Reprinted with permission from ref. 156. Copyright 2012 American Chemical Society.



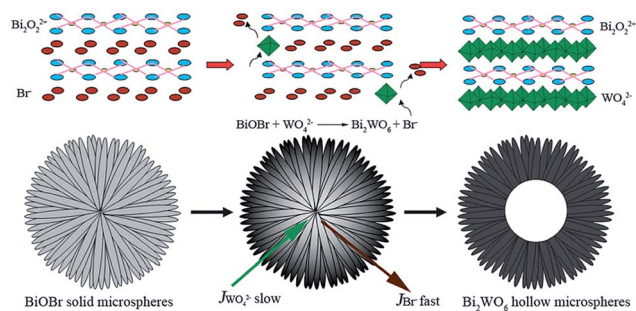


Fig. 14 Schematic of hollow Bi_2WO_6 microspheres formation through anion exchange of solid BiOBr microspheres. Reproduced from ref. 157 with permission from The Royal Society of Chemistry.

mesoporous array of crystallites (Fig. 15c and d). Such biomimetic SrTiO_3 and CaTiO_3 architectures outperformed corresponding reference titanates in CO_2 photoreduction to CO (major product) and CH_4 (secondary product) during UV illumination (300 W Xe arc lamp) under water vapour in a gas closed circulation system and 80 kPa of CO_2 . Incorporation of Au, Ag and Cu into these hierarchical titanates enhanced their photoactivity, and also led to the evolution of trace C_2H_4 and C_2H_6 , although the latter were proposed to arise *via* photocatalytic non-oxidative coupling of CH_4 rather than direct CO_2 photoreduction.¹⁵⁹

The excellent performance of these leaf-architected titanates presumably reflects their highly interconnected macroporous-mesoporous structure, which promotes gas diffusion in addition to increasing surface active sites. This sophisticated architecture may also enhance light absorption in a manner similar to that of natural leaves, by which incident light is scattered and transmitted into deeper layers of the network, thereby increasing the quantum efficiency and hence photocatalytic activity.

2.2.5. Hybrid structured photocatalysts. As touched upon in the preceding sections, semiconductor photocatalysts can be coupled with other materials which may comprise efficient charge carrier components (electron donor or acceptor), such as semiconductors, metal oxides or zeolites. Such combinations offer hybrid photocatalyst with superior physicochemical or optical properties to the parent active phase, *e.g.* a higher dispersion of active centres, enhanced accessibility of catalytic centres (*cf.* hierarchical architectures) or novel band structures. For instance, two semiconductors (SC) with different band gaps and valence/conduction band energy levels can be combined to create a staggered type II band structure as depicted in Fig. 16.¹⁶⁰ When light is absorbed by a small (visible) band gap semiconductor (SC_1), interparticle electron transfer can occur, in which photogenerated electrons are injected into the CB of a large band gap (SC_2) semiconductor, while photogenerated holes remain in the valence band (VB) of SC_1 , thereby effecting charge separation through spatial localisation, and hence maximising the lifetime of photoinduced charge carriers and photocatalytic efficiency. Direct particle-to-particle contact is generally held to be crucial for efficient operation of such hybrid systems.¹⁶¹

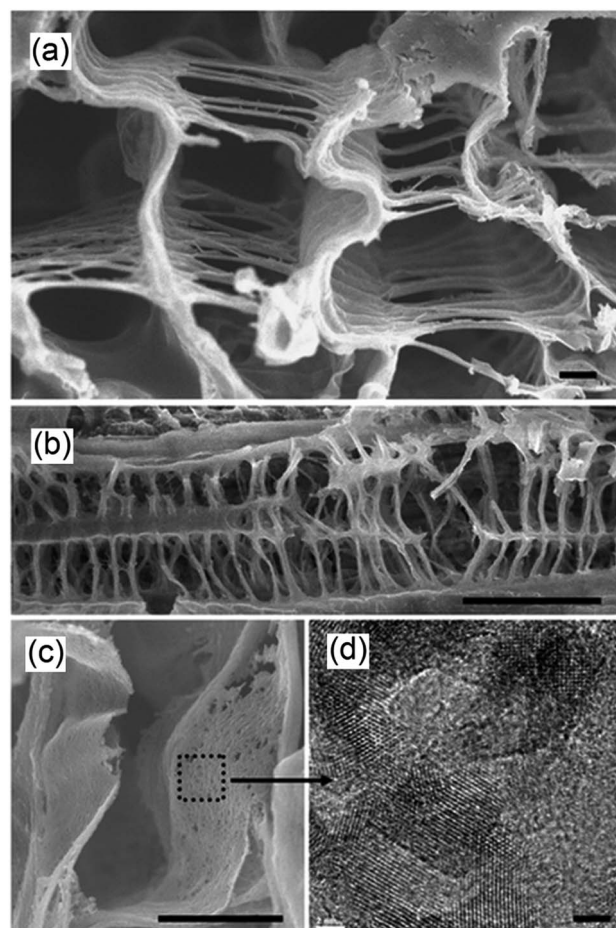


Fig. 15 FE-SEM images showing (a) the cross section of the porous venation architecture of SrTiO_3 (scale bar, 1 μm) (b) cross section of the porous network axially (scale bar, 10 μm), (c) magnified image of the wall of the network (scale bar, 1 μm) and (d) TEM image showing the mesoporous structure of SrTiO_3 (scale bar, 2 nm). Reprinted by permission from Macmillan Publishers Ltd ref. 158, copyright 2013.

2.2.5.1. Inorganic hybrid photocatalysts. A number of such SC_1/SC_2 hybrid systems have been developed for CO_2 photoreduction. Wang *et al.* prepared $\text{CdSe}/\text{Pt}/\text{TiO}_2$ heterostructures using commercially available CdSe quantum dots (QDs) of two different sizes (2.5 nm and 6 nm) and commercial P25 titania.¹⁶² The resulting heterostructures, containing 0.5 at% Pt and 1 at%

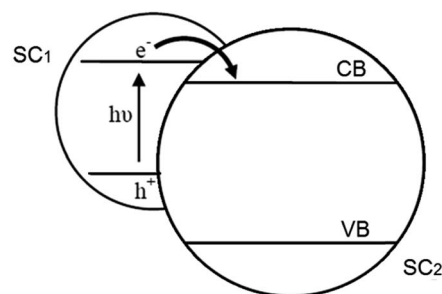


Fig. 16 Electron transfer pathway in a SC/SC hybrid system. Adapted from ref. 160, Copyright 1995, with permission from Elsevier.



Cd, were active for the photoreduction of CO_2 to CH_4 and CH_3OH (respective major and minor products) under visible light irradiation, with trace H_2 and CO also reported; neither Pt/ TiO_2 or CdSe components were individually active under identical reaction conditions. Consequently, the observed visible light photoactivity of the semiconductor heterostructures must arise from a synergy between CdSe and TiO_2 . It was proposed that photoexcited electrons promoted into the CB of CdSe under visible light irradiation, were subsequently injected into the CB of TiO_2 , increasing their lifetime and probability of transfer to CO_2 . However, these composites deactivated after 4–6 h irradiation, most likely due to oxidation of the QDs by the accumulated photoinduced holes in the VB of CdSe.

In other work, coupling of AgBr with P25 was also undertaken to form nanocomposites active for reducing CO_2 under visible light,¹⁶³ wherein the indirect band gap of AgBr, which spans wavelengths between 450–700 nm, was held responsible for the visible light activity. This hybrid was synthesised utilising a cetyltrimethylammonium bromide (CTAB) surfactant stabiliser to create well-dispersed AgBr NPs (of around 5 nm) decorating the surface of P25. The nanocomposites exhibited excellent visible light photoactivity (150 W Xe lamp with a 420 nm cut-off filter) and photostability in the presence of aqueous KHCO_3 , relative to pure AgBr, with CH_4 as the major product together with CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$ and CO under high CO_2 pressure (7.5 MPa). A composite containing 23.2 wt% of AgBr exhibited optimum performance, with the photocatalytic mechanism again proposed to involve visible light excitation of electrons into the AgBr conduction band and subsequent transfer into the TiO_2 CB with attendant charge separation. In addition to increasing charge carrier lifetime, these hybrid structures also impeded the formation of metallic Ag through photolysis, as was observed for pure AgBr.

Qin *et al.* followed a similar route employing CTAB to produce 14 nm CuO/TiO_2 composite nanostructures,¹⁶⁴ although here UV irradiation in the presence of methanol (rather than water) resulted in CO_2 photoreduction to methyl formate within a slurry reactor. A 1 wt% CuO/TiO_2 composite calcined at 450 °C exhibited the highest photoactivity, outperforming both pure TiO_2 and composites synthesised in the absence of CTAB, suggesting a role for both charge separation and particle size effects. Liu *et al.* also explored the synergy between copper and titania heterojunctions, employing a sol-gel route to prepare $\text{Cu}_2\text{O}/\text{TiO}_2$ composites which demonstrated superior photoactivity over pure TiO_2 in photoreducing CO_2 to CH_4 in a stirred batch, annular quartz reactor under 1 bar of CO_2 and low power (32 W) UVA illumination.¹⁶⁵ XPS and pulse chemisorption measurements identified the presence of a two-dimensional Cu_2O species decorating the surface of titania at extremely low doping levels (0.03 wt% Cu). Higher copper loadings resulted in a structural transformation to three-dimensional Cu_2O crystallites, which reduced the efficiency of photoinduced electron transfer from TiO_2 to Cu_2O , and hence lowered their activity. TiO_2 has also been coupled with iron to form $\text{FeTiO}_3/\text{TiO}_2$ hybrids able to photoreduce CO_2 to CH_3OH under high power UV (500 W Xe lamp) and visible light irradiation under basic conditions.¹⁶⁶ Materials synthesised with 20

mol% Fe gave the highest rate of CO_2 reduction. Under UV illumination, photoinduced electrons were proposed to transfer from the (higher energy) CB of TiO_2 to that of FeTiO_3 , with photoinduced holes returned from the VB of FeTiO_3 to that of TiO_2 , charge separation again inferred as improving the overall photoactivity. In contrast, under visible light irradiation, electrons were photoexcited into the FeTiO_3 CB, resulting in a partially vacant FeTiO_3 VB, which was charge compensated for by the consequential movement of electrons from the almost isoenergetic TiO_2 VB, leaving residual holes in the TiO_2 VB, and net electron-hole charge separation across the two semiconductors. Efforts have been made to couple TiO_2 with CdS and Bi_2S_3 in order to photoreduce CO_2 to CH_3OH .¹⁶⁵ Li *et al.* precipitated CdS or Bi_2S_3 onto TiO_2 NTs to yield visible light active CdS/ TiO_2 and $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterostructures, thereby delivering improved photoactivity relative to P25 or bare TiO_2 NTs (although activities were not normalised to take into account the two-fold higher surface areas of the nanorod morphologies). Photoinduced electrons from the CB of CdS or Bi_2S_3 could be injected into that of TiO_2 to achieve efficient charge separation. Nevertheless, these complex heterojunction nanorods failed to generate more CH_3OH than their respective pure CdS and Bi_2S_3 bulk analogues.

