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Spatial separation of oxidation and reduction cocatalysts for efficient charge separation: Pt@TiO₂@MnO_x hollow spheres for photocatalytic reactions†

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Efficient charge separation is a critical factor for solar energy conversion by heterogeneous photocatalysts. This paper describes the complete spatial separation of oxidation and reduction cocatalysts to enhance the efficacy of charge separation and surface reaction. Specifically, we design Pt@TiO₂@MnO_x hollow spheres (PTM-HSs) with Pt and MnO_x loaded onto the inner and outer surface of TiO₂ shells, respectively. Pt favours electron trapping, while MnO_x tends to collect holes. Upon generation from TiO₂, electrons and holes flow inward and outward of the spherical photocatalyst, accumulating on the corresponding cocatalysts, and then take part in redox reactions. Combined with other advantages, such as the large surface area and appropriate pore size, the PTM-HSs exhibit high efficiency for the photocatalytic oxidation of water and benzyl alcohol. The mechanism of the oxidation process of benzyl alcohol over the photocatalyst is also presented.

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Introduction

Efficient charge separation is a critical factor for solar energy conversion by semiconductor-based systems. It is crucial for increasing the performance of solar cells, photoelectrochemical and photocatalytic systems.^{1,2} As an important application, photocatalytic oxidation requires exceptionally efficient charge separation. Within photooxidation reactions, the photooxidation of water into O₂ has long been considered as the bottleneck of the water-splitting process, so the invention of highly active water oxidation catalysts is a key step in the development of light-driven water splitting.³ In addition, the photocatalytic oxidation system can also be used to produce highly valued chemicals such as aldehydes and ketones. Compared with traditional methods with high temperature, toxic oxidants and hazardous waste,⁴ photocatalytic oxidation processes can be performed under mild and environmentally friendly conditions. Substances unstable at high temperatures may also be synthesized by such selective light-assisted processes.⁴ Recently, the emergence of a new family of metal-free polymer photocatalysts provided fine methods to enhance charge separation.^{5,6} For instance, heterojunctions between carbon nitride

and sulfur-mediated carbon nitride have been constructed to promote photocatalytic reactions.⁶ Besides, many other strategies were adopted to improve charge separation, while the results remain unsatisfactory because of diverse problems.^{1,7–9}

Cocatalyst loading has been proved to be an effective approach to accelerate charge separation.¹ Cocatalysts can be designed for oxidation and reduction purposes. Oxidation cocatalysts tend to capture holes (PbO₂, MnO_x and PdS,¹⁰ *etc.*), while reduction cocatalysts prefer electrons (Pt, Pd,¹ *etc.*). Meanwhile, they can promote the surface reaction of the redox process.¹¹ Yu *et al.* have reported the fabrication of TiO₂ nanosheets loaded with Pt. Compared with pure TiO₂ nanosheets, the photocatalytic activity of Pt decorated nanosheets was obviously improved.²

Simultaneous loading of oxidation and reduction cocatalysts could further improve the photocatalytic activity. Colón *et al.* fabricated Pt–TiO₂/g–C₃N₄–MnO_x composites and successfully proved that Pt and MnO_x trap electrons and holes, respectively, leading to a further separation of charges.¹² However, both reduction and oxidation cocatalysts are randomly distributed in this case, which results in a random flow direction of charge carriers when they migrate to the cocatalysts. In such a scenario, the possibility of electron–hole recombination will be increased. In addition, the short distance between the reduction and oxidation cocatalysts is unfavorable for redox reactions, for close redox sites may lead to severe back-reactions.

