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### Introduction

Nanomaterials have attracted much interest as a result of their size-dependent optoelectronic, magnetic, chemical and physical properties.<sup>1-3</sup> The use of nanoscale semiconductor nanostructures will be essential in the fabrication of the next generation of optoelectronic devices and in fulfilling future energy demands.<sup>4-6</sup> Much work has been carried out on the synthesis of multi-functional nanomaterials. Nanostructured semiconductor materials act as efficient photocatalysts as a result of their high surface area and varied morphologies.<sup>7,8</sup> Many strategies have been used to develop efficient photocatalyst-based surface-tuning strategies for the synthesis of various oxides on the nanoscale.<sup>9</sup> In the past decade, most of the progress made in the field of photocatalysis<sup>10</sup> has been limited to the use of ultraviolet (UV) light rather than the more

# *In situ* preparation of a novel organo-inorganic 6,13-pentacenequinone–TiO<sub>2</sub> coupled semiconductor nanosystem: a new visible light active photocatalyst for hydrogen generation<sup>†</sup>

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Previous studies related to the synthesis of stable UV-visible light active photocatalysts for hydrogen generation have been limited to inorganic semiconductors and their nano- and hetero-structures. We demonstrate here the use of an organo-inorganic 6,13-pentacenequinone (PQ)–TiO<sub>2</sub> coupled semiconductor nanosystem as an efficient photocatalyst active in visible light for the production of hydrogen. Anatase TiO<sub>2</sub> nanoparticles (3–5 nm) were uniformly decorated on thin sheets of monoclinic PQ by an *in situ* solvothermal method. These as-prepared PQ–TiO<sub>2</sub> coupled semiconductor nanosystems had a band gap in the range 2.7–2.8 eV. The strong emission at 590 nm can be attributed to the transfer of electrons from the LUMO energy level of TiO<sub>2</sub> to combine with the holes present in the HOMO level of PQ. This electron–hole recombination makes availability of electrons and holes in LUMO of PQ and HOMO of TiO<sub>2</sub>, respectively. This hybrid semiconductor coupled nanosystem resulted in a rate of hydrogen evolution of 36 456 µmol h<sup>-1</sup> g<sup>-1</sup> from H<sub>2</sub>S under UV-visible light; this is four times higher than the rate obtained with TiO<sub>2</sub> in earlier reports of UV-visible light active photocatalysts. These results open up a new path to explore inorganic systems coupled with PQ as new photoactive hybrid catalysts in a number of chemical and physicochemical processes.

useful visible light region. Scientific and engineering interest in semiconductor photocatalysis has increased significantly<sup>10</sup> and the use of visible light (a renewable source of energy) active photocatalysts in the economic production of hydrogen has been explored.<sup>10,11</sup> Hydrogen is recognized as an important future fuel and is capable of meeting global energy demands. Using photocatalysis, H<sub>2</sub> can be economically produced from both  $H_2O$  and  $H_2S$ .  $H_2S$  is readily available as a waste gas from oil refineries and the alkali chemical industry; the ubiquitous Claus process is currently used to produce sulphur from H<sub>2</sub>S rather than hydrogen. The photocatalytic production of hydrogen from H<sub>2</sub>S using UV-visible light is therefore very important. The photocatalytic production of hydrogen from H<sub>2</sub>S and H<sub>2</sub>O is economically more viable than conventional hydrogen production methods such as steam reforming and electrolysis.8-12 We have previously reported the use of waste H<sub>2</sub>S to produce eco-friendly hydrogen under UV-visible light irradiation,<sup>8,13-16</sup> but few reports have been published on the use of a visible light active photocatalyst for the production of hydrogen from H<sub>2</sub>S. Metal oxide semiconductors have been doped with transition metals to narrow the band gap to be suitable for UV-visible light.17-23 As TiO2 is one of the most stable, eco-friendly and economic photocatalysts, much research has been carried out on the doping of TiO<sub>2</sub> with

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cations and anions to narrow the band gap.<sup>6,9</sup> TiO<sub>2</sub>–graphene nanocomposite particles and TiO<sub>2</sub> decorated with Ag, Au and Pt have been reported as visible light active photocatalysts.<sup>11,24–34</sup>