$\text{CuO}-\text{Cu}_2\text{O}$ thin film nanorod arrays prepared by Chadimkhani *et al.* were recently shown to photoreduce CO_2 into CH_3OH under simulated solar irradiation (AM 1.5) without a co-catalyst *via* photoelectrocatalysis.¹⁶⁷ Coupling of such small band gap semiconductors is advantageous in exploiting a larger fraction of the visible light region of the solar spectrum than achievable by either alone. CuO nanorods were first thermally grown over a Cu substrate, following which Cu_2O crystallites were electrodeposited on the nanorod surfaces to generate a CuO core/ Cu_2O shell hybrid thin film which outperformed a compact Cu_2O electrodeposited film. This enhancement may reflect more efficient transfer of photoinduced electrons from the CB of the Cu_2O shell to that of the CuO core and consequent increased probability of photoinduced electrons reacting with CO_2 . Such a model necessitates that the tips of CuO nanorods are exposed to a CO_2 saturated aqueous environment. The $\text{CuO}-\text{Cu}_2\text{O}$ thin film was reported to generate CH_3OH at a potential of only -0.2 V vs. SHE, lower than the standard redox potential for $\text{CO}_2/\text{CH}_3\text{OH}$ (-0.38 V vs. SHE), a feature characteristic of p-type semiconductors (such as CuO and Cu_2O).

Copper oxide has also been employed by In *et al.* to form hollow $\text{CuO}-\text{TiO}_{2-x}\text{N}_x$ hybrid nanocubes that are effective for photoreducing CO_2 to CH_4 .¹⁶⁸ As shown in Fig. 17a, Cu_3N nanocubes, synthesised through the thermal decomposition of $\text{Cu}(\text{NO}_3)_2$ in octadecylamine at 240 °C, were employed as the templating agent for subsequent TiO_2 deposition on their external surfaces through slow hydrolysis of titanium *n*-butoxide. The initial Cu_3N nanocubes were uniform in shape and around 27 nm across (Fig. 17b), and underwent significant roughening following TiO_2 coating ($\text{TiO}_2@\text{Cu}_3\text{N}$) as apparent in Fig. 17c. Subsequent heat treatment of the $\text{TiO}_2@\text{Cu}_3\text{N}$ powder at 450 °C under air transformed these phase-separated structures into hollow $\text{CuO}-\text{TiO}_{2-x}\text{N}_x$ hybrid nanocubes (Fig. 17d–f).



The final material was composed of hollow, truncated cuboidal CuO hollow cubes of ~ 57 nm diameter, decorated by small $\text{TiO}_{2-x}\text{N}_x$ particles. FE-SEM imaging confirmed the cubic morphology and hollow core of this hybrid material (Fig. 17g–f). The authors proposed that TiO_2 crystallised onto the surfaces of Cu_3N during thermal processing, but did not fully encapsulate the underlying nanocubes, permitting O_2 to diffuse into, and oxidise, the Cu_3N surface. Assuming that the inward rate of atomic oxygen diffusion is slower than the outward diffusion of N_2 , high temperature treatment would drive the formation of hollow cores through the Kirkendall effect.¹⁶⁹ As nitrogen atoms diffuse outward, they are able to react with TiO_2 and hence form an oxynitride $\text{TiO}_{2-x}\text{N}_x$ phase. Under simulated solar illumination and water vapour, this particular hybrid composite photoreduced CO_2 to CH_4 , and C_2H_6 , C_3H_8 and C_4H_{10} as minor products. The hollow $\text{CuO-TiO}_{2-x}\text{N}_x$ hybrid nanocubes outperformed P25, CuO (annealed Cu_3N), CuO@TiO_2 , Cu_3N and $\text{TiO}_2@\text{Cu}_3\text{N}$ in the photocatalytic generation of CH_3OH , likely due to their improved visible light absorption characteristics and the synergy between CuO and $\text{TiO}_{2-x}\text{N}_x$.

2.2.5.2. Organic hybrid photocatalysts. A hybrid catalyst composed of a Nafion (perfluorinated polymer with sulfonate groups, Nf) overlayer on TiO_2 with Pd co-catalyst was prepared by Kim *et al.* for CO_2 photoreduction¹⁷⁰ as illustrated in Fig. 18a. Pd was first impregnated onto P25, and subsequently coated with Nafion. The rationale for integrating Nafion with a photoactive semiconductor was that the superacidic polymer, which exhibits excellent proton conducting behaviour, would facilitate proton-coupled multielectron transfer (PCET) pathways during product (hydrocarbon) formation, thereby improving net CO_2 reduction. It was also believed that Nafion might inhibit the reoxidation of photoreduction products, and as a fluorinated polymer, be stable towards photocorrosion and redox reactions and thus a good host support. After catalyst pre-cleaning and UV irradiation the hybrid Nf/Pd- TiO_2 facilitated CO_2 photoreduction to CH_4 , C_2H_6 and H_2 (and trace C_3H_8) in a sodium carbonate aqueous solution. As shown in Fig. 18b, CO_2 reduction was highly sensitive to reaction pH, with photoactivity increasing at lower pH, the higher H^+ concentration aiding product generation. In the presence of Nafion, considerably more CH_4 was generated at pH 3 and 11 but the effect was less prominent at pH 1. However, Nafion significantly enhanced ethane production at pH 3 and 1, with propane only observed over the Nf/Pd- TiO_2 hybrid photocatalyst. The observation that Nafion favours longer chain hydrocarbons suggest that it may stabilise CO_2 reduction intermediates in a manner that promotes sequential multi-electron transfer. Additional experiments with Nf/Pd- TiO_2 under natural sunlight only resulted in CH_4 , C_2H_6 and C_3H_8 formation.

Sensitising large band gap semiconductors with transition metal complexes is another approach to designing visible light active materials.^{171–173} Yuan *et al.* recently demonstrated the utility of a $[\text{Cu}(\text{bpy})_2]^+$ dye-sensitised TiO_2 hybrid system for CO_2 photoreduction.¹⁷⁴ To obtain an air stable Cu complex, the 6- and 6'-position of the 2,2'-bipyridine (bpy) ligand were modified with a methyl group to protect the surroundings of the labile Cu(I) centre. This ligand was also designed to terminate in

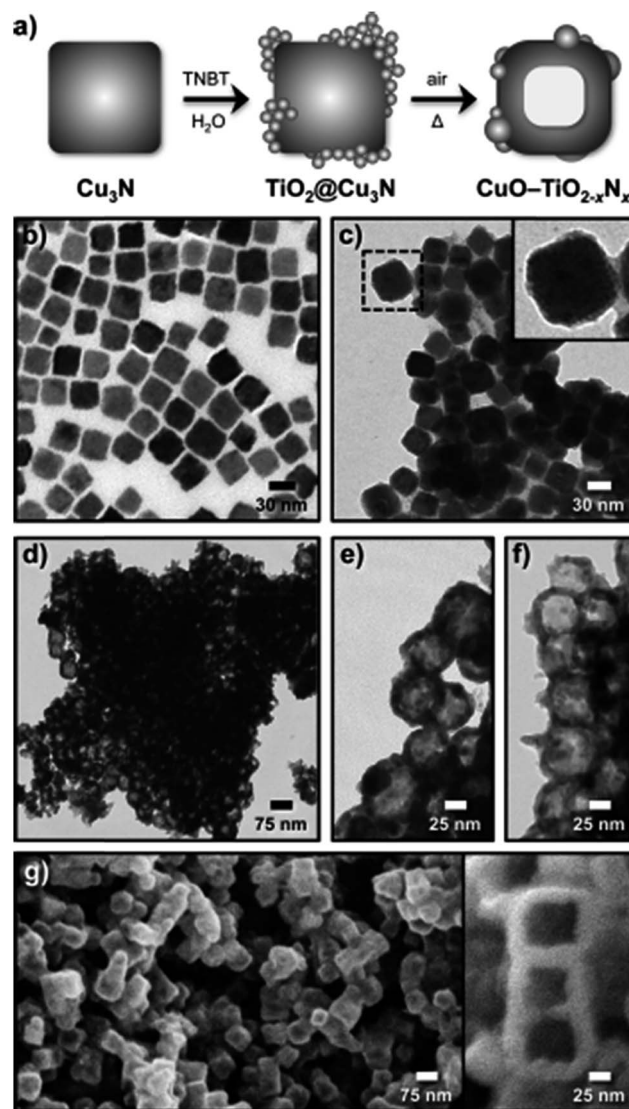


Fig. 17 (a) Schematic for the synthesis of hollow $\text{CuO-TiO}_{2-x}\text{N}_x$ hybrid nanocubes, and associated TEM images of (b) Cu_3N nanocubes, (c) $\text{TiO}_2@\text{Cu}_3\text{N}$ nanocubes, (d)–(f) hollow $\text{CuO-TiO}_{2-x}\text{N}_x$ hybrid nanocubes at different magnifications, and (g)–(h) FESEM images of the hollow hybrid nanocubes. Reproduced with permission from ref. 168. Copyright 2012 Wiley.

cynoacetic acid moieties, thus enabling efficient anchoring of the metal complex onto the semiconductor surface. The Cu(I) complex modified P25 hybrid successfully photoreduced CO_2 with water vapour into CH_4 in a gas–solid reaction system under visible light illumination. It is likely that the Cu(I) complex was responsible for harnessing photons from visible light, with the resulting photoexcited electrons rapidly injected into the conduction band of the visible-inactive TiO_2 , thereby prolonging the lifetime of photoinduced electrons to drive CO_2 reduction.

