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# Interfacial Band Alignment for Photocatalytic Charge Separation in TiO<sub>2</sub> Nanotube Arrays Coated with CuPt Nanoparticles†

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*n*-type anatase-phase one-dimensional TiO<sub>2</sub> nanostructure arrays coated with nanoparticles of Cu or CuPt have emerged as high performance photocatalysts for both photooxidation and photoreduction. The properties of the catalyst-promoter interface are recognized to be critical to this high performance but are largely unknown. Using X-ray and ultraviolet photoelectron spectroscopies (XPS/UPS), we probed the electronic properties of the CuPt-TiO<sub>2</sub> interface in transparent TiO<sub>2</sub> nanotube arrays (TTNTAs) coated with photodeposited CuPt nanoparticles (CuPt-TTNTA hybrids) as well as those coated with sputtered CuPt (Sput-CuPt-TTNTA hybrids). XPS and UPS spectra provided evidence of a Schottky barrier with a band-bending of 0.49-0.67 eV at the CuPt-TiO<sub>2</sub> interface in CuPt-TTNTA hybrids due to which photoexcited electrons are expected to be retained in the TiO<sub>2</sub> while photoexcited holes will be collected by the CuPt nanoparticles. For Sput-CuPt-TTNTA hybrids, no such band-bending was observed. These results point to the importance of metal nanoparticle preparation technique on interfacial band-alignments and challenge the conventional understanding of the promoting action of noble metal nanoparticles on TiO<sub>2</sub> photocatalysts as sinks for photoexcited electrons.

KEYWORDS: Electrochemical anodization, titania nanotubes, heterogeneous catalysis, internal electric fields, solar fuels.

The *n*-type semiconducting anatase phase of titanium dioxide (TiO<sub>2</sub>) is one of the most potent semiconductors for photocatalytic and photoelectrochemical device applications owing to its various advantageous properties such as the strong oxidizing power of photogenerated holes, nontoxicity, high resistance to photocorrosion, high chemical stability and low cost.<sup>1</sup> Most photocatalytic reactions are multi-step electron transfer reactions due to which electron-hole pair recombination losses, activation barriers at each step and back-reaction of intermediate products can have a catastrophic effect on overall reaction yields.<sup>2-5</sup> Furthermore, because of the way in which photocatalysts are deployed, an external bias to drive the separation of charge carriers is not present. In this context, nanostructuring the TiO<sub>2</sub> is highly effective for improving photocatalytic action because of the resulting high surface-to-volume ratio and the proximity of carrier photogeneration to carrier utilization. A high surface area increases the availability of reaction sites and enables a greater amount of co-catalyst/promoter loading to reduce activation barriers while the small particle size ensures that the distance from the site of carrier photogeneration to the site of chemical reaction is comparable to the minority carrier retrieval length (diffusion length + width of depletion region, if present).

Although zero-dimensional TiO<sub>2</sub> structures such as nanoparticles (NPs) and nanoshells benefit similarly from the advantages of nanostructuring outlined above and have been studied for a much longer duration both in isolation and with suitable noble metal co-catalysts, one-dimensional (1-D) TiO<sub>2</sub> structures such as nanorods (NRs) and nanotubes (NTs) loaded with suitable co-catalysts currently outperform TiO<sub>2</sub> nanoparticles and nanoparticulate films as photocatalysts for CO<sub>2</sub> photoreduction.<sup>6, 7</sup> There are several differences between the structure(s) and properties of TiO<sub>2</sub> NPs and those of NTs/NRs (with smallest dimension comparable to NP diameter). In nanorods and nanotubes, individual grains are

elongated along the NR/NT axis while their width is determined by the lateral dimension (diameter or wall-thickness) of the NR/NT. The anisotropy induced by the resulting high aspect ratios in the range 15-40, changes the interactions of charge carriers and the crystallographic texture of NT/NR surfaces due to which band densities of states, surface energies, work-functions and trap distributions are significantly different than in nanoparticles.<sup>8-11</sup> Indeed, the dynamics of carrier recombination in TiO<sub>2</sub> nanotube and nanorod arrays have been found to be significantly different from nanoparticles of comparable size.<sup>12-16</sup> The interactions of light with spherical and rod-type structures are different owing to the scattering of nanoparticles governed by the exact solutions given by Mie theory<sup>17</sup> and that of nanorods/nanotubes affected by optical anisotropy and approximately described by Gans theory.<sup>18</sup> While the co-catalysts in nanoparticulate photocatalysts are also nanoparticles of roughly the same size and present a single length scale, co-catalyst NPs are much smaller than the length of NRs/NTs resulting in multiple length scales, a desirable feature for high performance photocatalysis.<sup>19</sup>

When 1-D anatase-phase TiO<sub>2</sub> nanostructures are combined with a suitable co-catalyst, efficient photocatalytic activity results. Au and Pt nanoparticles formed on TiO<sub>2</sub> nanotubes by sputtering followed by thermal dewetting and dealloying showed a remarkable increase in efficiency for photocatalytic water splitting in comparison to TiO<sub>2</sub> nanoparticles.<sup>20, 21</sup> The highest reported values of CO<sub>2</sub> photoreduction ( $\sim 0.5 \mu\text{mol cm}^{-2} \text{hr}^{-1}$ ) for broad-band illumination in the scientific literature for any catalyst have been obtained using 1-D TiO<sub>2</sub> loaded with a nano-sized platinum-containing co-catalyst.<sup>22-</sup>  
<sup>27</sup> Yet, the exact electronic band-alignment at the Pt-TiO<sub>2</sub> interface is unknown. The Bardeen model for Fermi level pinning involving metal-induced gap states is known to be less relevant to large bandgap oxides.<sup>28</sup> The Shockley-Anderson model<sup>29</sup> for band-alignment at a semiconductor heterojunction, suggests the formation of a Schottky barrier between TiO<sub>2</sub> and high work-function noble metals resulting in a carrier-depleted interfacial region with an electric field that causes photogenerated holes to

transfer to the noble metal and photogenerated hot and equilibrated electrons to be injected into or retained in the  $\text{TiO}_2$  (Fig. S1 in ESI†). Cu-containing metallic and bimetallic photocatalysts are interesting for three reasons - the excellent selectivity toward specific photocatalytic reactions such as water-splitting and  $\text{CO}_2$  photoreduction,<sup>1, 30-33</sup> the lower cost of copper and the possibility of visible light absorption in Cu-based photocatalysts.<sup>34, 35</sup> Cu- $\text{TiO}_2$  catalysts have been used in a wide variety of industrial reactions<sup>36, 37</sup> such as hydrogenation of 1,3-cyclooctadiene and the CO-NO reaction. It is noteworthy that very high performance has been reported from CuPt- $\text{TiO}_2$  hybrid photocatalysts in both oxidative and reductive reactions.<sup>38, 39</sup>

There is some evidence in the scientific literature that  $\text{TiO}_2$  forms Schottky junctions with noble metals such as Au and Pt.<sup>40, 41</sup> These are also borne out by numerous recent reports of hot electron transfer from noble metals into  $\text{TiO}_2$  and concomitant photoelectrochemical or photocatalytic activity but mostly without quantification of the Schottky barrier heights involved.<sup>42-49</sup> On the other hand, femtosecond transient absorption spectroscopy, surface potential imaging and electron spin resonance studies suggest transfer of the photoexcited electron to the noble metal leaving the photogenerated hole in  $\text{TiO}_2$ .<sup>24, 50, 51</sup> Thus there exists a fundamental contradiction between the above two scenarios that needs resolving. Some reports claim that Pt NPs on *n*- $\text{TiO}_2$  act as electron sinks through Schottky barrier electron-trapping,<sup>52, 53</sup> which represents a lack of understanding of the difference between the two scenarios outlined. Furthermore, the photocatalytic activity is highly sensitive to the method of formation and deposition of the noble metal NPs. Since NTs differ in structure and properties from NPs, investigations on electronic interactions and charge transfer at the co-catalyst- $\text{TiO}_2$  interface specific to 1-D nanostructures and type of co-catalyst loading are quite important from the point of view of understanding and improving photocatalytic performance. The present study investigates the structure and electronic interactions at the CuPt NP-TTNTA hybrid interface wherein the CuPt NPs are