Based on the good stability of  $TiO_2$  and our earlier work<sup>16</sup> on the use of a 6,13-pentacenequinone (PQ) organic semiconductor as a photocatalyst for energy harvesting and environmental remediation, we investigated the organo-inorganic hybrid (PQ– $TiO_2$ ) nanosystem as a visible light active photocatalyst for the production of hydrogen. PQ has good thermal stability and a band gap around 2.8 eV. It is also simple to synthesize and has a high molar absorption coefficient, which makes it an efficient visible light active photocatalyst. The *in situ* preparation of a novel organo-inorganic (PQ– $TiO_2$ ) coupled semiconductor nanosystem was investigated using a facile solvothermal method. The interesting optical properties of this organo-inorganic coupled nanosystem and its enhanced photocatalytic activity were studied.

During the solvothermal preparation of  $TiO_2$ , PQ was introduced to produce the PQ– $TiO_2$  hybrid nanosystem. PQ– $TiO_2$ nanosystems were prepared using 5, 10 and 17 mmol of a titanium tetra-isopropoxide precursor (referred to as PT-5, PT-10 and PT-17, respectively). This unique nanosystem was characterized to identify the phases present.

### **Results and discussion**

These as-prepared PQ–TiO<sub>2</sub> nanosystems were characterized by X-ray diffractometry (XRD) (Fig. 1). The XRD patterns for pure PQ and TiO<sub>2</sub> are shown in Fig. 1a and e.

The diffraction peaks at  $2\theta = 25.3$ , 37.8, 48, 53.9 and 55° can be indexed as (101), (004), (200), (105) and (211) and correspond to anatase TiO<sub>2</sub> (JCPDS no. 21-1272). The diffraction peaks at  $2\theta = 14.7$ , 23.6 and 27.7° represent the (012), (112) and (104) planes and indicate the crystalline monoclinic phase of PQ (JCPDS no. 47-2123). The broadening of the XRD peaks of TiO<sub>2</sub> clearly shows the nanocrystalline nature of the material. The crystallite sizes of the TiO<sub>2</sub> in the PT-5, PT-10 and PT-17 hybrid nanosystems calculated using Scherrer's formula were 5.8, 6.6



Fig. 1 XRD patterns of the  $PQ-TiO_2$  hybrid nanosystems. (a) Pure PQ, (b) PT-5, (c) PT-10, (d) PT-17 and (e) pure  $TiO_2$ .

and 7.5 nm, respectively. However, with increasing  $TiO_2$  concentration, the overall intensity of the other  $TiO_2$  peaks also increased slightly while retaining their width. This difference was marginal and difficult to see because the difference in crystallite size was very small (about 1 nm). However, this was also studied using the SAED pattern (see later discussion). The existence of monoclinic PQ and anatase  $TiO_2$  in the XRD spectra clearly indicates the formation of the organo-inorganic (PQ– $TiO_2$ ) hybrid nanosystem.

Fig. 2 shows the field-emission scanning electron microscopy (FESEM) images of the as-prepared PQ-TiO<sub>2</sub> hybrid nanosystems PT-5, PT-10 and PT-17. Pristine PQ forms micronsized sheets with a smooth surface and a thickness in the range 50–200 nm (Fig. 2a and b). FESEM images of the PT-5 nanosystem indicate the formation of nanosized TiO<sub>2</sub> particles  $\leq 5$ nm in size on the surface of the PQ sheets (Fig. 2c and d). The images of the PT-10 and PT-17 hybrid nanosystems show 5–7 and 8–10 nm TiO<sub>2</sub> particles uniformly layered on the PQ sheets (Fig. 2e–h). All three hybrid nanosystems show the same morphology of nanosized TiO<sub>2</sub> particles on the surface of PQ sheets. Further high-resolution FESEM images are given in the ESI (Fig. S1†). The density of the nanoparticles increased from PT-5 to PT-17 as a result of the increase in the TiO<sub>2</sub>



Fig. 2 FESEM images of the  $PQ-TiO_2$  hybrid nanosystems. (a and b) PQ, (c and d) PT-5, (e and f) PT-10 and (g and h) PT-17.

concentration.  $\text{TiO}_2$  nanoparticle clusters were also seen sandwiched between the PQ sheets. The FESEM images clearly show the uniform distribution of the  $\text{TiO}_2$  nanoparticles on the PQ sheet for all the prepared nanosystems.