A visible light hybrid photocatalyst system, which utilised a naturally occurring enzyme CO dehydrogenase (CODH 1) to reduce CO_2 , was developed by Woolerton *et al.*^{175,176} This enzyme was homodimeric, such that each sub-unit contained a buried



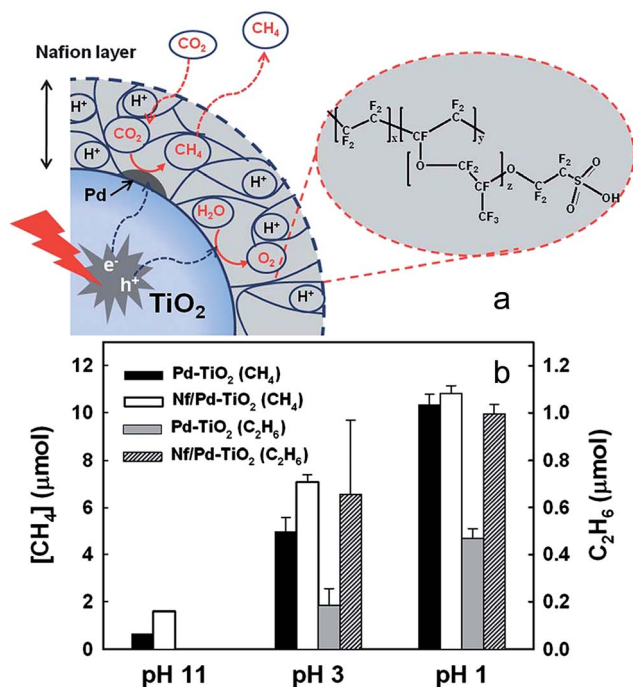


Fig. 18 (a) Schematic of CO₂ photoreduction on Nf/Pd-TiO₂ nanoparticles and (b) CH₄ (at 5 h) and C₂H₆ (at 1 h) production at different pH ranges on Pd-TiO₂ and Nf/Pd-TiO₂ NPs under UV illumination ($\lambda > 300$ nm) in the presence of 0.2 M Na₂CO₃ aqueous solution. Catalyst concentration was fixed at 1.5 g L⁻¹ (with 1.0 wt% Pd and 0.83 wt% Nafion). Reproduced from ref. 170 with permission from The Royal Society of Chemistry.

[Ni4Fe-4S] active site, wired to the protein surface through a series of [4Fe-4S] clusters that were also responsible for relaying electrons in and out of CODH 1. Fig. 19 illustrates the complete photosystem comprising CODH 1 modified, and Ru dye (RuP) sensitised, P25 NPs. During visible light irradiation, photoexcited electrons generated through metal-to-ligand charge-transfer on the RuP dye could be injected into the CB of TiO₂ and transferred through the [4Fe-4S] clusters to the CODH 1 active sites, with the resulting photo-oxidised RuP regenerated *via* 2-(*N*-morpholino) ethanesulfonic acid (MES) as a sacrificial electron donor. It was proposed that the reduction process was initiated through CO₂ binding as a bridging ligand between the Ni and dangling Fe atom of the enzyme. Under visible light illumination, TiO₂ thus functioned as a medium for relaying electrons between the dye and enzyme. It is noteworthy that CODH 1 usually oxidises CO to CO₂, but that the enzyme can be driven to catalyse the reverse reaction by applying a small overpotential.¹⁷⁷ Further investigations revealed P25 as the preferred semiconductor with respect to ZnO, SrTiO₃, rutile and anatase TiO₂.¹⁷⁵ Photoactivity was further enhanced through the addition of another sacrificial electron donor, ethylenediaminetetraacetic acid (EDTA). To improve CODH 1 attachment to titania, P25 was modified with various molecules, including polymyxin B sulphate and glutamic acid, albeit to no effect. On the other hand, functionalisation with *o*-phosphorylethanol led to a significant decrease in activity. Although this

particular system was capable of photoreducing CO₂ to CO, the photoconversion efficiency was lower than expected, and it was sensitive to O₂ passivation.^{175,176} Photoactivity decreased after 4 h on-stream, potentially due to the difficulty in regenerating oxidised RuP, or the ineffectiveness of CODH 1 in harnessing electrons for activating CO₂.

2.2.5.3. Carbonaceous media hybrid photocatalysts. Carbon nanomaterials, such as activated carbons, carbon monoliths, carbon NTs, graphene and graphites^{178,179} are promising candidates for catalyst supports, offering low cost, robust mechanical strength, high surface area, excellent porosity, chemical inertness and high electron conductivity. Moreover, carbons are amenable to the efficient recovery of precious metal promoters *via* combustion, and their surfaces may be readily functionalised by physical or chemical treatments, thereby modifying the resulting performance of hybrid catalysts. Significant work has been undertaken to integrate photoactive materials with carbonaceous media such as carbon NPs and graphene to deliver improved photocatalysts.

Covalently-functionalised carbon quantum dots (QDs) absorb and emit strongly in the visible light region.^{180–183} Because of these unique electronic properties, surface-passivated carbon QDs are a promising visible light harvesting medium. Surface-functionalised carbon NPs prepared by Cao *et al.* were active in photoreducing CO₂ under visible light illumination.¹⁸⁴ Sub-10 nm carbon NPs were functionalised with oligomeric poly(ethylene glycol) diamine (PEG_{1500N}), rendering the resulting nanoparticles photoactive and water soluble. PEG-functionalised carbon QDs readily generated surface confined electrons and holes under irradiation that recombined radiatively (Fig. 20). This recombination process can be quenched by either electron donors or acceptors. Efficient charge separation and suppressed radiative recombination was achieved through coated these surface-functionalised carbon NPs with Au or Pt through solution-phase photolysis; subsequent exposure to a light source would channel photogenerated electrons into the resulting metal nanoparticles, thereby prolonging the lifetime of charge carriers required for subsequent CO₂ reduction. Under visible light irradiation (425–720 nm), and in the presence of water, metal decorated and surface-functionalised carbon NPs proved active for photoreducing CO₂ to formic acid, although product analysis relied upon solution phase ¹H and ¹³C NMR spectroscopy, and hence was unable to quantify the

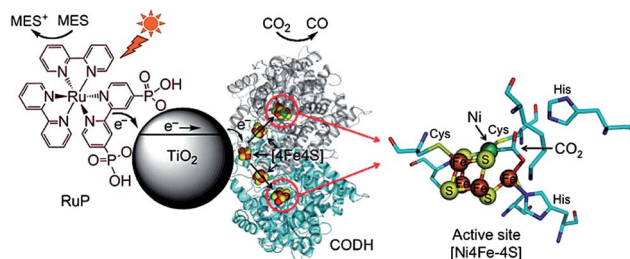


Fig. 19 Schematic illustrating the CODH 1 modified and Ru dye-sensitised TiO₂ NPs photoactive system. Reprinted with permission from ref. 176. Copyright 2010 American Chemical Society.



presence of potential gas phase reduction products such as light alkanes and alkenes.

As a conductive electron reservoir, carbon is also effective in channelling photoinduced electrons away from a photoactive host, thereby increasing the probability that photoexcited electrons reduce CO_2 rather than recombining with holes. Ong *et al.* reported a hybrid catalyst, composed of CNTs grown on a Ni impregnated TiO_2 composite, for CO_2 photoreduction to CH_4 under visible light.¹⁸⁵ The authors first deposited 10 wt% Ni onto commercial anatase *via* precipitation in the presence of glycerol. Carbon NTs were subsequently grown over the calcined Ni/ TiO_2 through chemical vapour deposition. The band gap of the resulting hybrid material was 2.22 eV, significantly smaller than that of anatase TiO_2 (3.32 eV). Hence CNT incorporation served to narrow the band gap and improve visible light absorption in the hybrid catalyst. Visible light irradiation under water vapour revealed the CNT/Ni/ TiO_2 hybrids were superior to either Ni/ TiO_2 or pure anatase TiO_2 , although progressive deactivation occurred after 4.5 h irradiation at which point CO_2 photoreduction activity was maximal. Photoactivity of the CNT/Ni/ TiO_2 hybrid catalyst originated from improved visible light absorption and the excellent electron storage and transfer properties of the CNTs which helped to suppress electron-hole recombination.

Graphene, a two-dimensional planar structure of sp^2 hybridised carbon, has received much attention in regard to photocatalytic applications for H_2 evolution,^{58,163,186–194} photocurrent generation,^{190,194–198} and dye degradation,^{90,144,145,163,189,199–201} due to its outstanding electronic properties.^{144,197} Graphene also offers extremely high specific surface areas²⁰² in excess of $2600 \text{ m}^2 \text{ g}^{-1}$, a good CO_2 and H_2 adsorption capacity,^{203,204} and has been reported to sensitise large band gap semiconductors for visible light photoabsorption.^{205–207} However, less work has been conducted into the integration of graphene with photoactive materials for CO_2 photoreduction. Nevertheless, it is known that graphene oxide (GO), an unreduced form of graphene, despite being a poor electrical conductor,¹⁹⁵ is capable of photoreducing CO_2 to CH_3OH .²⁰⁸ Liang *et al.* demonstrated that the photocatalytic activity of commercial P25 is greatly enhanced when used in conjunction with a low defect density, solvent-exfoliated graphene (SEG), compared to that achievable over defective, solvent-reduced graphene oxide (SGRO).²⁰⁶ The

photoactivities of these SEG-P25 and SGRO-P25 composite films, which were synthesised by blade-coating a physical mixture of different amounts of graphene and P25 ink and subsequent annealing, are shown in Fig. 21a. Note that under UV illumination the presence of SGRO exerted little impact upon the photoactivity of TiO_2 , whereas graphene possessing a low defect density exhibited better electrical mobility and concomitant superior photocatalytic efficiency under either UV or visible light.