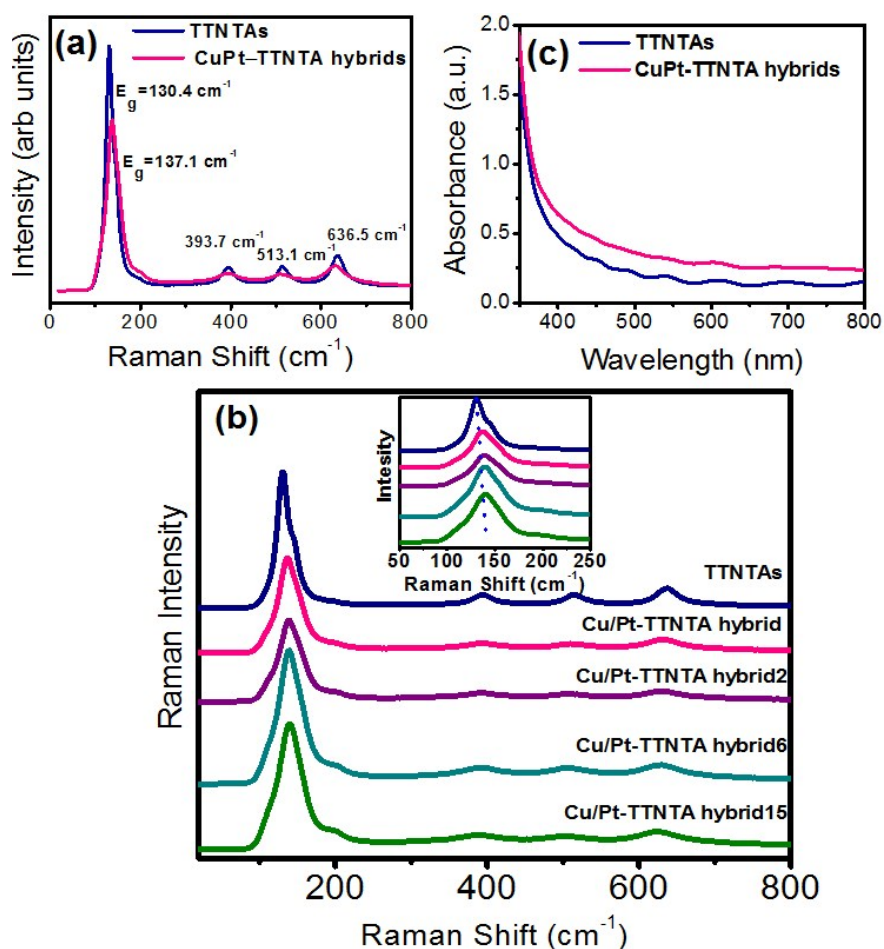
photodeposited onto the nanotube walls, and compares them to the electronic properties of Sput-CuPt-TTNTA hybrids wherein the noble metal nanoparticles are formed by sputtering followed by thermal dewetting. Transparent nanotubes on FTO-coated glass substrates are used in this study since they allow clear and quantitative measurement of the effect of CuPt loading on the optical absorption of the photocatalyst.

## Results And Discussion

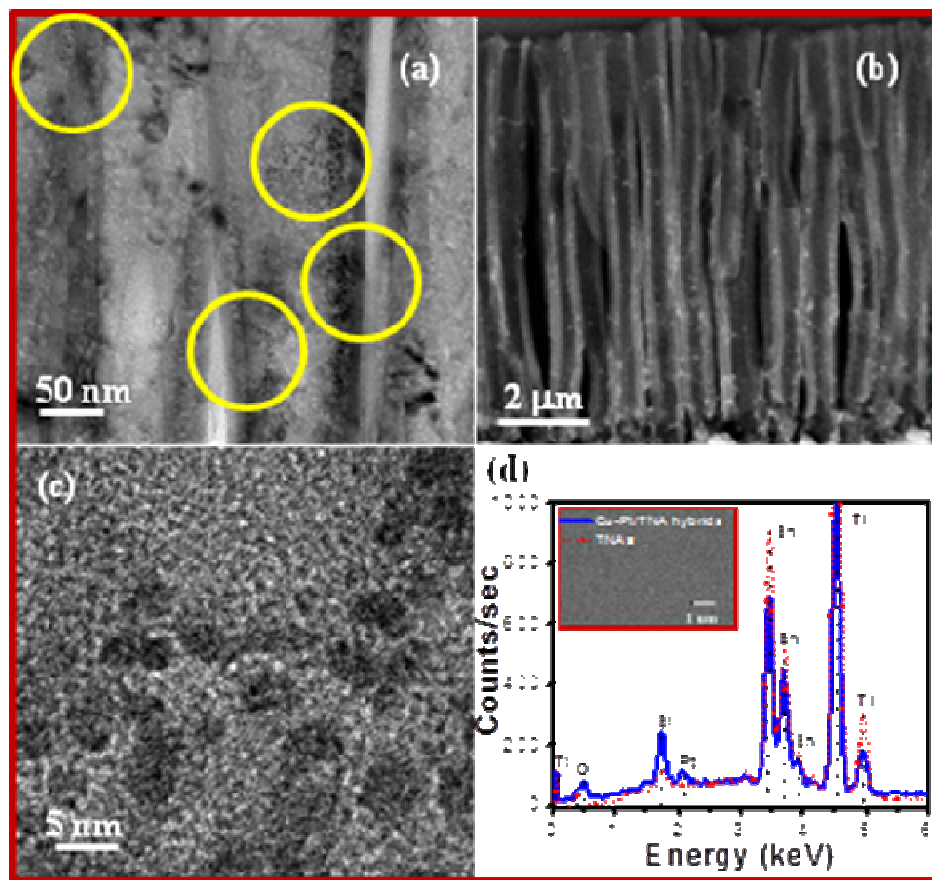
### 1. Morphology, structure and optical absorption of CuPt coated TTNTAs

MicroRaman spectroscopy is a sensitive and powerful technique to investigate defects, variations in local structure and phase transformations in  $\text{TiO}_2$  based materials. The Raman spectra of TTNTAs and CuPt-TTNTA hybrids are shown in Fig. 1. TTNTAs formed after anodization are amorphous in nature and their crystallization is achieved by annealing in air at  $550^\circ\text{C}$ . For crystalline anatase  $\text{TiO}_2$  phase, six Raman active phonon modes are present that correspond to  $A_{1g}$ ,  $B_{1g}$  and  $E_g$  modes, respectively. Fig. 1a shows a comparison of the Raman spectra of TTNTAs and CuPt-TTNTA hybrids. Raman spectra confirm the tetragonal anatase mode of TTNTAs with the presence of Raman active  $A_{1g}$ ,  $B_{1g}$  and  $E_g$  modes.<sup>54, 55</sup> It can be seen that the most intense peak for TTNTAs appears at  $130.4\text{ cm}^{-1}$  corresponding to the  $E_g$  mode. In addition to the  $E_g$  mode, the other less intense peaks can be seen at  $393.7\text{ cm}^{-1}$ ,  $513.1\text{ cm}^{-1}$  and  $636.5\text{ cm}^{-1}$  confirming the presence of  $B_{1g}$ ,  $A_{2g}$  and  $E_g$  modes, respectively. A shift in a peak position of  $7\text{ cm}^{-1}$  ( $137\text{ cm}^{-1}$ ) is found for CuPt-TTNTA hybrids for main  $E_g$  mode with a small broadening. This shift in CuPt-TTNTA hybrids is due to dispersion of bimetallic CuPt NPs over  $\text{TiO}_2$  producing a change in the local structure of  $\text{TiO}_2$ . Fig. 1b shows the Raman spectra of CuPt-TTNTA hybrids subjected to different irradiation times by the one sun output of a calibrated solar simulator together with heating at  $100^\circ\text{C}$ . Such a configuration to study the CuPt- $\text{TiO}_2$  interface was

chosen keeping in mind the fact that both photochemical and thermochemical interfacial reactions are possible upon illumination in TTNTA photocatalysts. The inset of Fig. 1b shows the broadening of the main  $E_g$  peak in case of hybrids irradiated with different times in correspondence to the TTNTAs, which we associate with increasing structural disorder upon prolonged exposure to ultraviolet photons in simulated sunlight.