Fig. 3 shows transmission electron microscopy (TEM) images with the SAED pattern of the prepared PQ–TiO<sub>2</sub> hybrid nanosystems. The images for the hybrid PT-5 nanosystem (Fig. 3a and b) confirm the formation of spherical TiO<sub>2</sub> nanoparticles in the size range 3–5 nm (inset, Fig. 3b). The TEM images of the PT-10 and PT-17 hybrid nanosystems confirm the existence of TiO<sub>2</sub> nanoparticles with sizes of 6–8 and 9–10 nm evenly distributed on the PQ sheets (Fig. 3c–f). High-resolution TEM images indicating the size and shape of TiO<sub>2</sub> particles are given in Fig. S2.†

Well-defined lattice fringes were seen in the HRTEM images (insets, Fig. 3b, d and f) and the inter-planar distance between the adjacent planes was 0.34 nm, corresponding to the 101 plane of anatase  $TiO_2$  and confirming the formation of this phase in all three hybrid PQ– $TiO_2$  nanosystems. The SAED pattern (insets, Fig. 3b, d and f) also shows the *d* spacings of 0.24 and 0.34 nm attributed to the (103) and (101) reflection planes, matching with anatase  $TiO_2$  in all three nanosystems. The SAED pattern clearly shows that the intensity of the bright



Fig. 3 TEM images of PQ-TiO<sub>2</sub> nanosystems. (a and b) PT-5, (c and d) PT-10 and (e and f) PT-17; the insets in (b), (d) and (f) show the HRTEM and SAED patterns of PQ-TiO<sub>2</sub>.

rings increases from PT-5 to PT-17, indicating the slight increase in crystallinity suggested by the XRD patterns. The HRTEM images clearly show the perfect interface between the  $TiO_2$  nanoparticles and the PQ nanosheets. This interface could provide a channel for the transfer of electrons and holes between the PQ and  $TiO_2$  semiconductors.

Fig. 4 shows the diffuse reflectance UV-visible absorbance spectra of PQ-loaded TiO<sub>2</sub>. Pristine PQ shows an absorbance edge at 449 nm, indicating a band gap around 2.8 eV.

The PT-5 nanosystem shows an absorption edge at 451 nm with a band gap of 2.74 eV. The PT-10 and PT-17 nanosystems show two distinct absorption edges at 380 nm (band gap 3.26 eV) and 455 nm (band gap 2.73 eV), corresponding to TiO<sub>2</sub> and PQ, respectively. The higher band gaps of TiO<sub>2</sub> in PT-10 and PT-17 result from a blue shift in the absorbance as a function of particle size. The band gap values were verified using Tauc's plot (Fig. S3†). This confirmed the formation of the coupled hybrid PQ-TiO<sub>2</sub> nanosystem (Fig. 4).

The increase in absorbance in the range 370–400 nm was attributed to the increased concentration of  $\text{TiO}_2$  in the nanosystem. We observed a clear single absorption peak in PT-5 as a result of the higher concentration of PQ. The absorbance peaks in the range 400–460 nm correspond to PQ and the peaks in the range 370–400 nm correspond to  $\text{TiO}_2$  in the PT-10 and PT-17 hybrid nanosystems.

Photoluminescence spectra are often used to study surface processes involving electron-hole interactions in semiconductors. Fig. 5 shows the photoluminescence spectra of the hybrid nanosystems PT-5, PT-10, PT-17, together with those for pure PQ and TiO<sub>2</sub>. The prepared nanosystems showed strong emission peaks at 550 nm, with a satellite peak at 590 nm. An increase in the PL intensity as a function of the TiO<sub>2</sub> concentration was observed.<sup>35–38</sup>

The peak at 550 nm may be due to the defects generated as a result of oxygen vacancies. Such defects can act as self-trap centres for the recombination of excitons as a result of the combined effect of defect centres generated from oxygen vacancies and the lower particle size. PT-5 showed a slightly



Fig. 4 Diffuse reflectance UV-visible absorbance spectra of the PQ- $TiO_2$  hybrid nanostructures PQ, PT-5, PT-10 and PT-17.