Despite the popularity of graphene-derived materials, a direct comparison between graphene and its carbon nanotube (CNT) allotrope has not been well-explored. Further work by Liang *et al.* extended their studies on CO_2 photoreduction catalysed by blade-coated films to examine the integration of titania nanosheets (TiNS) with SEG or single-walled carbon nanotubes (SWCNT) to form either a two-dimensional graphene-titania nanosheet composite, or a one/two-dimensional carbon nanotube-titania nanosheet composite, respectively.²⁰⁹ Fig. 21b shows that the SEG-TiNS composites outperformed SWCNT-TiNS in photoreducing CO_2 to CH_4 under UV irradiation. Conversely, composites of SWCNT-TiNS demonstrated better photoactivity under visible light illumination. It was proposed that the two-dimensional interface between SEG and TiNS facilitated intimate electronic and physical coupling relative to the one/two-dimensional interface within the SWCNT-TiNS composite. Consequently, interfacial electron transfer from TiNS to SEG was greatly improved, inhibiting the recombination of photogenerated electron-hole pairs. In contrast, the better visible light photoactivity from SWCNT-TiNS was proposed to originate from the increased optical absorption of the SWCNT component at longer wavelengths relative to that of SEG. Accordingly, it was proposed that under visible light irradiation, photoinduced electrons generated at the SWCNT

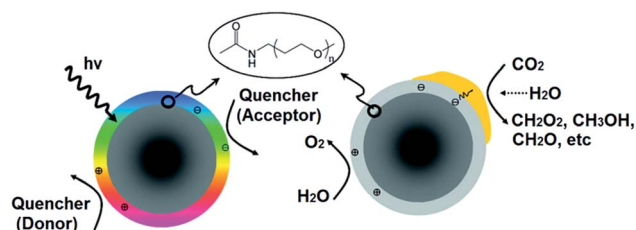


Fig. 20 PEG-functionalised carbon nanoparticles undergoing radiative recombination (left) and noble metal-coated & PEG-functionalised carbon nanoparticles photoreducing CO_2 (right). Reprinted with permission from ref. 184. Copyright 2011 American Chemical Society.

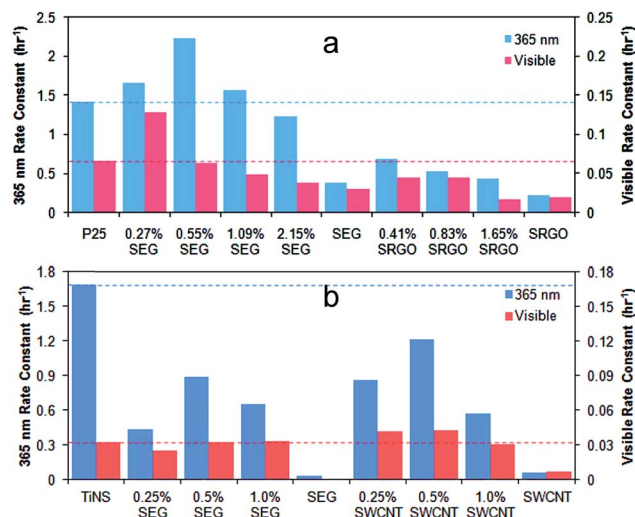


Fig. 21 Methane formation rate of (a) SEG-P25 and SGRO-P25 films under UV and visible light illumination, and (b) SEG-TiNS and SWCNT-TiNS films under UV (100 W Hg vapour lamp, 365 nm) and visible light irradiation (natural daylight bulb, ~400 to 850 nm). Reprinted with permission from ref. 206 and 209. Copyright 2011 and 2012 American Chemical Society.



surface were transferred to the TiNS substrate for subsequent CO₂ photoreduction.

A series of graphene-Ta₂O₅ composites, with different loadings of the carbon, were prepared by Lv *et al.* through a hydrothermal route.²⁰⁷ Impregnation with a Ni/NiO co-catalyst activated these composites for CO₂ photoreduction to CH₃OH and H₂ under UV-Vis illumination under aqueous conditions. Composites with 1 wt% graphene exhibited the highest photoactivity; in CO₂-aerated water the composite produced 3.4 times and 2.3 times the amount of CH₃OH and H₂ respectively than achieved over pure Ta₂O₅. This enhanced photocatalysis was attributed to the benefits of the graphene support in promoting effective interfacial charge transfer, as illustrated in Fig. 22. Photoinduced electrons generated at the Ta₂O₅ surface could be effectively transported to the surfaces of either graphene or the Ni/NiO dopant for subsequent transfer and CO₂ reduction.

Unlike the preceding materials, wherein as-synthesised graphene nanosheets were integrated with semiconductor particles through a simple impregnation/adsorption process, Tu *et al.* followed an alternative approach to prepare hollow spheres of alternating titania and graphene nanosheets for CO₂ photoreduction.²¹⁰ Fig. 23 shows how the surface of a poly(methyl methacrylate) (PMMA) template was first modified with a cationic polyelectrolyte, *e.g.* polyethylenimine (PEI) which electrostatically attracted negatively charged Ti_{0.91}O₂ nanosheets onto their surface. Subsequent surface modification of these titania-coated PMMA beads with PEI facilitated coating by negatively charged graphene oxide (GO) nanosheets. This process was repeated multiple times to thereby prepare a PMMA core composite with five alternating layers of (PEI/Ti_{0.91}O₂/PEI/GO)₅. Subsequent microwave treatment under an Ar environment decomposed the PMMA template, removed the PEI moiety, and reduced the GO to graphene (G). TEM (Fig. 23b and c) revealed that these Ti_{0.91}O₂ and graphene nanosheets alternated in a parallel, ordered lamellar arrangement, with a repeat distance estimated to be around 1.15 nm. Catalytic screening

under UV-Vis illumination showed that the (G/Ti_{0.91}O₂)₅ hollow spheres were superior for CO₂ photoconversion *versus* (Ti_{0.91}O₂)₅ hollow spheres (synthesised without GO) and P25 titania in a glass reactor filled with CO₂ at ambient pressure, albeit the principal photolysis product was CO not CH₄. A number of explanations for the excellent behaviour of these (G/Ti_{0.91}O₂)₅ hollow composites were advanced. The ultrathin nature of the Ti_{0.91}O₂ nanosheets likely drove rapid transfer of charge carriers to active sites, increasing the probability of the photogenerated electrons participating in subsequent photo-reduction chemistry; the compact stacking of Ti_{0.91}O₂ and graphene nanosheets would allow efficient interfacial electron transfer from the Ti_{0.91}O₂ to graphene layers, this spatial separation increasing the lifetime of photoexcited electrons. Hollow composite cores may also trap and multiply scatter incident photons, thereby improving light absorption and quantum efficiency.

Reduced graphene oxide (RGO) has also been employed within unique heterostructured optoelectronic materials, in which “tree”-like three-dimensional hierarchical titania nanorods,²¹¹ or one dimensional ZnO nanorods²¹² (as wide-band-gap UV absorbing semiconductors) are contacted with CdS visible light sensitising nanoparticles *via* a suspended, RGO film. The resulting architectures ensure precise spatial localisation of each component and tunable charge-transport properties, facilitating a 100–150 % increase in the associated photocurrent density relative to the metal oxide/chalcogenide system alone, and 25% increase in methylene blue decomposition (ZnO/RGO/CdS), and 240% increase in the applied bias to photo-electrochemical hydrogen generation efficiency for hydrogen production *via* water-splitting (TiO₂/RGO/CdS).

2.3. Co-catalysts and plasmonic photocatalysts

Co-catalysts, typically Platinum Group and noble metals, are frequently deposited on semiconductor surfaces in order to (i) maximise the lifetime of photogenerated charge carriers, (ii) to activate reactants, and (iii) to improve the absorption of incident light.^{213–216} Noble metals such as Au and Ag have lower Fermi levels than their partnered semiconductors, and hence can act as electron sinks that accept photoexcited electrons,^{217,218} thereby retarding electron–hole recombination and

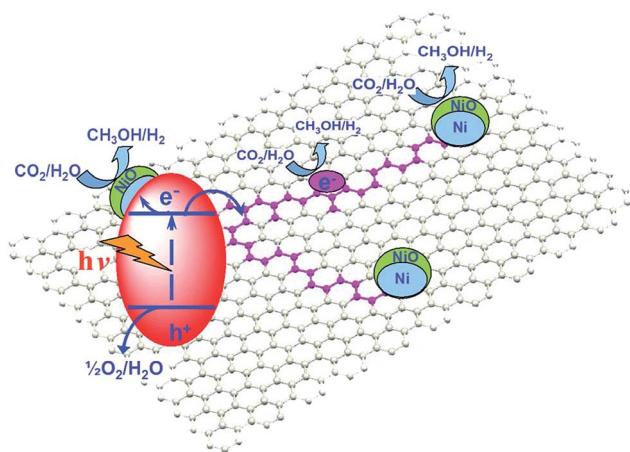


Fig. 22 Schematic of potential pathways for the transport of photo-induced electrons from a Ta₂O₅ semiconductor nanoparticle to active CO₂ photoreduction sites mediated by graphene. Reproduced from ref. 207 with permission from The Royal Society of Chemistry.

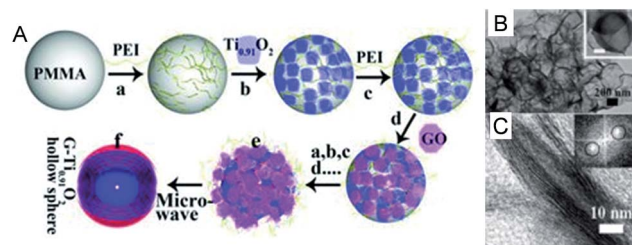


Fig. 23 (A) Stepwise preparation of alternating TiO₂ and graphene nanosheet hollow sphere assemblies, (B) TEM and (C) HR-TEM images of (G–Ti_{0.91}O₂)₅ hollow spheres. Scale bar of the inset in (c): 100 nm. Inset in (C) is the fast Fourier Transform pattern of the ordered lamellar structures exhibited by the (G–Ti_{0.91}O₂)₅ hollow spheres. Reproduced with permission from ref. 210. Copyright 2012 Wiley.



increasing the availability of electrons for CO₂ photoreduction. It is generally held that, when co-catalysts are employed, photoconversion efficiency varies with the co-catalyst particle size, in turn usually governed by the method of their incorporation,^{75,157,219} albeit the nature of this relationship (proportional or inversely proportional), magnitude and origin remains poorly studied and understood.