**Fig. 1** Counter-clockwise from top-left (a) Comparison of the room temperature Raman spectra of TTNTAs and CuPt-TTNTA hybrids (b) microRaman spectra of CuPt-TTNTA hybrids heated to 100°C with different light exposure times, here 2, 6 and 15 corresponds to hours of illumination; inset figure shows the broadening in the  $E_g$  peak of  $\text{TiO}_2$  with time. (c) UV-Vis spectra of TTNTAs and CuPt-TTNTA hybrids.



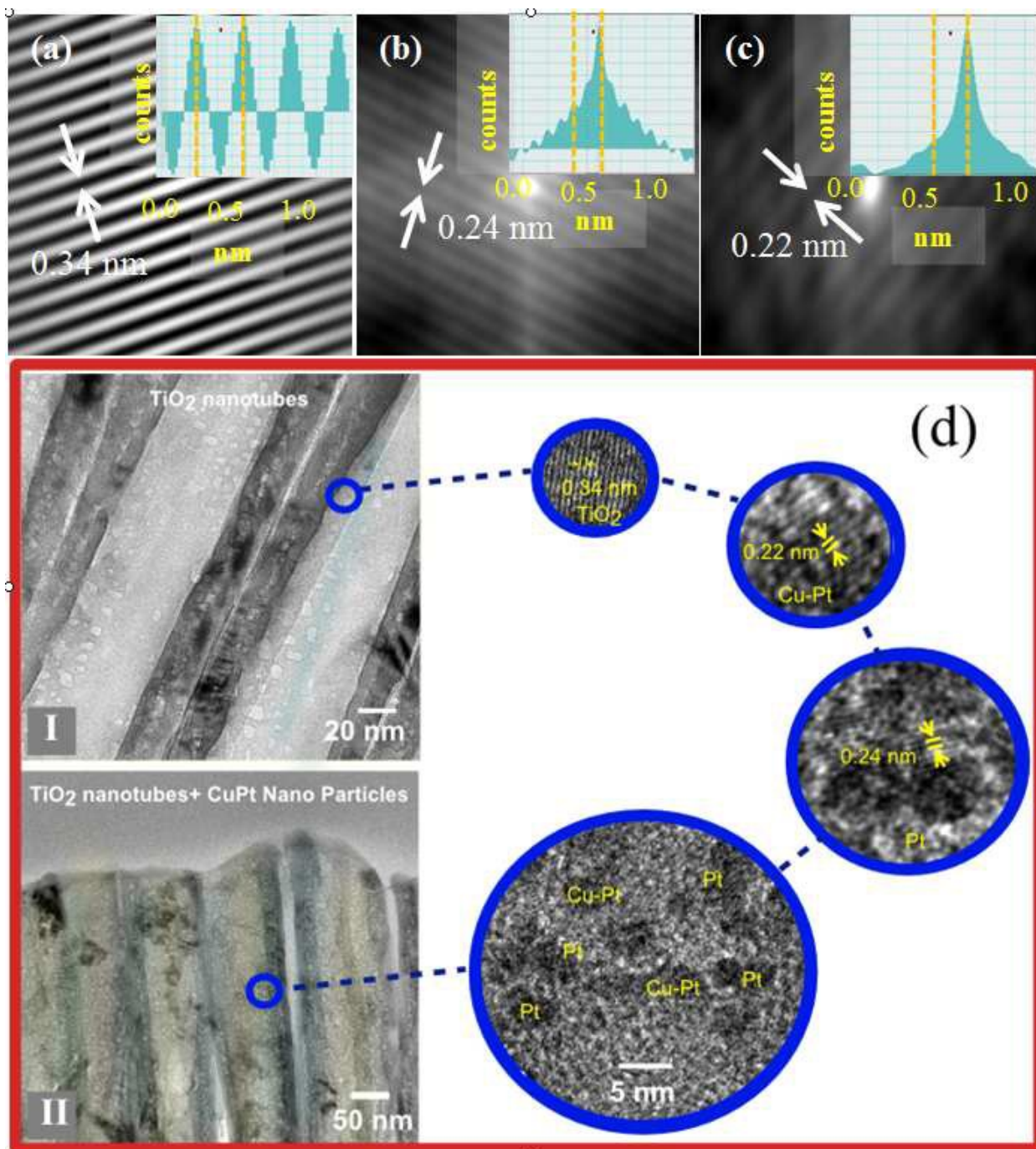
**Fig. 2** Low and high resolution transmission electron microscope images showing (a) CuPt nanoparticle loaded TTNTAs, (b) HAAFD image in STEM mode presenting the CuPt-TTNTA hybrids, (c) close knit attachment of CuPt nanoparticles along the walls of TTNTAs and (d) EDAX spectra confirming the presence of Pt.

The UV-Vis spectra in Fig. 1c show a strong sub-bandgap absorption in the bare TTNTAs due to an extended Urbach tail. No pronounced additional optical transitions were found in the CuPt-TTNTA hybrids. Intra- and interband absorption in CuPt NPs resulted in a slightly increased absorption of light throughout the visible spectra range in CuPt-TTNTA hybrids in comparison to TTNTAs. The morphology of the as-prepared TTNTAs was imaged using FESEM (Fig. S2 in ESI†) where closed packed TTNTAs with an average outer diameter  $\sim 105$  nm are seen. An inset image in top left corner of Fig. S2a in ESI† shows a cross section of TTNTAs with a tube-length of 1  $\mu\text{m}$ . Not much change is



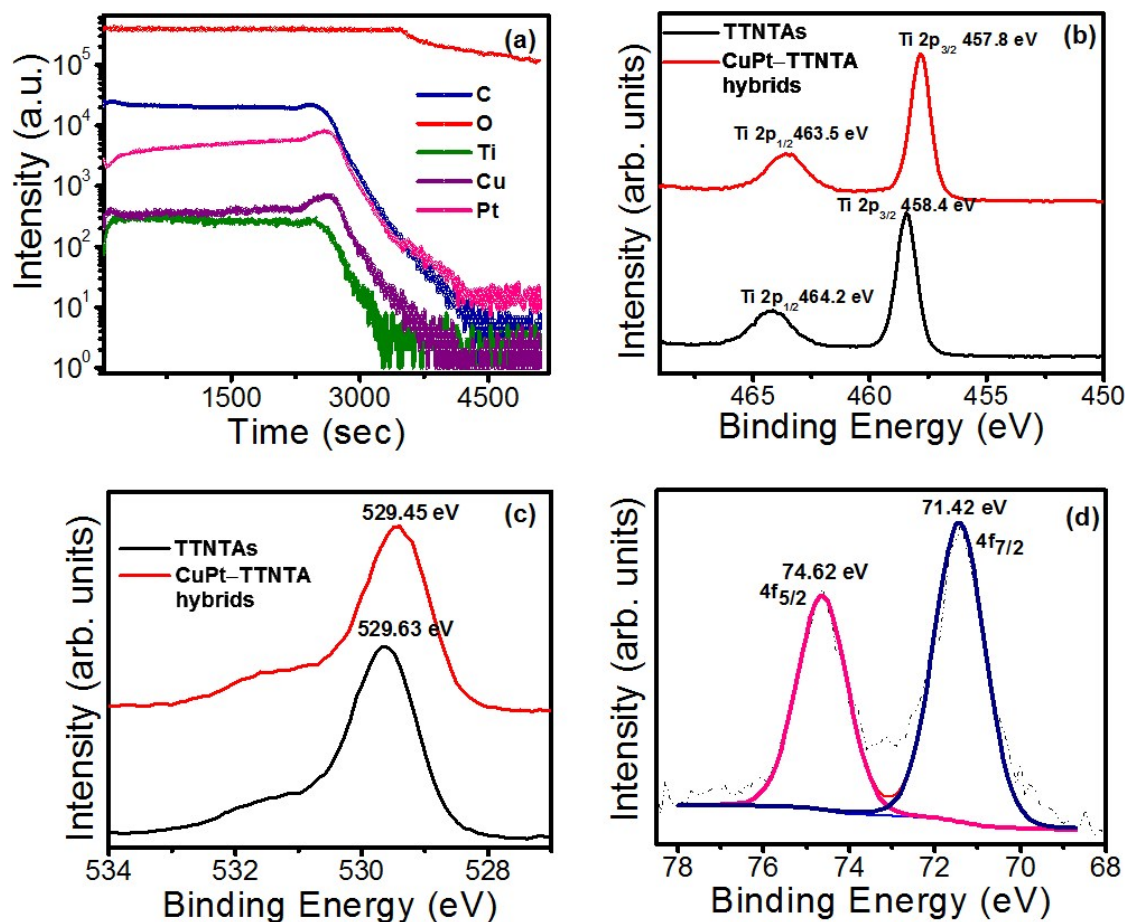
observed in the morphology of TTNTAs after CuPt loading. The nanoparticles of bimetallic alloys that form CuPt-TTNTA hybrids are too small to be seen in SEM images. Low and high resolution-TEM images and EDAX spectra of TTNTAs and their hybrids are displayed in Fig. 2. A direct attachment of CuPt-NPs is clearly seen along the walls of TiO<sub>2</sub> nanotubes (Figure 2a). The encircled regions in this image show CuPt NPs that are 2 - 5 nm in diameter, which is further confirmed through HRTEM images (Fig. 2c). However, there likely are several NPs similar in size to, or just below, the microscope resolution limit of 1 nm. The presence of these is inferred through features in the electronic spectra discussed later in this report.