Fig. 5 Photoluminescence spectra of the PQ–TiO\_ hybrid nano-systems PQ, PT-5, PT-10 and PT-17.

higher PL emission at 550 nm than PT-10, which might be a result of the smaller particle size of  $TiO_2$  leading to the recombination of self-trapped excitons. Ho *et al.*<sup>40</sup> reported that the emission peak at 550 nm can be attributed to electronic transitions involving trap states. The photoluminescence study of anatase  $TiO_2$  nanoparticles of Bian *et al.*<sup>32</sup> is in good agreement with our results. The satellite peak at 590 nm may be due to electron-hole recombination.

For simplicity, we studied the HOMO and LUMO energy levels of PQ and  $TiO_2$ . Fig. 6 shows the band diagram for the coupled nanosystems.

The LUMO energy levels of PQ and TiO<sub>2</sub> are at 3.29 and 4.20 eV, whereas the HOMO levels are at 6.29 and 7.40 eV.<sup>16,39</sup> Electron–hole pairs were generated in both PQ and TiO<sub>2</sub> on excitation with 350 nm light. As a result of the coupling of these two semiconductors, the electrons from the LUMO energy level of PQ transferred to the LUMO of TiO<sub>2</sub>; these may later combine with the holes present in the HOMO level of PQ. This electron–hole recombination might be responsible for the emission peak at 590 nm seen in the PL study (Fig. 5).



Fig. 6 Schematic band structures of PQ-TiO<sub>2</sub> hybrid nanosystem.

In the present nanosystems, spherical nanoparticles of  $TiO_2$  3–5 nm (PT-5) in size are intact on the plate-like structure of PQ (organic semiconductor); the generated electron–hole pairs can therefore be easily moved across the organic–inorganic interface.

It has been reported that the emission peak at 550 nm may be due to mid-trap states.<sup>34</sup> Pristine PQ has emission peaks at 408, 432 and 574 nm; the peaks at the lower wavelengths are due to  $\pi$ - $\pi^*$  and n- $\pi^*$  transitions, whereas the emission peak at 574 nm might be due to mid-trap centres. The enhancement in the PL intensity in the prepared hybrid system is a result of electron transfer between the organic-inorganic semiconductors, which may inhibit the non-radiative electron-hole pair recombinations. The observed results are in agreement with previously reported results for hetero-systems of TiO<sub>2</sub> with particle sizes <10 nm, which showed intense yellow-green emissions.<sup>37-39</sup>

#### Photocatalytic study

A photocatalytic study was performed using the synthesized PQ–TiO<sub>2</sub> hybrid nanosystems (PT-5, PT-10 and PT-17) under UV-visible light for hydrogen generation from  $H_2S$ .

Fig. 7 is a graph of the time-dependent photodecomposition of H<sub>2</sub>S and clearly shows a stable linear increase in the evolution of hydrogen. The highest rate of evolution of hydrogen (36 456  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup>) was obtained for the PT-5 hybrid nanosystem (Table 1); slightly lower rates were obtained for PT-10 and PT-17. This rate of evolution of hydrogen is four times higher than that obtained for TiO<sub>2</sub> and is higher than reported previously.<sup>13-16,24</sup>

The rate of evolution of hydrogen obtained is much higher than reported previously for P-25 Degussa  $TiO_2$  and PQ for a feed rate of  $H_2S$  of 0.5 mL min<sup>-1</sup>. Continuous hydrogen production has been monitored at this minimum  $H_2S$  flow-rate. As the initial rate of feeding  $H_2S$  becomes higher, the rate of hydrogen evolution also increases and hence a 0.5 mL min<sup>-1</sup> feeding rate was maintained throughout the experiment.<sup>16</sup> Excellent hydrogen evolution rates were observed at this feed



Fig. 7 Photocatalytic activity of PQ-TiO<sub>2</sub> hybrid nanosystems (250 mL reactor; 0.1 g catalyst; feed rate of H<sub>2</sub>S gas 0.5 mL min<sup>-1</sup>).