Recent work by Iizuka *et al.* has shown that the photoactivity of plate-like AlA₄Ti₄O₁₅ (A = Ca, Sr, and Ba) layered perovskites impregnated with a Ag co-catalyst varies with the method of co-catalyst loading.⁷⁵ Silver modification of AlA₄Ti₄O₁₅ with a AgNO₃ precursor was achieved *via*: (i) wet impregnation followed by H₂ reduction; (ii) *in situ* photodeposition; or (iii) liquid phase reduction using NaPH₂O₂. Under UV illumination and water, all these Ag-loaded AlA₄Ti₄O₁₅ materials were active in photoreducing CO₂ into CO predominantly, and a small amount of HCOOH, accompanied by H₂ and O₂ evolution, under a constant CO₂ flow rate of 15 mL min⁻¹. Ag loaded by liquid phase reduction demonstrated the highest photoactivity, followed by that through impregnation/H₂ reduction, ahead of those photodeposited. When photodeposition was employed, Ag NPs of around 30–40 nm populated edges of the as-prepared BaLa₄Ti₄O₁₅, while liquid phase reduction resulted in a homogeneous dispersion of <10 nm nanoparticles over the layered perovskite. Materials prepared *via* impregnation/H₂ reduction produced large aggregates of ~50 nm Ag particles, although some 10–20 nm Ag particles were observed at the edges of impregnated/reduced samples after photolysis. The basal plane and edges of plate-like BaLa₄Ti₄O₁₅ were suggested as the respective active sites for photooxidation and photoreduction. Accordingly, Ag deposited at the basal plane may undergo photodissolution and redeposition at the semiconductor edges during photocatalysis, with the particle size of such redeposited Ag dependent upon the concentration of dissolved silver ions. Consequently, *in situ* photolysis modified the Ag particle size to increase in the order: liquid phase reduction < impregnation/H₂ reduction < photodeposition. It was concluded that the photoactivity of Ag/BaLa₄Ti₄O₁₅ varied inversely with Ag particle size, a function of the co-catalyst incorporation route.

TiO₂ NTs arrays promoted by ultrafine Pt NPs, uniformly deposited *via* a rapid, microwave-assisted solvothermal approach, were investigated by Feng and co-workers.²²⁰ In this method, the crystalline nanotube arrays were first loaded in a Teflon reaction chamber containing a 0.15 M H₂PtCl₆/CH₃OH solution. After an overnight immersion process, the reaction chamber was rapidly heated to 120 °C and held for 20 min before cooling. The resulting Pt/TiO₂ NTs arrays were isolated, washed and dried prior to catalytic testing. Dark field (S)TEM shown in Fig. 24a highlights the uniform distribution of Pt NPs (with an average diameter of 3.4 nm) across the TiO₂ NTs arrays. While such wet impregnation is simple to conduct and yields small Pt NPs, they exhibited a broad size distribution spanning 1.8–4.9 nm. Nevertheless, under irradiation by a solar simulator and water vapour, these Pt/TiO₂ NTs arrays were superior to unpromoted TiO₂ NTs arrays in photoreducing CO₂ to CH₄ and trace C₂H₆ at 45 °C. The excellent photoactivity of Pt/TiO₂ NTs arrays was attributed to the high Pt nanoparticle dispersion

(and hence density of surface active sites), coupled with efficient electron diffusion properties through the nanotube arrays.

In contrast, Wang *et al.* utilised a unique gas phase technique, tilted-target sputtering (TTS), to deposit size-controlled ultrafine Pt NPs onto a single crystalline titania thin film comprised of 1-D TiO₂ columns.⁵¹ TTS enables precise control over both the flux of sputtered metal atoms and their radial distribution. Locating the TiO₂ film in the outer region of the deposition flux zone, where low energy atoms participate in nanoparticle formation, permitted the selective growth of ultrafine Pt NPs on the semiconductor surface as shown by TEM in Fig. 24b; Pt NPs with an average particle size of 1.04 ± 0.08 nm were uniformly coated on anatase TiO₂. It was claimed that such Pt NPs were preferentially deposited at surface defects on the titania substrate. While this gas-phase method necessitates high vacuum instrumentation, and hence is not readily scalable, it does offer Pt NPs possessing a narrow size distribution and tunable diameter (through varying the deposition time). The smallest and largest nanoparticles reported *via* this approach exhibited mean particle diameters of 0.63 ± 0.06 nm and 1.87 ± 0.31 nm, respectively (albeit a narrow range spanned). Subsequent exposure of Pt/TiO₂ catalyst films to water vapour and UV irradiation evidenced improved photoactivity compared with P25 and an analogous bare TiO₂ film for CO₂ photoreduction, forming predominantly CH₄ with trace CO under a slow CO₂ stream in a continuous flow reactor. Optimal photoactivity was achieved for a 1.04 ± 0.8 nm Pt/TiO₂ catalyst film, which delivered a remarkable combined quantum efficiency to CO and CH₄ of 2.41%. The observed photoactivity enhancement reflected a combination of the high surface area and single crystalline nature of the TiO₂ thin film, and excellent charge carrier separation characteristics conferred by the ultrafine Pt NPs. However, photocatalysis deteriorated after 5 h of irradiation, attributed to saturation of reactive sites by strongly-bound intermediate products, and consequent site-blocking.

Noble metals are often employed as co-catalysts to effect charge separation, but have been recently established to play an additional role as plasmonic photocatalysts in their own right, owing to the ability of gold and silver to absorb visible light through their localised surface plasmon resonance (LSPR).^{96,145,221–225} This latter hot topic requires an

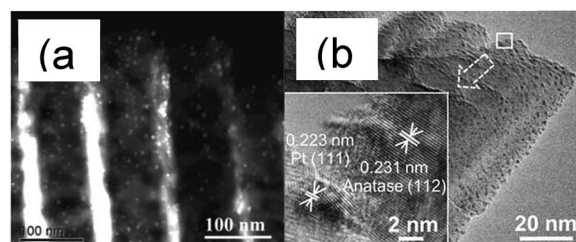


Fig. 24 (a) Dark field (S)TEM image of ultrafine Pt NPs deposited on TiO₂ nanotube arrays,²²⁰ and (b) TEM image of size-resolved ultrafine Pt NPs on TiO₂ film. Inset: HRTEM image showing the lattice fringes corresponding to anatase TiO₂ (112) and Pt (111) NPs. Reproduced from ref. 157 with permission from The Royal Society of Chemistry.



understanding of the basic principles underlying the plasmonic phenomenon. The LSPR is a collective oscillation of free electrons within metal structures, established when the natural oscillation frequency of surface electrons (induced by charge density redistribution), resonates with the frequency of incident photons. The free electrons of plasmonic Au, Ag, and Cu nanostructures can be excited by the electromagnetic field of incident visible light; as the light wavefront impinges, the electron density is polarised across these metal nanostructures, such that free conduction electrons coherently oscillate in phase with the light, creating a dynamic dipole oscillator at the metal surface (Fig. 25).^{225–227} Such intraband LSPR absorption (e.g. by Au 6sp electrons) induced by visible light is fundamentally different from the interband absorption caused by ultraviolet light (Au electrons excited from the 5d to 6sp bands).²²⁸

The strength and frequency of plasmon resonances depends on the size, shape, composition (for alloys) and local dielectric environment of the associated nanoparticles (see Fig. 26). These variations in LSPR peak positions and strengths strongly influence the photocatalytic capacities of such plasmonic nanomaterials.^{215,230}

On the basis of the literature, at least three mechanisms have been proposed to account for the enhanced visible light photoactivity of noble metal/semiconductor plasmonic photocatalysts. First, it is hypothesised that visible light photoexcited electrons at the surface of the plasmonic metal can migrate across the metal–semiconductor interface into the conduction band of the associated semiconductor, or transferred directly to adsorbates, providing a source of localised, energetic reductants.²³¹ Second, the polarised electric field induced by the LSPR of metal NPs could enhance reactant activation over neighbouring supports by the interplay between the resonating electron cloud of the metal NPs and nearby adsorbates (polarisable or possessing polar functional groups). Finally, photoexcited electrons may not actually transfer from plasmonic metal NPs to adjacent semiconductors/reactants nor interact with them indirectly *via* field effects, but may rather liberate heat during relaxation of photoelectrons to their groundstate, thereby promoting thermal catalysis, although it has proven extremely difficult to qualitatively or quantitatively determine any such heating effect.²³² All these models account for an increase in the photoexcited electrons available for chemical reduction.²²⁷

Plasmon-enhanced CO₂ photoconversion has been recently reported,^{233,234} exemplified by AgX : Ag (X = Cl or Br) plasmonic

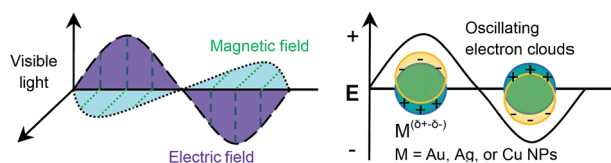


Fig. 25 Electromagnetic field of visible light interacting with plasmonic metal NPs: a dipole oscillator forms and resonates with the electromagnetic field of the incident visible light. Reproduced with permission from ref. 229.