A high angle annular dark field scanning TEM (HAADFSTEM) image, shown in Fig. 2b corresponds to the tiny bright spots demonstrating the dispersion of CuPt NPs on TTNTAs. A close knit attachment of CuPt NPs with the TTNTAs can be seen in Fig. 2c, favoring the CuPt NPs and TiO<sub>2</sub> nanotube array structures to form hybrids with a strong interaction. EDX spectra, shown in Fig. 2d confirm the elemental state of Pt only, due to a very small concentration of Cu. However, the HRTEM images shown in Fig. 3 confirm the presence of CuPt bimetallic alloy. Figs. 3a - 3c display the auto correlated lattice spacing, analyzed from HRTEM pictures. The anatase phase of TiO<sub>2</sub> with *d*-spacing 0.34 nm corresponding to the (101) plane, is confirmed through high resolution lattice fringes (Figure 3a). The presence of Pt and CuPt alloy is also confirmed from the *d*-spacing of the lattice fringes to be 0.24 nm (111) and 0.22 nm (111), respectively (Fig. 3b and Fig. 3c). The *d*-spacing of 0.22 nm from the lattice fringes reveals the formation of a Pt rich alloy with very small concentrations of Cu. A complete chain of TTNTAs and the CuPt-TTNTA hybrids with their corresponding *d*-spacing is summarized in Fig. 3d. Thus HRTEM results confirm the intimate nature of the CuPt-TiO<sub>2</sub> hybrid structure interface that is the foundation for the further set of studies.



**Fig. 3** High-resolution autocorrelated images of (a) TiO<sub>2</sub> lattice planes (b) Pt NPs (c) CuPt NPs (d) HRTEM images displaying the crystalline planes for (I) TTNTAs and (II) CuPt-TTNTA hybrids.

## 2. Elemental composition and photoemission spectra in CuPt–TTNTA hybrids



**Fig. 4.** TOF-SIMS and XPS data from CuPt-TTNTA hybrids (a) TOF-SIMS and core-level spectra of (b) Ti 2p (c) O 1s and (d) Pt 4f.

XPS, which is a highly surface sensitive technique, was performed to investigate the difference in the chemical states of different elements present in TTNTAs and CuPt-TTNTA hybrids. XPS is also used as a means to understand the charge transfer and electronic interactions between the metal and the support in the mentioned hybrid structure (Figs. 4b-4d). The survey scans on TTNTAs and CuPt-TTNTA hybrids confirmed the presence of Ti, O and Pt. Cu peak was not observed in the XPS survey scans owing to its very small concentration. To confirm the presence of Cu, time of flight-SIMS in depth profiling mode was performed on the sample that confirmed the presence of Cu by mass (Fig. 4a).

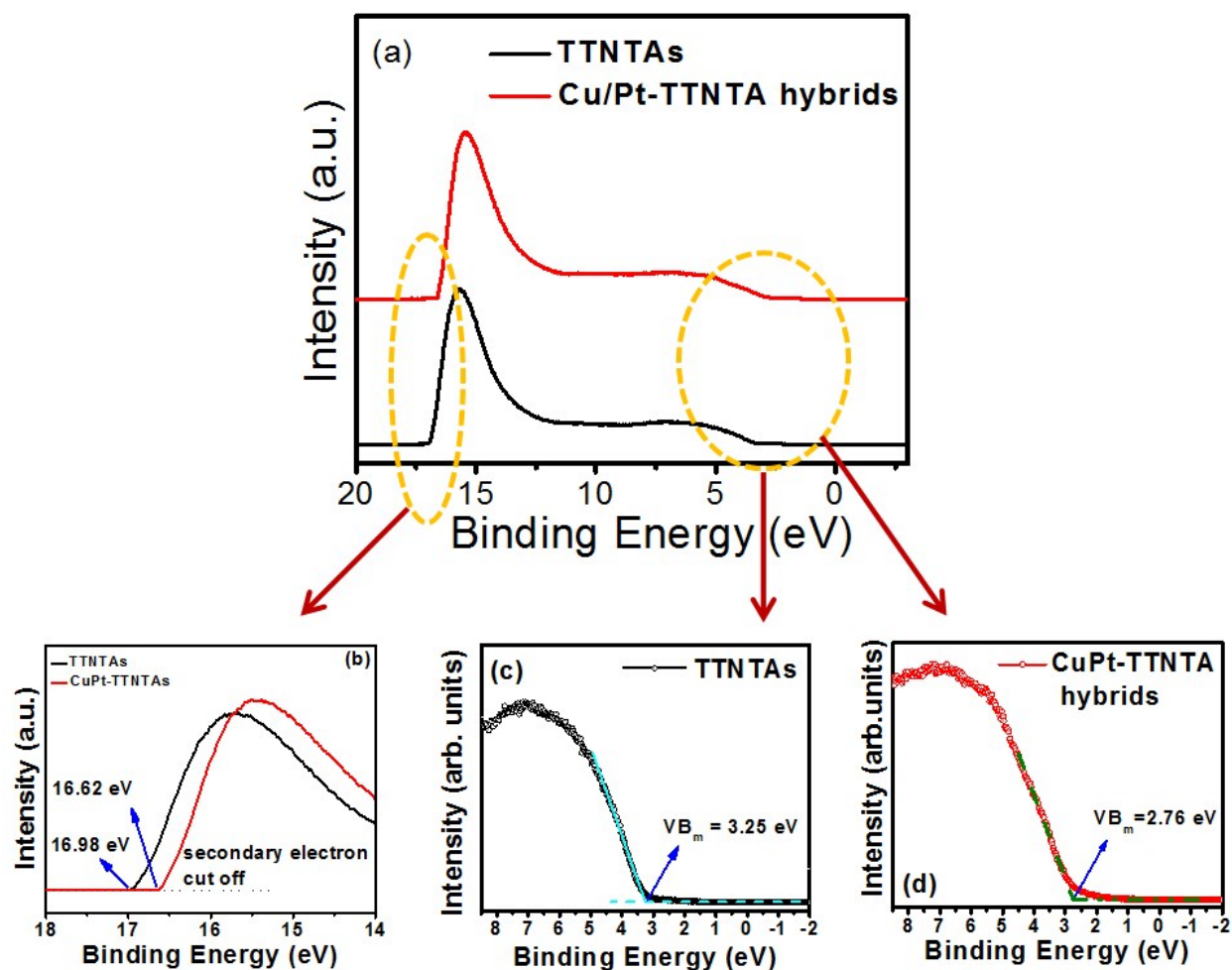
TOF-SIMS spectra (Fig. 4a) confirm the presence of all the materials present in the sample along with the substrate up to a sputtering time of  $\sim 2600$  s, which corresponds to the transition from the TiO<sub>2</sub> nanotube barrier layer to the FTO layer below. Furthermore, the intensities of Cu and Pt obtained through SIMS profiling correlate well with that of Ti, indicating a fairly uniform loading of CuPt NPs along the nanotube walls with a slight increase in Pt concentration closer to the barrier layer. The core level spectra of Ti, O and Pt are seen in Figs. 4b-4d. In Fig. 4b, the Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  states in TTNTAs present at 458.4 eV and 464.2 eV, respectively, correspond to Ti<sup>4+</sup> states.<sup>56</sup> The Ti<sup>4+</sup> surface state shifts to 457.8 eV and 463.5 eV in CuPt-TTNTA hybrids. Fig. 4c displays the O 1s spectra with the presence of Ti-O peak at 529.63 eV and 529.45 eV for TTNTAs and for CuPt-TTNTA hybrids, respectively. While the binding energy shift in this case appears to be a mere  $-0.18$  eV, measurements over a number of samples and peak decomposition of the resulting O 1s spectra show that TTNTAs without an oxygen plasma treatment exhibit peaks at 531.90 eV and 530.14 eV, which correspond to O-Ti (3+) and HO-Ti (3+) respectively (Fig. S5 in ESI†). Oxygen plasma treatment of the surface changes the relative weighting of the two peaks but leaves the peak positions almost unchanged (Fig. S5 in ESI†). On the other hand, photodeposition of CuPt consistently shifts both the peaks constituting the O 1s spectrum to lower binding energies (top panel of Fig. S6 in ESI†). This shift to lower binding energies after CuPt loading is characteristic of *n*-type semiconductors forming a Schottky junction with high work function metals, and occurs as a result of lattice distortion of TiO<sub>2</sub> surface that generates oxygen vacancies. The oxygen vacancies in TiO<sub>2</sub> correspond to the formation of Ti<sup>3+</sup> states. Such a charge transfer process results in the shifting of binding energy of Ti to the lower energy side in CuPt-loaded TTNTAs. Measurements of multiple CuPt-TTNTA hybrid samples yielded band bending of 0.4-0.7 eV from the shifts in the Ti  $2p$  core-level spectra. The Pt  $4f$  spectra can exhibit both initial and final state effects. The electric field due to the depletion region shifts the  $4f_{7/2}$  and  $4f_{5/2}$  peaks at 71.0 eV