Spatial separation of oxidation and reduction cocatalysts is a method to solve this problem, yet limited success has been

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reported. Carbon nitride nanosheets have been fabricated to separate different cocatalysts, promoting the locally-incompatible oxidation and reduction reactions on the two surfaces.⁵ In addition, Pt particles (reduction cocatalyst) and MnO_x particles (oxidation cocatalyst) have been nicely deposited on different facets of BiVO_4 , exhibiting increased performance when compared to the randomly deposited counterparts.¹ To achieve more complete spatial separation of oxidation and reduction cocatalysts, as well as to make full use of the photocatalyst, we design and synthesize $\text{Pt@TiO}_2\text{@MnO}_x$ hollow spheres (PTM-HSs) with Pt particles and MnO_x loaded onto the inner and outer surfaces of TiO_2 hollow spheres, respectively. Different cocatalysts can be completely separated by the TiO_2 shells without intermixing. The photocatalytic material can be fully used owing to the thin shell (about 40–60 nm) of TiO_2 hollow spheres. TiO_2 is chosen in this study since it serves as an excellent benchmark photocatalyst for comparison purposes.^{13–15} Additionally, as a model structure, this concept (*i.e.*, different cocatalysts are separated by TiO_2 shells completely) can be extended to other redox cocatalysts such as Au, Ag, PbO_2 , *etc.*¹

Upon generation from TiO_2 , electrons and holes will flow inward and outward of the spherical TiO_2 shells, respectively, accumulating on corresponding cocatalysts and then taking part in redox reactions (Fig. 1). Electrons can promote the photo-reduction, while holes participate in the photo-oxidation.¹⁶ Thus, the oxidation of benzyl alcohol accompanied by the elimination of electrons by O_2 is described in Fig. 1a. The reduction and oxidation reactions take place at different sides of the TiO_2 shells, which is critical for effective charge separation. In addition, light will pass through the thin TiO_2 shell and keep reflecting in the cavity, increasing the scattering length for enhanced light-absorption. Combined with the large surface area, the PTM-HSs exhibit high efficiency for the photocatalytic oxidation of benzyl alcohol, a representative alcohol containing phenyl groups. Generally, the appropriate catalysts for benzyl alcohol oxidation can also perform well in the oxidation of other similar chemicals.¹⁷ Thus, the current photoredox catalysis system can be expanded for other relevant organic synthesis of fine chemicals. Additionally, we propose a two-step

photooxidation mechanism for PTM-HSs, which may provide inspiration for the design of similar catalysts with high activity.

Results and discussion

The synthesis of PTM-HSs (Fig. 2) starts from SiO_2 nanospheres prepared by a modified Stöber method, with H_2PtCl_6 adsorbed on the surface of SiO_2 .¹⁸ Then they were calcined at 500 °C for 2 hours (h) under H_2 atmosphere to form Pt particles anchored on SiO_2 (Fig. 2a and f). Subsequent coating of an amorphous TiO_2 shell was performed by the hydrolysis of titanium *tert*-butoxide (TBOT) (Fig. 2b and g). Then the samples were calcined to improve the crystallinity of TiO_2 . It should be noted that direct calcination would destroy the structure of the TiO_2 shells (Fig. S2†). To preserve the morphology, another layer of SiO_2 was added as a coating to form the outermost protective layer (Fig. 2c and h). After calcination, the outer and inner silica layers were removed by NaOH (1.67 M) etching at 70 °C for 8 h to form Pt@TiO_2 hollow spheres (PT-HSs) (Fig. 2d and i). Finally, MnO_x was selectively deposited on the outer surface of PT-HSs to form PTM-HSs (Fig. 2e and j and S3†) by a photo-deposition method (Fig. S1†).

The successful synthesis of the PT-HSs is further validated. Fig. 3a shows that most Pt particles with an average size of $ca.$ 3.2 ± 1.3 nm (Fig. 3c) are uniformly loaded onto the inner surface of TiO_2 shells. A few Pt particles agglomerate to form larger ones. The high resolution transmission electron microscopy (HRTEM) image of the area near the inner surface of TiO_2 shells (Fig. 3b) shows that the lattice spacing of 0.2227 nm and 0.3520 nm match well with the (111) planes of Pt and the (101) planes of anatase. It can be seen that a hexagonal Pt particle is coated by a layer of TiO_2 (Fig. 3b), resulting from the strong interaction between Pt and TiO_2 . A STEM-energy-dispersive X-ray spectroscopy (EDS) line scan was performed through the center of an individual PT-HS particle (inset in Fig. 3d and e), which further confirms the position of Pt particles relative to the TiO_2 shell. Fig. 3d shows strong signals of Ti and O at the edge of the PT-HS, which reveals a typical structure of TiO_2 hollow spheres. The TiO_2 shell is marked in Fig. 3d by