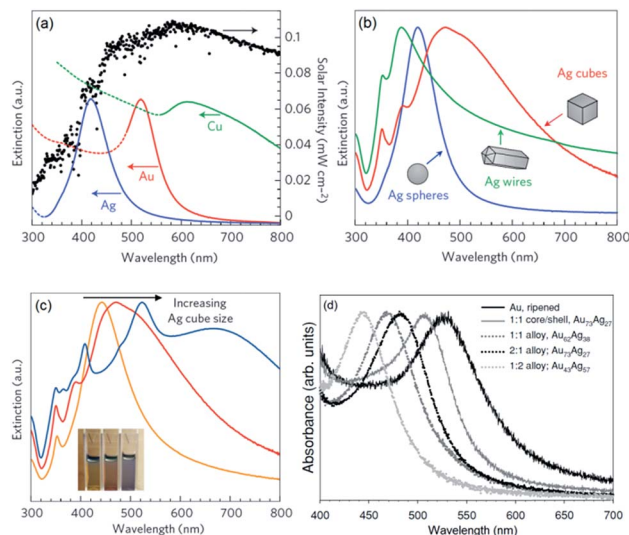


Fig. 26 The LSPR bands of plasmonic metal nanostructures with different shapes, sizes or compositions (for alloys): (a) nanoparticles of Au, Ag, and Cu; (b) Ag nanostructures with various shapes; (c) nanocubes of Ag with different cubic sizes; and (d) alloy of Au–Ag with different Au : Ag ratios. Reprinted by permission from Macmillan Publishers Ltd. Ref. 227, copyright 2011. Reproduced with permission from ref. 230. Copyright 2011 Wiley.

NPs synthesised through a glycerol-mediated precipitation route in the presence of polyvinylpyrrolidone.²³⁵ Despite their similar synthetic protocols, AgCl : Ag and AgBr : Ag exhibited cube-tetrapod-like and hexagonal nanoplates respectively. XPS and XRD confirmed the presence of metallic Ag on the as-prepared AgX : Ag NPs, with UV-Vis revealing significantly different band gaps of 3.95 (AgCl) and 3.45 eV (AgBr). When dispersed in NaHCO₃ aqueous medium under visible light, the AgX : Ag plasmonic photocatalysts were active for photo-reducing CO₂ into CH₃OH, attributed to the metallic Ag LSPR influencing the contacted AgX : Ag NPs. Recycling experiments indicated that these plasmonic catalysts were stable under the screening conditions, although *in situ* Ag⁺ reduction to additional silver metal is a plausible deactivation pathway following prolonged irradiation.

Hou *et al.* deposited islands of plasmonic Au NPs onto a sol-gel prepared TiO₂ thin film *via* electron beam evaporation.¹⁴⁸ Under visible light illumination and water vapour the resulting Au-promoted TiO₂ thin film exhibited a 24-fold activity enhancement relative to a bare TiO₂ thin film for CO₂ photo-reduction to CH₄ in a stainless steel reactor at 75 °C. The low, but finite, photoactivity of the parent TiO₂ film was attributed to defect-induced, sub-band gap photoexcitation. Complementary calculations suggested that direct electron transfer from Au NPs to TiO₂ was not feasible under plasmonic excitation, and hence the superior photoactivity was ascribed to an increased sub-band gap charge carrier formation rate, indirectly induced by the LSPR of gold. Methane was the only reductant formed over the bare TiO₂ thin film under UV irradiation, however a range of products were formed over the Au/TiO₂ thin film wherein the production rate followed CH₄ > C₂H₆ > HCHO > CH₃OH.



Surprisingly, the pure Au NPs were also reported to generate these aforementioned organic products, although the overall productivity was lower than that of the Au/TiO₂ composite. The photocatalytic activity of Au NPs was proposed due to interband electronic transitions (and not the LSPR) wherein electrons were photoexcited to a potential more negative than the TiO₂ conduction band and redox potential required to form desired reduction products. The synergy between Au NPs and the TiO₂ film under UV irradiation was attributed to improved charge carrier separation.

Small Cu and Ag NPs which exhibit plasmonic effects have also been successfully loaded onto TiO₂ nanorod films by an electrochemical method.^{219,236} Tan *et al.* loaded Cu NPs onto a TiO₂ film *via* a 0.01 mM CuSO₄ and 0.1 M K₂SO₄ mixed electrolyte at a pulse potential of -0.8 V for between 0–300 s.²³⁶ Under UV illumination and water, the resulting composite film (prepared at the optimum 100 s deposition time) demonstrated superior activity to a bare TiO₂ or P25 film in photoreducing CO₂ into CH₄. The copper co-catalyst benefits were again ascribed to efficient charge separation due to plasmonic effects. However, it was reported that surface oxidation of Cu NPs to copper oxide occurred during photocatalytic screening. An electrochemical deposition method known as the double-potentiostatic method was also used to deposit Ag NPs onto a TiO₂ nanorod film.²¹⁹ This method favoured the formation of uniform and dense metallic nanoparticles due to quick nucleation and slow nanoparticle growth at high potential and low precursor concentration. Accordingly, Kong *et al.* loaded silver onto a TiO₂ film employing a 0.1 M KNO₃/0.2 mM sodium citrate/0.05 mM AgNO₃ electrolyte at nucleation potentials from -1.4 V to -0.8 V for 100 s, followed by a growth potential of -0.2 V for 2400 s. TiO₂/Ag films prepared at the optimum nucleation potential of -1.0 V exhibited improved photoactivity relative to a bare TiO₂ film in photoreducing CO₂ into CH₄ under UV illumination and water vapour. Photocatalytic performance was again postulated to arise from efficient charge separation due to silver plasmonic effects. Moreover, alloy or bimetallic plasmonic nanostructures, such as Au–Pt (as shown in Fig. 27a)²³⁷ and Ag–Pt (as shown in Fig. 27b),²³³ have also been discovered to enhance CO₂ the photoreduction by titania. In both cases, the introduction of plasmonic Au or Ag particles increased photocatalytic efficiency in terms of product selectivity and/or yield, ascribed to the LSPR effect of Au (Ag) NPs significantly increasing light absorption and charge separation of the photoexcited titania. Co-deposition of Au/Pt on TiO₂ NFs considerably enhanced photocatalytic activities for both H₂ generation and CO₂ reduction compared to singly decorated (Pt/TiO₂ or Au/TiO₂) fibres. Bijith and co-workers' study demonstrates that Ag, Pt and bimetallic Ag–Pt NPs enable CH₄ and CO product selectivity to be tuned:²³³ product yields were enhanced more than seven-fold compared with native TiO₂, with a high CH₄ selectivity. This was attributed to the enhanced availability of photoexcited electrons *via* improved electron–hole pair generation, and surface trapping of photoexcited electrons within the titania lattice, enabling the necessary accumulation of charge to drive the eight-electron CH₄ forming process from adsorbed CO₂.

2.4. Miscellaneous photocatalysts

Cationic and/or anionic doping is commonly employed to decrease semiconductor band gaps.^{238–242} Richardson *et al.* co-doped TiO₂ with Cu and Ga *via* a sol–gel route to form composites that were active in CO₂ photoreduction at longer wavelengths than possible utilising P25.¹³⁹ The absorption band edge wavelength of doped photocatalysts increased in the order P25 < Ga/TiO₂ < Cu/TiO₂ < Cu, Ga/doped TiO₂, with a corresponding decrease in the band of the doped-materials relative to P25. It should be noted that the absorption band edges of doped materials still resides in the UV region despite their modified optical properties. Under 200 W near-UV (350–450 nm), 350 W mid-UV (280–350 nm) or 500 W deep-UV (240–260 nm) irradiation, and immersion in a NaOH and KHCO₃

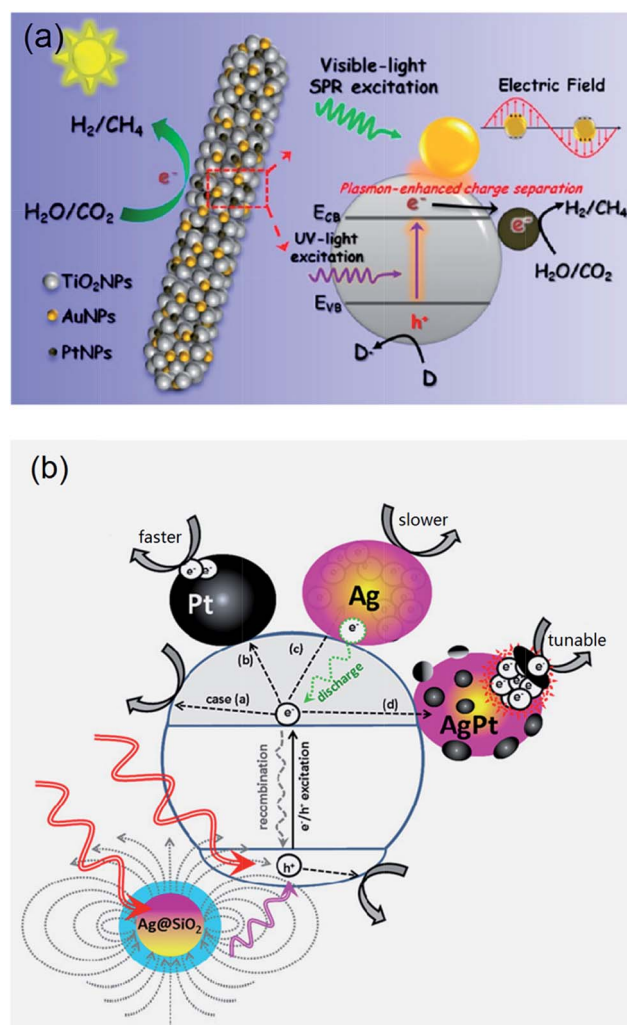


Fig. 27 (a) Illustration of the photocatalytic process to produce H₂ and to reduce CO₂ over Au/Pt/TiO₂ NFs. Reprinted with permission from ref. 237. Copyright 2010 American Chemical Society. (b) Illustration of different photoexcited charge pathways following electron–hole generation assisted by plasmonic nanoparticles over core–shell Ag@SiO₂: transfer to the [a] semiconductor surface, [b] Pt NP surface, [c] Ag NP surface, and [d] bimetallic Ag–Pt surface. Reproduced with permission from ref. 233. Copyright 2013 IOP Publishing Ltd.