and 74.4 eV in bulk Pt to lower binding energies while the size-dependent screening effect shifts the peaks to higher binding energies. The width (FWHM) of the Pt  $4f_{7/2}$  peak in bulk Pt is smaller than 0.5 eV. However, in Fig. 4d and for other samples of photodeposited CuPt-TTNTA hybrids (see Fig. S8a in ESI†), the FWHM is *ca.* 1.5 eV which is indicative of the presence of Pt clusters of size 1 nm and smaller.<sup>57</sup> In Fig. 4d, the binding energy shifts in the two Pt  $4f$  peaks are +0.2 to +0.4 eV. However, for samples with band bending towards the lower end of the range (0.4-0.5 eV), the peak shifts are +1.2 to +1.5 eV as shown in Fig. S8a in ESI†, which we attribute to the final state effect being less obscured by the initial state effect.<sup>57</sup> The data obtained by us strongly indicates that metallic behavior is not fully developed in the photodeposited CuPt nanoparticles.

## 2.1 Band alignment in CuPt coated TTNTAs

A clear difference in the UPS spectra of transparent TiO<sub>2</sub> nanotubes before and after the photodeposition of CuPt nanoparticles is evident in Fig. 5 with both the secondary electron cut-off and the valence band edge red-shifted to lower binding energies. The valence band maximum, which was previously located 3.25 eV below the Fermi level ( $E_f$ ), is shifted to 2.76 eV below the Fermi level. By examining UPS spectra from multiple CuPt-TTNTA hybrid samples, a range of 0.49 - 0.67 eV was obtained for the observed band bending following CuPt photodeposition. The close agreement between the band-bending values obtained from XPS core-level spectra and UPS valence band spectra is noteworthy, and confirms the formation of a depletion region at the CuPt-TiO<sub>2</sub> interface following photodeposition. The resolution of the UPS spectra is slightly superior to that of XPS spectra (see Methods section) making the narrower UPS range more reliable. The work-function of a semiconductor surface is given by  $\phi_s = h\nu - E_{SE}$  where the first term represents the energy of the photons used to probe the band-structure (He I:21.21 eV in our case) and the second term is the secondary electron cut-off energy. The work function of the

transparent titania nanotubes is found to be 4.23 eV (implied electron affinity of 4.17 eV) in agreement with most prior studies on anatase thin films and nanostructures,<sup>58, 59</sup> and increased by 0.36 eV upon photodeposition of CuPt to 4.59 eV. The difference of 0.13-0.31 eV between the estimated band-bending and the change in work-function indicates the formation of a surface dipole ( $\Delta$ ) at the CuPt nanoparticle-decorated TiO<sub>2</sub> surface (see Fig. S1 in ESI†).<sup>60</sup>



**Fig. 5** UPS spectra of CuPt-TTNTA hybrids. For each spectrum, the valence band maximum was estimated using the intercept on the abscissa obtained by extrapolating the low binding energy edge to the baseline.

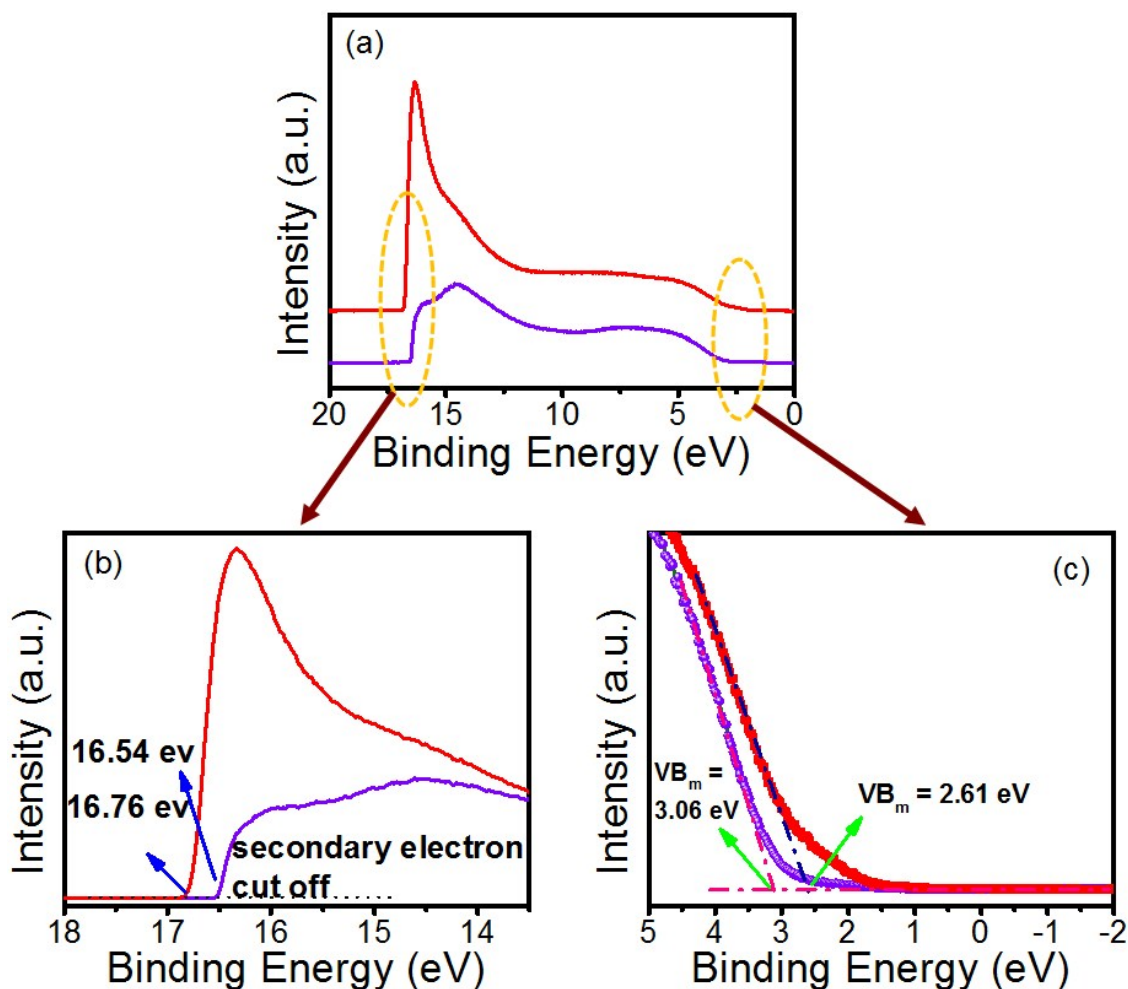
To understand the effect of Cu in CuPt-TTNTA hybrids, UPS data was collected from Pt-TTNTA hybrids wherein TiO<sub>2</sub> nanotube arrays were coated with monometallic Pt nanoparticles

using a near-identical photodeposition process. This data (see Fig. S12 in ESI†) indicates the valence band edge in Pt–TTNTA hybrids to be shifted upward toward to the Fermi level by a much larger amount than in CuPt–TTNTA hybrids indicating a band bending as large as 1.6 eV. This observation can be rationalized using the Anderson model<sup>29</sup> based on the much higher work function of monometallic Pt which is reduced by the addition of Cu in bimetallic alloys.