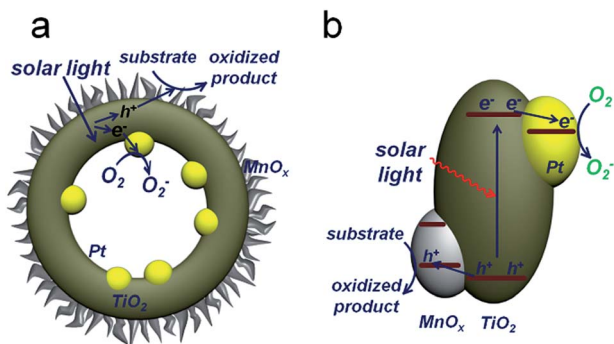


Fig. 1 Proposed mechanism for photocatalytic oxidation by PTM-HSs. Pt and MnO_x are spatially separated by TiO_2 . (a) The reaction process. (b) Band structure of the catalyst.

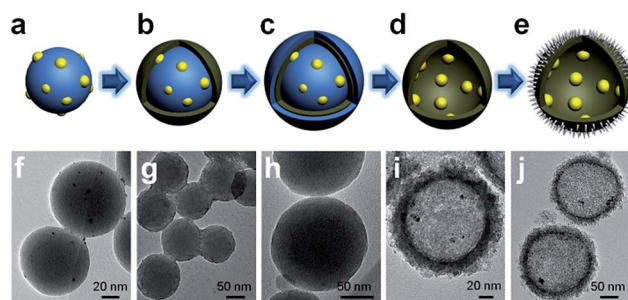


Fig. 2 Schematic illustration and TEM images of the formation process of PTM-HSs. (a) and (f) Pt loaded onto SiO_2 nanospheres to form $\text{SiO}_2\text{-Pt}$. (b) and (g) TiO_2 layers were coated on $\text{SiO}_2\text{-Pt}$ to form $\text{SiO}_2\text{-Pt@TiO}_2$. (c) and (h) SiO_2 protective layers were coated on $\text{SiO}_2\text{-Pt@TiO}_2$ to form $\text{SiO}_2\text{-Pt@TiO}_2\text{@SiO}_2$. (d) and (i) PT-HSs. (e) and (j) PTM-HSs. The outermost spine-like layer in image (j) is the MnO_x layer.



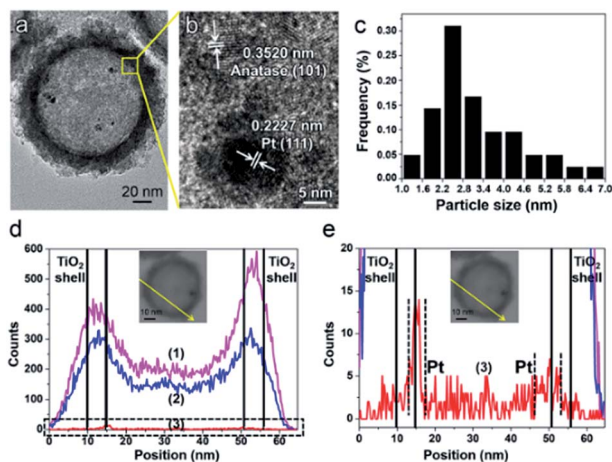


Fig. 3 The confirmation of PT-HS structures. (a) TEM image of a PT-HS. (b) HRTEM image of the area near the inner surface of the TiO₂ shell. (c) The distribution of the particle size. (d) EDS line scan of a PT-HS. The part in the dotted pane is magnified in image (e). (e) The magnified patterns of the EDS line scan. Inset in image (d) and (e): the path of the EDS line scan. Curves (1), (2) and (3) in image (d) and (e) refer to the signals of Ti, O and Pt, respectively.

two groups of vertical lines, indicating the wall of the TiO₂ shell based on Ti and O signals in the EDS line scan. Fig. 3e shows the magnified Pt EDS signal, demonstrating that Pt particles are loaded onto the inner surface of the TiO₂ shell. It is not possible to use an EDS area scan to perform such confirmation because of the low loading of Pt (1%, measured by ICP) (Fig. S4d†).