Table 2 Photocatalytic reaction conditions and CO₂ reduction performance of exemplar nanostructured materials

Material	Light source	T/°C	P _{CO₂} /bar	Product yield/ $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	Selectivity (product)/mol%	Quantum efficiency/%	Reference
ZnGa ₂ O ₄	300 W Xe	—	1	1 wt% RuO ₂ 7245, mesoporous 762	100 (CH ₄)	—	113
Pt/TiO ₂	400 W Xe (20 mW cm ⁻² 250–388 nm)	22–32	1	1361 (CH ₄), 180 (CO)	88.5 (CH ₄), 11.5 (CO)	2.33 (CH ₄)0.077 (CO)	51
Zn ₂ SnO ₄	300 W Xe	—	1	Bulk 17.0 (CH ₄), atactic 34.5, micro-octahedra 54.6, nanoplate/micro-octahedra 288.9, RuO ₂ /Pt 1246.3	100 (CH ₄)	—	155
W ₁₈ O ₄₉	300 W Xe(30 mW cm ⁻²)	70	1	11.31 (CH ₄ , visible) 858 (CH ₄ , UV-visible)	95 (CH ₄), 5 (ethanol, acetone...)	0.03 (CH ₄ , visible)	65
Au/Pt-TiO ₂	500 W Xe	—	—	114 (CH ₄), 20 (CO)	85 (CH ₄),15 (CO)	—	234
(RuO ₂ + Pt)-Zn ₂ GeO ₄	300 W Xe	RT	1	25	100 (CH ₄)	—	94
Nafion layer-enhanced Pd-TiO ₂	300 W Xe ($\lambda > 300$ nm)	—	—	21.9 (CH ₄), 1.03 (C ₂ H ₆)	95.5 (CH ₄), 4.5 (C ₂ H ₆)	—	170
Pt-Cu/TiO ₂	200 W Xe (320–780 nm)	50	2	9.8 (CH ₄), 5.9 (CO), 51 (H ₂)	14.7 (CH ₄), 8.8 (CO)	—	249
0.5 wt% Cu/TiO ₂ -SiO ₂	Xe (2.4 mW cm ⁻² 250–400 nm)	—	—	10 (CH ₄), 60 (CO)	14.3 (CH ₄), 85.7 (CO)	0.56 (CH ₄), 0.85 (CO)	121
0.5 wt% Pt ZnAl ₂ O ₄ -ZnGaNO	300 W Xe ($\lambda \geq 420$ nm)	—	1	9.2	100 (CH ₄)	—	111
0.5 wt% Pt/NaNbO ₃	300 W Xe ($\lambda > 300$ nm)	—	0.8	0% cubic 2.19 (CH ₄), 15 (CO), 45 (H ₂), 69% cubic 5.86 (CH ₄), 16 (CO), 42 (H ₂), 98% cubic 4.91 (CH ₄), 12 (CO), 25 (H ₂)	12.7 (CH ₄), 87.3 (CO), 26.8 (CH ₄), 73.2 (CO), 29 (CH ₄) 71 (CO)	—	250
AgBr/TiO ₂	150 W Xe ($\lambda > 420$ nm)	RT	75	5.71 (CH ₄), 15.57 (CH ₃ OH), 2.66 (C ₂ H ₅ OH), 6.43 (CO)	18.8 (CH ₄) 51.3 (CH ₃ OH) 8.8 (C ₂ H ₅ OH)	—	163
Amine-functionalised TiO ₂	Xe ($\lambda > 302$)	—	—	3.08 (CH ₄), 11.92 (CO)	20.5 (CH ₄), 79.5 (CO)	—	67
Pt-, Au-, or Ag-TiO ₂	350 W Xe (35 mW cm ⁻²)	60	—	0.2% Pt 2.85, 0.2% Au 1.51, 0.1% Ag 0.65, TiO ₂ 0.238	100 (CH ₄)	0.68,0.36, 0.15, 0.06	123
Ti _{0.91} O ₂	300 W Xe	—	1	Graphene 1.14 (CH ₄), 8.91 (CO), Ti _{0.91} O ₂ 1.41 (CH ₄)	11.4 (CH ₄), 88.6 (CO), 100 (CH ₄)	—	210
Cu(i) dye-sensitised TiO ₂	300 W Xenon ($\lambda > 420$ nm)	—	1	0.725	100 (CH ₄)	—	174
Ga ₂ O ₃	300 W Xe (500 mW cm ⁻²)	—	—	0.3935	100 (CH ₄)	0.007	107
RuO ₂ -Zn ₂ GeO ₄	300 W Xe	—	1	0.39 (CH ₄), 1.01 (CO)	25.5 (CH ₄), 74.5 (CO)	—	97
Carbon nanotubes@ Ni/TiO ₂	75 W visible daylight lamp ($\lambda > 400$ nm)	50	1	0.145	100 (CH ₄)	—	185
Pd-TiO ₂	500 W Hg ($\lambda > 310$ nm)	5	0.867	1% Pd 0.037 (CH ₄), 0.06 (C ₂ H ₆), 0.04 (CO), TiO ₂ 0.027 (CH ₄), 0.353 (CO)	78.9 (CH ₄), 12.7 (C ₂ H ₆), 8.4 (CO), 7.1 (CH ₄), 92.9 (CO)	—	68
N-doped ZnO	8 W fluorescent tube 7 mW cm ⁻²	50	2	0.01 (CH ₄), 0.03 (CH ₃ OH), 0.04 (CO), 0.09 (H ₂)	4.8 (CH ₄), 19.0 (CH ₃ OH), 23.8 (CO)	—	112
CdS/TiO ₂ , Bi ₂ S ₃ /TiO ₂	500 W Xe ($\lambda \geq 400$ nm)	—	1	CdS 40.1, TNTs-Cds 32.2,Bi ₂ S ₃ 64.5, TNTs-Bi ₂ S ₃ 45.3, TNTs 20.5, P ₂₅ 18.2	100 (CH ₃ OH)	—	165
Graphene-modified NiO _x -Ta ₂ O ₅	400 W Metal halogen lamp	RT	1	52 (CH ₃ OH), 41 (H ₂)	55.9 (CH ₃ OH)	—	207
AgCl : Ag, AgBr : Ag	300 W Xe, ($\lambda \geq 400$ nm)	0	1	AgCl 37.7, AgBr 21.7	100 (CH ₃ OH)	1.3 0.97	235
Bi ₂ WO ₆	300 W Xe ($\lambda \geq 420$ nm)	0	—	Hollow microspheres 16.3, bulk 0.64	100 (CH ₃ OH)	—	157

Table 2 (Contd.)

Material	Light source	$T/^\circ\text{C}$	$P_{\text{CO}_2}/\text{bar}$	Product yield/ $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	Selectivity (product)/mol%	Quantum efficiency/%	Reference
$\text{g-C}_3\text{N}_4$	300 W Xe ($\lambda \geq 420 \text{ nm}$, 267 mW cm^{-2})	20	1.013	$\text{u-g-C}_3\text{N}_4$ 6.28 (CH_3OH), 4.51 ($\text{C}_2\text{H}_5\text{OH}$), 21.33 (O_2), m-g- C_3N_4 3.64 ($\text{C}_2\text{H}_5\text{OH}$), 10.29 (O_2), trace (CH_3OH)	19.6 (CH_3OH), 14 ($\text{C}_2\text{H}_5\text{OH}$), 26.1 ($\text{C}_2\text{H}_5\text{OH}$)	0.04 (CH_3OH + $\text{C}_2\text{H}_5\text{OH}$), 0.018 ($\text{C}_2\text{H}_5\text{OH}$)	120
TiO_2	500 W Xe ($\lambda > 300 \text{ nm}$, 2.5 mW cm^{-2})	—	1	Anatase-brookite 0.59, flower-like rutile 0.32, rutile 0.30, anatase 0.19, P_{25} 0.18	100 (CH_3OH)	0.0059, 0.0032, 0.0030, 0.0019, 0.0018	79
$\text{FeTiO}_3/\text{TiO}_2$	500 W Xe ($\lambda > 300 \text{ nm}$)	—	—	TiO_2 0.175 (UV-visible), 10% $\text{FeTiO}_3/\text{TiO}_2$ 0.338 (UV-visible), 20% $\text{FeTiO}_3/\text{TiO}_2$ 0.462 (UV-visible), 50% $\text{FeTiO}_3/\text{TiO}_2$ 0.298 (UV-visible), TiO_2 0.141 (visible), 10% $\text{FeTiO}_3/\text{TiO}_2$ 0.319 (visible), 20% $\text{FeTiO}_3/\text{TiO}_2$ 0.432 (visible), 50% $\text{FeTiO}_3/\text{TiO}_2$ 0.352 (visible)	100 (CH_3OH)	—	166
$\text{ZIF-8}/\text{Zn}_2\text{GeO}_4$	500 W Xe	—	—	Zn_2GeO_4 0.14 (CH_3OH), $\text{Zn}_2\text{GeO}_4/\text{ZIF-8}$ 0.23 (CH_3OH), 1 wt% Pt/ $\text{Zn}_2\text{GeO}_4/\text{ZIF-8}$ 0.27 (CH_3OH)	100 (CH_3OH)	—	95
Graphene oxide (GO)	300 W halogen lamp	25	—	GO-3 0.172, GO-1 0.110, GO-2 0.089	100 (CH_3OH)	—	208
Zn-Cu-M(III) ($\text{M} = \text{Al, Ga}$) layered double hydroxides	500 W Xe (UV-visible)	32–40	0.023	$[\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga}(\text{OH})_8]^{2+}$ 0.17 (CH_3OH), 0.079 (CO), $[\text{Zn}_3\text{Ga}(\text{OH})_8]^{2+}$ 0.051 (CH_3OH), 0.080 (CO), $[\text{Zn}_3\text{Al}(\text{OH})_8]^{2+}$ 0.039 (CH_3OH), 0.62 (CO), $[\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Al}(\text{OH})_8]^{2+}$ 0.13 (CH_3OH), 0.37 (CO)	68.3 (CH_3OH), 31.7 (CO), 38.9 (CH_3OH), 61.1 (CO), 5.9 (CH_3OH), 94.1 (CO), 26 (CH_3OH), 74 (CO)	0.00015 (CH_3OH), 0.000019 (CO), 0.00028 (CH_3OH), 0.000083 (CO), —	134
$\text{Ag}/\text{Ala}_4\text{Ti}_4\text{O}_{15}$ ($\text{A} = \text{Ca, Ba}$ and Sr)	400 W Hg	RT	1	Ca 4.3 (HCOOH), 3.3 (CO), 18.7 (H_2), 7.0 (O_2), Ba 10 (HCOOH), 14.3 (CO), 33.3 (H_2), 23.3 (O_2), Sr 16.7 (HCOOH), 6.0 (CO), 9.0 (H_2), 6.0 (O_2)	HCOOH : 12.9, CO : 9.9, HCOOH : 82.3, CO : 17.7, HCOOH : 44.3, CO : 15.9	—	75
BiVO_4	300 W Xe ($\lambda \geq 400 \text{ nm}$, or without UV filter)	0	1	Monoclinic BiVO_4 110 (visible), tetragonal BiVO_4 12.5 (visible), monoclinic BiVO_4 2150 (UV-visible), tetragonal BiVO_4 250 (UV-visible)	100 ($\text{C}_2\text{H}_5\text{OH}$)	—	77
Dye-sensitised + dehydrogenase TiO_2 KTaO_3 by SSR or solvothermal	Halogen lamp ($\lambda > 420 \text{ nm}$ 45 mW cm^{-2}) 300 W Xe	20 —	— —	287.2 SSR- KTaO_3 0.436 (H_2), 0.041 (CO), 0.173 (O_2), hexane- KTaO_3 0.088 (CO), 40.13 (H_2), 0.4 (O_2), ethanol- KTaO_3 0.283 (CO), 84.7 (H_2), 0.2 (O_2)	100 (CO) 6.3 (CO), 0.2 (CO), 0.6 (CO)	— —	176 74