Table 1 Photocatalytic evolution of hydrogen

Sample no.	Catalyst	$H_2$ evolution (µmol h <sup>-1</sup> g <sup>-1</sup> )
1	PT-17	18 600
2	PT-10	24 552
3	PT-5	36 456

rate. In 0.25 M KOH solution (pH 12.5), the weak diprotic acid  $H_2S$  (p $K_a$  values 7.0 and 11.96) dissociates and maintains an equilibrium with hydrosulfide (HS<sup>-</sup>) ions (eqn (1)). The PQ-TiO<sub>2</sub> hybrid nanosystem absorbs light and generates electronhole pairs (eqn (2)). The photogenerated valence band hole (h<sup>+</sup>VB) formed by band gap excitation of the PQ-TiO<sub>2</sub> hybrid nanosystem oxidizes the HS<sup>-</sup> ion to the disulfide ion (S<sub>2</sub><sup>2-</sup>), liberating a proton from the HS<sup>-</sup> ion (eqn (3)). The conduction band electron (e<sup>-</sup>CB) from the PQ-TiO<sub>2</sub> hybrid nanosystem photocatalyst reduces protons to produce molecular hydrogen (eqn (4)).

$$H_2S + OH^- \leftrightarrow HS^- + H_2O$$
 (1)

Semiconductor PQ-TiO<sub>2</sub>  $\leftrightarrow$  h<sup>+</sup>VB + e<sup>-</sup>CB (2)

Oxidation:  $2HS^- + 2h^+VB \leftrightarrow S_2^{2-} + 2H^+$  (3)

Reduction:  $2H^+ + 2e^-CB \leftrightarrow H_2$  (4)

We did not observe any hydrogen evolution without a catalyst in the dark; this clearly indicates that the evolution of hydrogen was a result of the PQ–TiO<sub>2</sub> hybrid nanosystems.

Fig. 8 shows the mechanistic approach for the photocatalytic generation of  $H_2$  *via* the decomposition of  $H_2S$  over prepared PQ-TiO<sub>2</sub> hybrid nanostructures. PT-5 shows a higher photocatalytic activity than the other prepared nanosystems. The conduction band (CB) of TiO<sub>2</sub> is 0.91 eV lower than the CB of PQ and the valence band (VB) of TiO<sub>2</sub> is about 1.11 eV lower than the VB of PQ. On excitation with light, there are two



Fig. 8 Mechanism of H<sub>2</sub> generation.

possibilities: (1) the electron-hole pairs generated in both the semiconductors and the generated species will act as reducing as well as oxidizing agents to generate  $H_2$ ; and (2) the CB electrons of TiO<sub>2</sub> will recombine with the VB holes of PQ. The  $H_2$  generation takes place at the CB of PQ and the oxidation reaction occurs at the VB of TiO<sub>2</sub>.

This process results in the availability of electrons for H<sub>2</sub> generation by inhibiting electron-hole recombination in the individual semiconductors. The PL study supports the reaction mechanism and revealed that the activity of the nanosystem decreased with increasing PL emission. The PL study clearly supported that view that the emission peak around 550 nm represents the recombination of electron-hole pairs when large numbers of electrons transfer from the CB of PQ to the CB of TiO<sub>2</sub> and recombine with holes present in the VB of PO or TiO<sub>2</sub>. The PT-17 nanosystem had a higher PL intensity and showed a lower rate of H<sub>2</sub> generation. The reduction in the intact nanoparticle size of TiO<sub>2</sub> on PQ in samples PT-5 and PT-10 also affected the generation of H<sub>2</sub>. The reduction in PL intensity in these samples may be due to the smaller size of the TiO<sub>2</sub>, which creates defects. These defects are responsible for the suppression of charge carrier recombination, which ultimately enhances the photocatalytic activity.15 However, although PT-5 had a slightly higher intensity than PT-10, the combined effect with a smaller particle size enhanced the inhibition in charge carrier recombination, which ultimately resulted in the highest activity.<sup>40</sup> Another advantage of coupled semiconductor systems is that they allow inter-particle electron transfer, which increases the charge separation and helps to enhance the photocatalytic activity. Considering the very small size of the  $TiO_2$  nanoparticles (3-5 nm) in intimate contact with PQ, the surface trapping of electrons and holes before recombination will also be more efficient.40 The photogenerated electron-hole pairs have a much shorter distance to travel to reach the surface in a small cluster. Once the charged carriers (electron and holes) reach the interface, they can participate in redox reactions and contribute to the enhancement in the photocatalytic activity.