The structure of the PTM-HSs is confirmed by the same method (Fig. 4), where MnO_x is identified on the outer surface of TiO₂ shells. The universal existence of PTM-HSs can be demonstrated by the TEM image of a larger area (Fig. S3†).

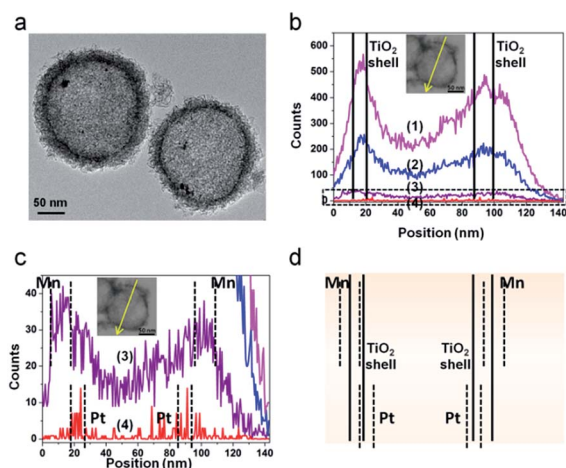


Fig. 4 The confirmation of PTM-HS structures. (a) TEM image of PTM-HSs. (b) EDS line scan of a PTM-HS. The part in the dotted pane is magnified in image c. (c) The magnified patterns of the EDS line scan. (d) The relative positions of Mn, Pt and the TiO₂ shell. Inset in (b) and (c): the path of the EDS line scan. Curves (1), (2), (3) and (4) in images (b) and (c) refer to the signals of Ti, O, Mn and Pt, respectively.

The pore size and Brunauer–Emmett–Teller (BET) surface area of PTM-HSs are measured by N₂ adsorption, and determined to be 5.0 nm (average pore size) and 298 m² g⁻¹, respectively (Fig. S5a†). The results indicate a mesoporous structure, which is the prerequisite for effective immigration of reactants. Additionally, X-ray diffraction (XRD, Fig. S5b†) and HRTEM of the spine-like layer (Fig. S5c and d†) prove that the PTM-HSs consist of Pt, anatase and MnO_x, where *x* is between 1.0 and 2.0. Highly crystallized anatase instead of a rutile shell is formed, which is capable of achieving higher photocatalytic activity.^{19,20} The components of the catalysts can be further confirmed by X-ray photoelectron spectroscopy (XPS, Fig. S8†).

For comparison, reference catalysts such as pure TiO₂ hollow spheres (T-HSs) (Fig. S6a and b†) and TiO₂/Pt/MnO_x hollow spheres (T/P/M-HSs) (Fig. S6c–f†) were synthesized by a similar method. PT-HSs were also used as reference catalysts. T/P/M-HSs were synthesized by impregnating T-HSs in solutions of H₂PtCl₆ and MnSO₄ in sequence to form a structure in which the Pt particles and MnO_x distributed randomly on both the inner and outer surfaces.

Catalysts containing Pt and TiO₂ can exhibit activity in the photooxidation of alcohols (details are discussed in Fig. S12†) and water (Fig. 5a) under visible light, because of the surface plasmonic resonance effect (SPR) of Pt (Fig. S12e†).^{17,21,22} As shown in Fig. 5a, the highest water oxidation activity is achieved for the PTM-HSs. The deposited Pt on the inner surface can collect electrons to reduce IO₃⁻ ions, and the MnO_x photo-deposited selectively on the outer surface can accumulate holes for water oxidation. For PT-HSs, although the amounts of loaded species and the topography of the catalysts are similar, the promotion effect of the cocatalysts is not as evident as that of PTM-HSs, indicating that the photocatalytic performance can