aqueous medium, Cu and Ga co-doped TiO_2 photocatalysts were superior to P25 and the monometal-doped titanias in photoreducing CO_2 to HCOOH and other carbonic products (determined by TOC) in a continuous flow reactor at room temperature. Highest photoactivity was observed for the $\text{Cu}_{0.78}\text{-Ga}_{0.22}/\text{TiO}_2$ catalyst, with Cu the proposed CO_2 adsorption and reduction site for HCOOH and other organic products which include trace CH_3OH and HCHO .

Anion doping by Tsai *et al.* improved the visible light absorption properties of InTaO_4 . Doping was performed by nitridation of SSR prepared InTaO_4 under flowing NH_3 at 800°C ,²⁴³ resulting in the absorption band edge shifting to longer wavelengths in comparison to pure InTaO_4 . Results were attributed to hybridisation between the N 2p and O 2p orbitals, which shifts the valence band upwards, thereby narrowing the InTaO_4 band gap. Under visible light illumination (390 to 770 nm) and in the presence of water, the prepared N-doped InTaO_4 outperformed pure InTaO_4 in photoreducing CO_2 into CH_3OH in a continuous flow reactor. XANES analysis indicated that N doping narrowed the band gap, and induced oxygen vacancies, the latter possibly contributing to photocatalytic enhancement. The photoactivity of the N-doped InTaO_4 was further improved by the addition of a Ni@NiO core-shell co-catalyst, incorporated through a sequence of wet impregnation, chemical reduction and final calcination. Promotion by the Ni@NiO core-shell co-catalyst was ascribed to enhanced charge separation and light harvesting.

Solid solutions formed between wide and narrow band gap semiconductors have been reported to possess valence and conduction bands that provide smaller gaps than their parent materials.^{244–247} In general, the component semiconductors must possess the same crystal structure and similar lattice parameters. Liu *et al.* recently reported the application of $\text{Cu}_x\text{-Ag}_y\text{In}_z\text{Zn}_k\text{S}_m$ solid solutions as visible light photocatalysts for CO_2 photoreduction.²⁴⁸ The band gap of this composite was a strong function of composition, and spanned 1.33–1.44 eV. Visible light irradiation (1000 W Xenon lamp at $\lambda > 400$ nm) in a NaHCO_3 aqueous medium of these solid solution photocatalysts facilitated CO_2 photoreduction to CH_3OH in a closed glass gas circulation system. Systematic relations could not be derived between the catalyst composition and photoactivity, although photoactivity was composition dependent. A range of co-catalysts were investigated, including RuO_2 and $\text{Rh}_{1.32}\text{Cr}_{0.66}\text{O}_3$, although these did not promote CO_2 conversion. Methanol productivity was enhanced under a H_2 environment, wherein a higher density of protons was formed.

3. Conclusions and future directions

A wide variety of approaches have been developed for the synthesis of photocatalytically active materials for CO_2 reduction to solar fuels and chemicals. To date, there is no standard protocol for evaluating photocatalytic performance, or single parameter that enables quantitative benchmarking of CO_2 conversion efficiencies to specific carbon-containing solar fuels or chemicals. In a first step towards addressing these deficiencies, Table 2 compares a range of the nanomaterials

discussed in this review, with a view to informing on which show the most promise with respect to productivity per unit catalyst mass, and thus provide a strong rationale for future development. Of course, many additional factors such as earth abundance, cost, toxicity, and scalability will also influence which materials are ultimately best suited to commercialisation. However, a step-change in photoactivity, and comprehensive mechanistic insight into the catalytic cycle and nature of the surface sites participating in CO_2 adsorption and reduction, is required before such considerations should influence ongoing fundamental research efforts.

The optoelectronic properties of crystalline materials, and hence their photoactivity, are a strong function of the crystal structure, with different semiconductor polymorphs exhibiting disparate photocatalytic behaviour reflecting their surface atom arrangement and attendant electronic band structure. Although surface defects may serve as electron-hole recombination centres detrimental to the achievement of high quantum efficiencies, such sites can also promote visible light absorption and hence photocatalysis. Band gap engineering of earth abundant, large band gap semiconductor to facilitate visible light photocatalysis remains an important barrier to visible light absorption properties, although transition metal and p-block dopants provide a simple route to band-gap narrowing. Integrated dyes or small band gap semiconductors may also be employed as visible light sensitizers of conventional semiconductor photocatalysts, with the resulting hybrid, composite materials facilitating both UV and visible light capture and efficient charge carrier separation *via* preferential transfer of photoexcited electrons into one material and of holes into the other. In the latter regard, one- and two-dimensional semiconductor nanostructures, exhibiting high surface to volume ratios, can promote efficient transport of charge carriers to adsorbates during photocatalysis.

Integration of photoactive semiconductors with electrically conductive materials such as graphene offers new routes to maximising charge carrier lifetimes and consequent electron transfer to CO_2 . High surface area and porous materials increase the density of surface active sites available to chemically bind and activate CO_2 , its reactive intermediates, and water. Such nanostructures can be created through the synthesis of semiconductors with intrinsic porosity on the micro-, meso- or macroscale, or *via* immobilisation (embedding) of photocatalysts onto (within) an inert, high area architecture. Three-dimensional hierarchical materials epitomise catalyst engineering, affording rapid molecular transport to/from active sites, enhanced light harvesting, and superior charge carrier transport and recombination characteristics. It seems extremely unlikely that any single semiconductor composition or structure can deliver the requisite optical, material and catalytic properties necessary to harness sunlight under ambient conditions for the rapid and selective photoreduction of CO_2 into the key chemical targets of methane, methanol, formaldehyde or ethene, hence the majority of promising systems employ co-catalysts whose contributions depend strongly on their method of incorporation.



Noble metal co-catalysts in particular offer exciting possibilities for visible light absorption through plasmonic effects, and indeed have even proven efficient photocatalysts in their own right for the selective oxidation of CO, ethene and ammonia²⁵¹ and reduction of nitroaromatics.²⁵² Photoreactor design will play an increasingly important role in ensuring optimum light (and catalyst) utilisation for CO₂ reduction, and enable quantitative benchmarking of different photocatalysts in terms of their absolute productivity, selectivity and quantum efficiency. Innovation is required to facilitate CO₂ separation/recycle, on-stream gas/liquid product separation, and optical materials to avoid losses in transmission to the internal reactor volume.

Ultimately, the final selection and commercialisation of the most promising (*i.e.* highly active, selective and stable) photocatalysts will be dictated by process economics, since even the highest value oxygenate or olefin products directly derivable from CO₂ will continue to face stiff competition with low cost fossil fuel sources for the foreseeable future. Indicative 2015 prices per metric ton are: methanol \$420; formaldehyde \$420; formic acid \$500, and ethylene/propylene \$800–1100. Overall process costs will be a strong function of the choice of chemical precursors, type and recyclability of solvents, (re)use of textural templates, mechanothermal processing, photocatalyst forming, and reactor operating conditions (temperature, pressure, separation and recycle). Many of the most promising photocatalysts described in this review utilise noble metal co-catalysts,^{40,51,94,123,161,213,220,234,249} and with common H₂PtCl₆ and HAuCl₄ prices in excess of \$10 000 per kg, high turnover numbers per metal atom (>3000) would be essential to even recoup the precursor costs. An obvious target for synthetic improvement is thus maximising noble metal efficiency through *e.g.* lowering the size/dimensionality of associated nanostructures, or atomically dispersing noble metal atoms exclusively within the terminating layer of catalysts.^{253–256} Soft and hard templating methods are widely adopted in heterogeneous catalysis to introduce porosity, and hence enhance the surface density and accessibility of active sites.¹³⁷ A number of photocatalysts for CO₂ reduction employ such templates to similar effect, typically surfactants (*e.g.* TTAB,¹⁰⁷ CTAB^{77,163,164} and P123 (ref. 78 and 112)) or polymers.²¹⁰ While their costs are comparatively low (\$150–350 per kg), in the majority of cases such surfactants are removed through combustion and hence are not recoverable, and even solvent-extraction protocols rarely recover sufficiently pure and chemically unaltered templates amenable to re-use, though ultrasonic template removal shows promise as an energy and atom efficient solution.²⁵⁷ The majority of synthetic strategies for nanostructure photocatalysts employ solvothermal processing, and hence comparatively low (<200 °C) temperatures (in the absence of a template calcination step) offering little scope for cost savings *via* energy input reduction. As with all syntheses, Green Chemistry principles provide the best general guidelines to reduce the number of reaction steps and minimise associated waste generation and the use of auxiliaries,²⁵⁸ in concert with lower production costs.

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