## 2.2 Examination of the effect of illumination in pure methanol on the TiO<sub>2</sub> surface

Photodeposition was performed by us in a methanolic medium and involved the photocatalytic reduction of the noble metal precursors (acetylacetonate salts of Cu and Pt). A question that arises is whether the TiO<sub>2</sub> nanotubes also experience chemical reduction of the surface during this process through the ultraviolet photon-mediated photocatalytic oxidation of methanol. The significance of this question lies in the determination of whether the observed Ti<sup>3+</sup> states in CuPt–TTNTA hybrids arise from charge transfer to the metal or from reduction by methanol. Therefore photoemission spectroscopic measurements were performed in methanol under identical conditions without the metal precursors, and the resulting spectra were compared to TTNTAs and CuPt–TTNTA hybrids. The UPS spectra for methanol illuminated samples (Fig. 6) are very dissimilar to those of TTNTAs and CuPt–TTNTA hybrids (Fig. 5) with regards to the shape and locations of peaks and energy cut-offs. The valence band maximum for the methanol illuminated transparent titania nanotube array samples occurred at 3.10 eV, indicating a maximum band-bending of 0.15 eV produced by chemical reduction of the TiO<sub>2</sub> surface. For the same sample preparation and illumination conditions, the valence band maximum for CuPt–TTNTA hybrids occurred at 2.76 eV. As seen in Fig. S7 in ESI†, transparent TiO<sub>2</sub> nanotube samples illuminated in methanol under identical conditions but without the metal precursors do not show a shift unlike the CuPt–TTNTA hybrids in Fig. 5. Thus significant band bending is indicated only in the

presence of CuPt nanoparticles. The increase in work function of the methanol illuminated samples implied by the secondary electron cut-offs occurring at lower binding energies in the UPS spectrum of Fig. 6b is attributed to surface adsorbates formed during the photochemical oxidation of methanol. The detailed study of such adsorbates is outside the scope of this work, but we will mention here that the dramatic attenuation of the secondary electron emission peaks in Fig. 6a is a well-known sign of the presence of such adsorbates.<sup>61, 62</sup>



**Fig. 6** Counter-clockwise from top (a) whole UPS spectra (b) magnified view of secondary electron cut-off region and (c) valence band edges of transparent TiO<sub>2</sub> nanotube samples following photodeposition of CuPt NPs (red curve) and subsequent to illumination under identical conditions in methanol but without the presence of metal precursors (purple curve).



The deposition of CuPt nanoparticles is not purely a chemical reduction of the complexed Cu(II) and Pt(II) species in the respective acetylacetonates because the presence of ultraviolet radiation is essential. Therefore, the reaction is photo-induced, and it is possible to have one or both of photochemical reduction and photocatalytic deposition.<sup>63</sup> In photochemical reduction, the illuminated solvent (MeOH, a potent hole scavenger) is the reducing agent and it is conceivable that the TiO<sub>2</sub> too gets reduced in addition to the Cu(II) and Pt(II) ions. On the other hand, in photocatalytic deposition, it is illuminated TiO<sub>2</sub> that is the reducing agent (through photogenerated electrons). Therefore, TiO<sub>2</sub> can get oxidized at best but is more typically unchanged (since the reduction is performed by photogenerated excess charge carriers).<sup>56</sup> The data presented here enables clear differentiation between the two phenomena under consideration. In particular, the band alignments produced by the photodeposition of CuPt on TiO<sub>2</sub> nanotube arrays are shown to be totally different from the corresponding alignment produced by pure photochemical reaction in methanol.

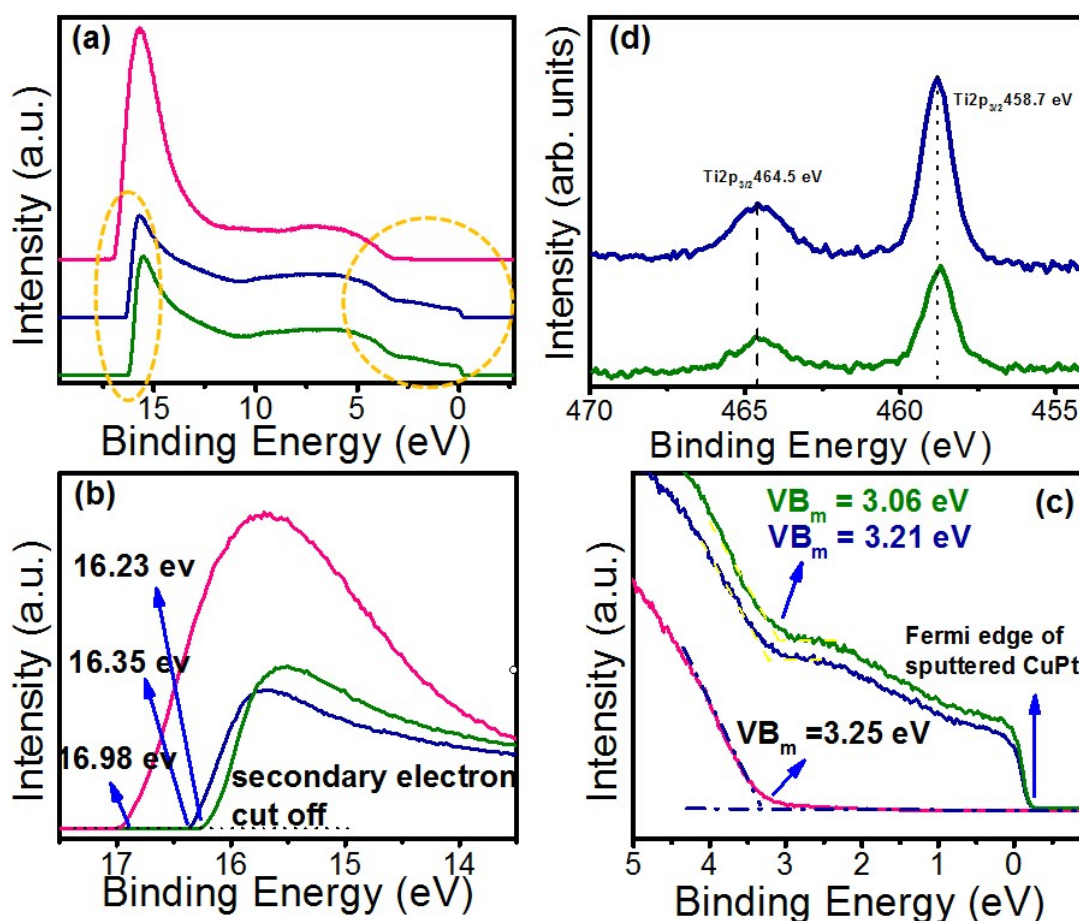
### 2.3 Comparison of photodeposited CuPt NPs to sputtered CuPt NPs

Fig. 7 displays the transformation in the UPS valence band spectra of transparent TiO<sub>2</sub> nanotubes after the formation of 2-5 nm sized CuPt nanoparticles by sputtering. The morphology and structure of such vacuum deposited mono- and bimetallic noble metal nanoparticles deposited on to one-dimensional titania nanostructures have been reported on elsewhere.<sup>24, 64-66</sup> For sputtered CuPt, the UPS spectra at low binding energies show a clear Fermi edge close to  $E_f = 0$  eV, which is a strong manifestation of metallic behavior. Likewise, the Pt 4*f* spectra in Fig. S8b (in ESI†) show peaks at 71.0 eV and 74.4 eV corresponding to those of bulk platinum. These findings are in line with prior reports that show the metallic behavior of metal-semiconductor heterojunctions dominating at metal coverages exceeding 2 nm. The FWHM of the Pt 4*f*<sub>7/2</sub> peak is ~1 eV for the sputtered CuPt NPs, less than that of