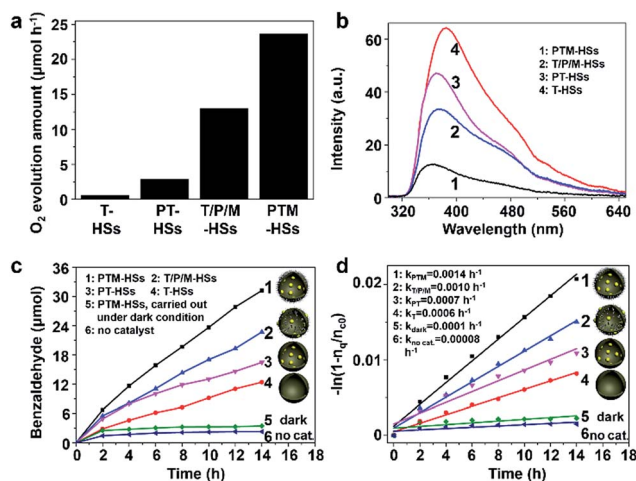


Fig. 5 (a) The activity for photocatalytic water oxidation under visible light ($\lambda > 420$ nm). 0.03 g of catalyst was used. (b) The PL spectra (excited at $\lambda = 235$ nm) of diverse catalysts. (c) The activity for photocatalytic alcohol oxidation under UV light. (d) The corresponding kinetic rate plots. Traces 1–6 refer to PTM-HS, T/P/M-HSs, PT-HSs, T-HSs, PTM-HSs under dark conditions, and no catalyst, respectively. Traces 1–4 and trace 6 are carried out under UV irradiation. 0.03 g of catalyst was used.



be greatly enhanced when the reduction/oxidation cocatalysts are spatially separated. The activity of T-HSs and PT-HSs is even lower. These results can be explained by the improvement of the charge separation, which can be demonstrated by the photoluminescence (PL) spectra (Fig. 5b). The emission intensity of T-HSs is the strongest, resulting from the severe recombination of photogenerated charges. In contrast, the intensity of PT-HSs, T/P/M-HSs and PTM-HSs are reduced by about 25%, 45% and 80%, respectively, indicating an enhanced suppression of the recombination process.

To illustrate that the enhancement of activity is indeed caused by the improvement of charge separation, the oxidation of benzyl alcohol was performed under UV light ($\lambda < 420$ nm). UV light (1.46 mW cm^{-2}) was adopted to ensure that light absorption remained the same (Fig. S7†) when different catalysts were used. Thus, the influence of light absorption can be eliminated. Benzyl alcohol was oxidized to benzaldehyde without any over-oxidized products such as benzoic acid (explained in Fig. S9†). Besides, the structure of the catalysts remained unchanged after the reaction, indicating excellent stability (Fig. S10†). As shown in Fig. 5c, negligible amounts of benzaldehyde were detected without the catalyst or in the dark condition (traces 5 and 6, Fig. 5c), indicating the importance of catalysts and light. The T-HSs display a moderate photocatalytic activity (trace 4, Fig. 5c, $12.39 \mu\text{mol}$ of product, 14 h), while the activity of PT-HSs is increased (trace 3, Fig. 5c, $22.72 \mu\text{mol}$ of product, 14 h). By loading Pt and MnO_x simultaneously (T/P/M-HSs), the activity is further enhanced (trace 2, Fig. 5c). The highest activity ($31.22 \mu\text{mol}$ of product, 14 h) is achieved when PTM-HSs were used (trace 1, Fig. 5c). The corresponding study on kinetics (Fig. S14†) shown in Fig. 5d exhibits the same trend (*i.e.*, activity: PTM-HSs > T/P/M-HSs > PT HSs > T-HSs).