#### Conclusions

Novel organo-inorganic PQ-TiO<sub>2</sub> hybrid semiconductor nanosystems were successfully synthesized by a facile solvothermal method. The nanosystems were used as photocatalysts for the photodecomposition of H<sub>2</sub>S to produce hydrogen under UVvisible light. The highest rate of hydrogen evolution (36 456  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup>) was observed over a PQ-TiO<sub>2</sub> hybrid nanosystem without a co-catalyst under UV-visible light. In this hybrid nanosystem, very small intact nanoparticles of TiO<sub>2</sub> on sheets of PQ exhibited the most efficient inhibition of the charge carrier recombination, which is responsible for the enhanced photocatalytic activity. These results suggest that this organo-inorganic hybrid nanosystem is a promising and efficient UV-visible light active photocatalyst. Other hybrid nanosystems with different semiconductor oxides can be synthesized using the same technique.

### Experimental

#### **Catalyst preparation**

To synthesize the PQ-TiO<sub>2</sub> nanosystem, 5 mL of titanium tetraisopropoxide (17 mmol) in methanol and 2 mL of hydrazine hydrate were stirred in a beaker. Guanidine carbonate solution (3.05 g, 17 mmol) in acetic acid was then added to this solution. The solution was stirred for a further 15 min and then the appropriate amount (0.25 g) of freshly prepared PQ was added and the stirring continued for another 15 min. PQ was prepared by a previously reported method.<sup>16</sup> The resultant reaction mixture was transferred to a Teflon-lined autoclave, which was sealed and heated at 150 °C for 15 h in an oven. The precipitate of PQ-TiO<sub>2</sub> obtained was washed and dried at 80 °C. A similar procedure was followed for concentrations of titanium tetra-isopropoxide of 10 and 5 mmol. The PQ-TiO<sub>2</sub> nanosystem prepared using 5, 10 and 17 mmol of the titanium tetra-isopropoxide precursor were referred to as PT-5, PT-10 and PT-17, respectively.

#### **Catalyst characterization**

Structural studies of the as-synthesized products were performed using an X-ray diffractometer (XRD-D8, Advance, Bruker-AXS). The samples were studied morphologically using FESEM (Hitachi S-4800) and TEM (Philips, EM-CM-12). The UV-visible absorbance spectra were recorded using a Shimadzu UV-visible-NIR spectrophotometer (Model UV-3600) in the wavelength range 200–800 nm.

#### Photocatalytic study

Hydrogen evolution was carried out in a quartz photo-reactor using 0.1 g of PQ–TiO<sub>2</sub> under irradiation from a 450 W Xe lamp light source (Oriel). The cylindrical quartz reactor was filled with 250 mL of 0.25 M aqueous KOH and purged with Ar for 30 min. H<sub>2</sub>S was bubbled through the solution for 60 min at a rate of 0.5 mL min<sup>-1</sup>. A 0.1 g mass of the photocatalyst (PQ–TiO<sub>2</sub>) was introduced into the reactor and irradiated with the visible light source with stirring and the continuous bubbling of H<sub>2</sub>S at a rate of 0.5 mL min<sup>-1</sup>. The excess H<sub>2</sub>S was trapped in a 0.5 M NaOH solution. The amount of H<sub>2</sub> evolved was measured with a graduated gas burette and analysed by gas chromatography (Model Shimadzu GC-14B, MS-5 Å column, TCD, Ar carrier).

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