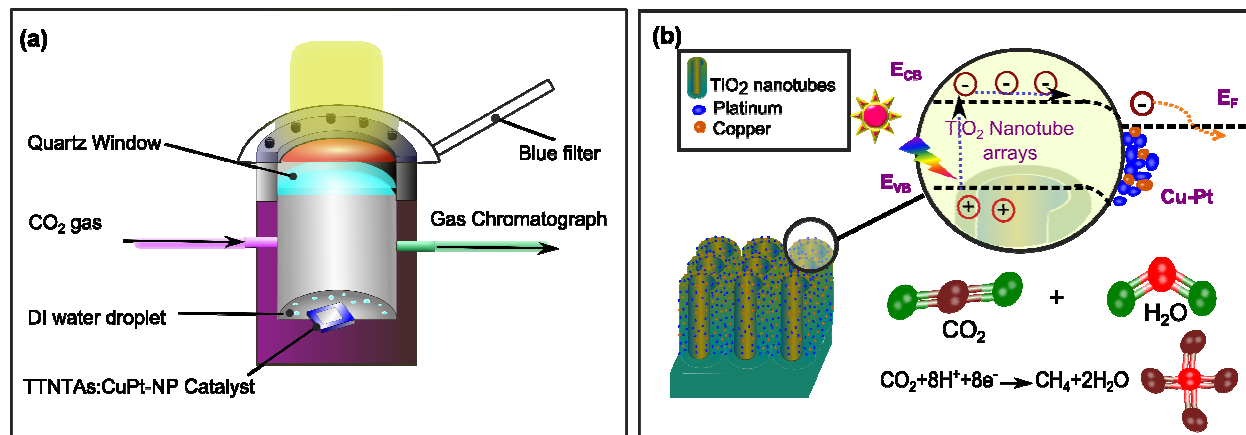
photodeposited CuPt NPs by  $\sim 0.5$  eV but not quite approaching the value of bulk Pt (0.5 eV). In Fig. 7, the valence band of TiO<sub>2</sub> is not completely obscured by the metallic behavior and is seen to be mostly unchanged by the formation of the heterojunction with sputtered CuPt. Furthermore, Fig. S9 (in ESI†) highlights the vast differences in the low binding energy XPS spectra of Sput-CuPt-TTNTA hybrids and the other types of TTNTAs studied in this report. CuPt-TTNTA hybrids formed by photodeposition show a rich collection of features in the 0-60 eV binding energy range, rather similar to those exhibited by TTNTAs subjected to ultraviolet radiation in methanol albeit shifted. However, these features in the 0-60 eV spectral range are mostly absent or smeared out for the Sput-CuPt-TTNTA hybrids in Fig. S9 (in ESI†), which provides further confirmation of the manifestation of bulk metallic behavior in the sputtered samples and the lack thereof in the photodeposited samples. In Fig. 7d, the Ti 2*p* binding energies for Sput-CuPt-TTNTA hybrids are slightly blue-shifted by 0.3 eV from the corresponding binding energies observed for bare TTNTAs in Fig. 4b. In the absence of concomitant shifts in the Pt 4*f* spectra (Fig. S8b in ESI†) to support the formation of an accumulation layer (downward band-bending), such a shift may indicate a healing of the TiO<sub>2</sub> surface by scavenging of remnant Ti<sup>3+</sup> species by the deposited noble metal nanoparticles. Thus, the sputtered CuPt nanoparticles certainly do not exhibit upward band-bending (i.e. depletion) as manifested by shifts in either core-level spectra or the valence band spectra.

The study of interfacial band alignment in TTNTA:CuPt hybrids was accompanied by CO<sub>2</sub> photoreduction studies and were compared with Sput-CuPt-TTNTA hybrids. Fig. 8a illustrates a photoreactor used for the reduction studies and the mechanism for a photoreduction process. The photoreduction of CO<sub>2</sub> to CH<sub>4</sub> is a complex that involves at least eight electron transfer steps. TTNTA:CuPt NPs demonstrated a higher CH<sub>4</sub> yield ( $\sim 600$  nmol cm<sup>-2</sup> hr<sup>-1</sup>) in comparison to TTNTAs coated with sputtered CuPt ( $\sim 30$  nmol cm<sup>-2</sup> hr<sup>-1</sup>) during 6 hours of illumination under AM 1.5 one sun

illumination, in agreement with previous reports.<sup>22, 64</sup> More details related to how this experiment was performed are provided in ESI†. Despite CuPt-NPs not acting as electron sinks at moderate illumination intensities, such TiO<sub>2</sub> nanotube-CuPt NP heterojunctions have demonstrated excellent performance for both photooxidation and photoreduction reactions. We hope our results will highlight the importance of preparation technique on band alignment in heterojunctions and stimulate the search for reaction mechanisms where noble metals behave as hole-sinks.



**Fig. 7** Counter-clockwise from top-right (a, b and c) Survey and magnified UPS valence band spectra of transparent TiO<sub>2</sub> nanotubes (pink-colored curve), sputtered CuPt nanoparticles formed on transparent TiO<sub>2</sub> nanotubes subsequent to an oxygen plasma clean (green-colored curves) and sputtered CuPt nanoparticles formed on transparent TiO<sub>2</sub> nanotubes without an oxygen plasma clean (blue-colored curves). In (d), the high resolution XPS core-level spectra of the Ti 2p peak is shown for sputtered CuPt nanoparticles formed on TiO<sub>2</sub> nanotube arrays.



**Fig. 8** Schematic illustrations displaying the (a) photoreactor used for reduction experiments using TTNTA:CuPtNP hybrids as a photocatalyst for the sunlight-driven conversion of CO<sub>2</sub> into methane and (b) conventional mechanism used to explain the conversion of carbon dioxide to methane by photoreduction on TiO<sub>2</sub>.

#### 2.4 Work functions, Schottky barriers and surface dipoles at TiO<sub>2</sub> nanotube surfaces

A number of samples examined in this study exhibit divergent behavior in their work-functions (as obtained from the secondary electron cut-off in the UPS spectra) and their band-bending (as obtained from shifts in the core-level binding energies and the UPS valence band edges). For instance, TTNTA samples illuminated by UV photons in methanol (Fig. 6c), the valence band edge is slightly red-shifted by 0.19 eV to 3.06 eV from 3.25 eV in TTNTAs (Fig. 5c) but with a red-shift of 0.44 eV in the secondary electron emission cut-off from 16.98 eV (Fig. 5b) to 16.54 eV (Fig. 7b). Therefore, the change in the work-function is significantly larger than the magnitude of the band-bending, and indicates the formation of a  $-0.25$  eV surface dipole. The surface dipole does not affect the core-level binding energies of photoelectrons generated interior to itself.<sup>67</sup> The absence of exact correlation between the work-function and the band-bending may be related to the orientation sensitivity of the work-function and the charge transfer.<sup>68</sup> In polycrystalline TiO<sub>2</sub> nanotube arrays, the crystal planes exposed to the vacuum that determine the work function can be different from the crystal planes which have contributed the bulk of the transferred electronic charge. Sput-CuPt-TTNTA hybrid samples too

exhibit significant shifts to higher work-functions with small or negligible band bending. However, these samples also show prominent bulk metallic character in their UPS spectra as manifested by their Fermi edges. Therefore the work functions of 4.86-4.98 eV measured here (Fig. 7c) are that of the bimetallic nanoparticles, and explained by the reduction of the platinum work-function of 5.5 eV due to the addition of lower work-function copper ( $\phi_{\text{Cu}} = 4.6$  eV).