To further confirm the enhancement of separation efficiency (η_s), the apparent quantum efficiency (AQE) of PTM-HSs and T/P/M-HSs at 254 nm were determined to be 63.14% and 45.94%, respectively, which is higher than that of conventional TiO_2 -based catalysts (often in the range 4.3–39%).²³ Because of the similar structure of the two kinds of catalysts and the same loading amount of cocatalyst, the efficiency of adsorption (η_a) and surface-reaction (η_c) remain the same between the catalysts (Fig. S7†). Considering the overall efficiency is determined by η_a , η_s and η_c simultaneously, the enhancement of AQE can be attributed to the enhancement of η_s . Thus, we can quantitatively demonstrate that the spatial separation of cocatalysts indeed leads to an efficient charge separation for photocatalytic oxidation. Moreover, even under visible light ($\lambda > 420$ nm), the electrons (generated from catalysts containing Pt and TiO_2) still flow from TiO_2 to Pt (instead of the hot electrons injected into TiO_2), which can be proved by a probe experiment (Fig. S12†).

In order to investigate the mechanism of photocatalytic benzyl alcohol oxidation, particularly the main active species, phenol, and 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl free radical (4-OH-TEMPO) were used as the scavengers of holes (h^+) and superoxide radicals (O_2^-), respectively. As shown in Fig. 6a, when phenol (h^+ scavenger) was added into the photocatalytic system, an extremely low oxidation activity was observed, indicating that h^+ plays an indispensable role in the oxidation

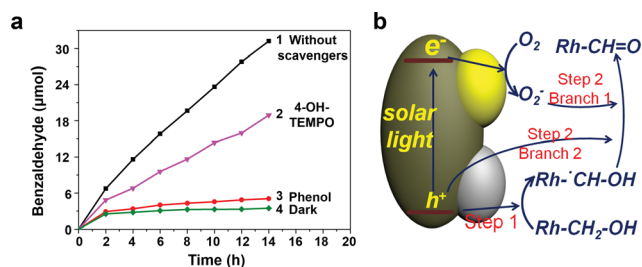
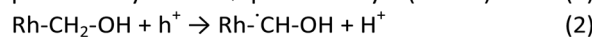


Fig. 6 (a) Effects of diverse scavengers on the photooxidation of benzyl alcohol in the presence of PTM-HSs (0.03 g). Traces 1–3 were obtained under UV light, while trace 4 was under dark conditions. (b) The proposed mechanism of photocatalytic benzyl alcohol oxidation.

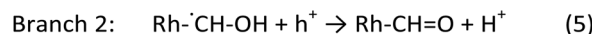
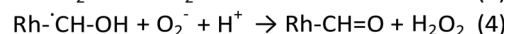
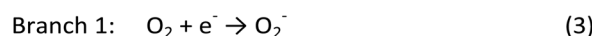
process. However, when 4-OH-TEMPO (O_2^- scavenger) was added, the activity only partly decreased, indicating that O_2^- also takes part in the reaction, while it is not indispensable. These observations suggest that two photocatalytic steps might be involved. The first step primarily depends on h^+ , while the second step is driven by h^+ and O_2^- simultaneously. An intermediate would be formed in step 1 and be oxidized in step 2, bridging the two steps.

To determine the intermediate species, a kinetic isotope effect (KIE) study was conducted for PTM-HSs with benzyl alcohol under aerobic conditions. The KIE value was 0.78, suggesting the breaking of a C–H bond instead of an O–H bond (see ESI†). Accordingly, the intermediate was determined to be $\text{Rh}^-\text{CH}-\text{OH}$ (Rh stands for the benzene ring). The speculated mechanism of photocatalytic benzyl alcohol oxidation is shown in Fig. 6b and eqn (1) to (5):

Step 1:



Step 2:



Upon the separation of photo-induced electrons and holes over the PTM-HSs, the holes react with benzyl alcohol molecules to form intermediate free radicals ($\text{Rh}^-\text{CH}-\text{OH}$). Subsequently, some of the free radicals react with O_2^- , while others are further oxidized by holes to form the ultimate products ($\text{Rh}-\text{CH}=\text{O}$). Meanwhile, oxy species finally exist as H_2O_2 after a series of changes, which are discussed in detail in the ESI.†²⁴

Conclusions

In summary, the PTM-HS catalyst with Pt and MnO_x loaded separately onto the inner and outer surfaces of TiO_2 hollow spheres was successfully synthesized for the photooxidation of