The Schottky barrier height is given by  $\Phi_B = \phi_{bi} + \phi_n$  where  $\phi_n (= E_C - E_F)$  depends on the intrinsic carrier concentration in the  $n$ -TiO<sub>2</sub> nanotubes and  $\phi_{bi}$  is the maximum band-bending in the semiconductor.  $\phi_{bi}$  is given by  $kT \ln N_c/n$  where  $k$  is Boltzmann's constant and  $T$  is the absolute temperature, and estimated to be 0.06 eV at room temperature based on a conduction band density of states ( $N_c$ ) of  $10^{21}$  cm<sup>-3</sup>. In this study, we used TiO<sub>2</sub> nanotubes formed in ethylene glycol electrolytes and annealed in air, for which a carrier concentration ( $n$ ) in the range  $1.4 \times 10^{19}$ – $3.5 \times 10^{20}$  cm<sup>-3</sup> has been measured.<sup>69, 70</sup> The bandgap ( $E_g$ ) of anatase phase TiO<sub>2</sub> nanotubes (3.32 eV) is known to be slightly larger than that of bulk anatase.<sup>32, 71</sup> Thus, a range of 0.55-0.73 V is estimated for the Schottky barrier height. For a point-contact Schottky diode such as the one formed by isolated CuPt NPs decorating the walls of titania nanotube arrays, a hemispherical depletion region is obtained as shown in Fig. S10 (in ESI†).<sup>72</sup> We extracted the depletion region widths of such point-contact Schottky junctions with a barrier height of 0.4-0.7 V for 1 nm, 2 nm and 5 nm sized metal NPs for a range of equilibrium carrier concentrations in  $n$ -TiO<sub>2</sub> (Fig. S11 in ESI†). The resulting depletion widths are 2-10 nm (inset of Fig. S11 in ESI†). Since the wall-thickness of the TiO<sub>2</sub> nanotubes is in the range 25-35 nm (see Fig. 2 and Fig. 3), the nanotubes will not be fully depleted by the surface band bending.

## 2.5 Schottky Barrier Electron Trapping ?

Internal electric fields are vital in photocatalysts to separate charge carriers so that photogenerated electrons and holes drive chemical reactions instead of being lost to recombination. The electronic band-alignment at the support-promoter hetero-interface is needed in order to understand the correct photocatalytic mechanism of operation and also to improve the catalytic activity. The magnitude and direction of electric fields in a vast majority of photocatalysts based on *n*-type anatase-phase TiO<sub>2</sub>–noble metal nanoparticle (*nm-NP*) heterojunctions are undetermined yet an assumption is made in many reports that *nm-NPs* act as sinks for photogenerated electrons while photo-holes remain in TiO<sub>2</sub> based on spectroscopic evidence in a restricted set of idealized TiO<sub>2</sub>-noble metal junctions where the noble metal is deposited by high vacuum deposition. The term "Schottky-Barrier Electron Trapping" is used quite frequently in the photocatalytic literature to describe the electron sink effect of noble metal nanoparticles.<sup>73-77</sup> But a Schottky barrier would indicate electron transfer to surface reactants on TiO<sub>2</sub> surfaces and hot hole injection into the CuPt NPs where they might participate in further reactions,<sup>78</sup> opposite to the aforementioned electron sinking effect. At moderate incidence intensities of supra-bandgap photons (a carrier generation rate  $< 10^{19} \text{ cm}^{-3}$ ), the term "Schottky-barrier electron trapping" would be wholly incorrect due to its implication that noble metal nanoparticles trap photogenerated electrons due to the built-in field of the Schottky junction when it is actually photogenerated holes that would be trapped by the noble metal. At high illumination intensities, flat band conditions are created which may favor electron trapping at the noble metal due to kinetic rather than energetic conditions if the hole is scavenged quickly enough by surface-bound species. But the electron trapping here would occur due to kinetic factors rather than the Schottky barrier. Likewise flat band conditions exist in very small anatase nanoparticles ( $r < 20 \text{ nm}$ ) with a relatively low intrinsic carrier concentration that are unable to support a depletion region. But flat band conditions are unlikely to prevail in larger-sized,

moderately-to heavily *n*-type TiO<sub>2</sub> crystallites or on single crystal anatase surfaces. Therefore we suggest that the term "Schottky-Barrier Electron Trapping" be used with extreme caution with *n*-type semiconductor photocatalysts if used at all.

In the conventional understanding of photocatalysis, noble metal NPs act as electron sinks<sup>79, 80</sup> due to which transfer of photogenerated electrons to reactants occurs primarily on metal surfaces while the high oxidizing power of photogenerated holes is used in reactions on TiO<sub>2</sub> surfaces. The efficiency of charge-separation processes in such a scenario is kinetically controlled by parameters such as the minority carrier diffusion length, photoinduced electron transfer rate to the metal, trapping cross-sections and time-constants, etc. However, our XPS studies of the CuPt-TiO<sub>2</sub> interface in transparent TiO<sub>2</sub> nanotube arrays (TTNTAs) coated with photodeposited CuPt NPs (CuPt-TTNTA hybrids) show the existence of a depletion region with a built-in potential of 0.49-0.67 V. Under actual photocatalytic reaction conditions, further variation of the interfacial electronic properties is possible due to adsorption of reactant species. Notwithstanding this, the Schottky barrier at the CuPt-TiO<sub>2</sub> interface detected by our studies would direct photoexcited electrons toward the TiO<sub>2</sub> and photoexcited holes toward the CuPt NPs (Fig. S1 in ESI†), which would require a review of the commonly accepted mechanistic routes for various photocatalytic reactions that are almost exclusively based on hole-mediated oxidation on TiO<sub>2</sub> and electron-mediated reduction on the noble metal surface. The conventional model of noble metal electron sinks may still be applicable to the case of Sput-CuPt-TTNTA hybrids for which upward band bending was not detected.

## Conclusions

The structure and electronic properties of the TiO<sub>2</sub>-noble metal interface are important in both photocatalysis and conventional catalysis. Most of the work in this area considers single crystals of rutile

- reports on other forms and phases of  $\text{TiO}_2$  are scarce. Likewise, the majority of photoemission spectroscopic studies consider metal nanoparticles or films deposited under high vacuum conditions. However alternative methods of noble metal impregnation such as electrodeposition, photodeposition, wet impregnation, deposition-precipitation and colloidal synthesis are being extensively used to prepare photocatalysts, and the electronic properties of the resulting interfaces with semiconductor supports are largely unknown. Anodically formed  $\text{TiO}_2$  nanotube arrays coated with noble metal nanoparticles (NPs) formed by non-vacuum processes are being researched intensively for photocatalytic applications and have shown exceptional performance in recent studies. Cu-Pt bimetallic nanoparticles (NPs) were decorated over transparent  $\text{TiO}_2$  nanotube arrays via a facile approach of photodeposition to investigate their influence on the structural and electronic properties of CuPt-TTNTA hybrids. HRTEM studies revealed that Cu-Pt NPs were closely attached to the walls of  $\text{TiO}_2$  nanotubes. The crystalline structure of nanotubes and the local changes at the interface of CuPt-TTNTA hybrids were confirmed by microRaman spectroscopy. A shift in the  $E_g$  Raman mode along with a narrow broadening for CuPt-TTNTA hybrids was found due to dispersion of bimetallic CuPt nanoparticles over  $\text{TiO}_2$  nanotubes. The lack of manifestation of metallic behavior in the XPS and UPS spectra were used to infer that the majority of photodeposited CuPt NPs had a size of 1 nm or smaller, even though 2-5 nm NPs were detected in electron micrographs. On the other hand, 2-5 nm sputtered and thermally dewetted CuPt manifested clear metallic behavior. The formation of a Schottky barrier at the CuPt- $\text{TiO}_2$  interface with a band bending of 0.49-0.67 eV was confirmed through XPS and UPS studies in the photodeposited CuPt-TTNTA hybrids in comparison to sputtered CuPt-TTNTA hybrids, where no appreciable band bending was present. A close agreement between the band-bending values obtained from XPS and UPS results corroborates the formation of a depletion region at the photodeposited Cu-Pt  $\text{TiO}_2$  nanotube interface. This study also points to the strong effect of the preparation conditions of the noble metal promoter on



the electronic structure of the resulting photocatalyst. We show that sputtered CuPt and photodeposited CuPt have substantially different band-alignment in heterojunctions with TiO<sub>2</sub> nanotubes. Photochemical reduction by methanol was ruled out as a cause for the observed difference. On the other hand, the different size-scales of the sputtered and photodeposited CuPt nanoparticles was shown to be a contributing factor. Finally, the errors associated with the use of the term "Schottky barrier electron trapping" were highlighted.

†Electronic supplementary information (ESI) available: Experimental details and supplementary figures relating to the electronic band-structure, nanotube morphology, photoemission spectra and depletion region formation.

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