Monolayer of TiO_2/PbS coupled semiconductor nanoparticles

Yipeng Sun,[a,b] Encai Hao,[b] Xi Zhang,[a,b] Bai Yang,[b] Mingyuan Gao[b] and Jiacong Shen*[a,b]

[a] *Key Lab of Supramolecular Structure & Spectroscopy, Jilin University, Changchun, 130023, PR China*
[b] *Department of Chemistry, Jilin University, Changchun, 130023, PR China*

A new type of coupled semiconductor nanoparticle TiO_2/PbS monolayer is prepared based on electrostatic interactions and characterised by UV–VIS, IR, EDS, TEM and XPS.

Coupled semiconductor nanoparticle systems have recently received a great deal of attention in research.[1–3] Combining a small-bandgap semiconductor with a large-bandgap semiconductor offers an opportunity to sensitize the latter, which may find potential applications in photocatalysis, solar energy conversion, *etc.* Organizing such types of materials into layered structures provides the possibility to fabricate new types of molecular or supramolecular devices.

In our previous work, we reported the build-up of nanoparticle multilayer assemblies based on electrostatic interactions.[4–6] Here, we further develop our concept and have succeeded in depositing a new type of coupled semiconductor nanoparticle, TiO_2/PbS, as a monolayer film for the first time. UV–VIS spectra, IR spectra, energy dispersive X-ray spectra (EDS) and X-ray photoemission spectroscopy (XPS) confirmed the coexistence of TiO_2 and PbS nanoparticles in the films. Transmission electron micrographs (TEM) gave a direct observation of the morphology of the coupled semiconductors.

The TiO_2 colloidal solution was prepared by the forced hydrolysis technique.[7] Fresh doubly distilled $TiCl_4$ (5.2 ml) was slowly added to vigorously stirred water (200 ml) maintained at 0 °C. The mixture was then dialysed to yield a suspension of 15 g l^{-1} TiO_2 particles dispersed in water at pH 2. The mean diameter of the particles was 14 mm, as determined by TEM, with a size distribution of ±20%. In a typical preparation process of the TiO_2/PbS coupled semiconductor, 2.7 ml of concentrated TiO_2 solution was diluted to 0.2 g l^{-1}, after which 12 ml of 1.0×10^{-2} mol dm^{-3} $SHCH_2CO_2H$ and 1 ml of 5×10^{-2} mol dm^{-3} $PbNO_3$ was added. To the resulting solution under vigorous stirring, 5 ml of 1×10^{-2} mol dm^{-3} Na_2S was injected and the solution was further stirred for 15 min to obtain a brown colloidal solution of pH 3, which was stable in a refrigerator (5 °C) for at least 2 weeks. UV–VIS spectra revealed the obvious absorption in the visible region, confirming the formation of PbS nanoparticles. The above preparation process is different from that of Lawless *et al.* for the TiO_2/CdS system,[3] in which the two types of nanoparticles were prepared separately and subsequently mixed. In our case, we took advantage of the stabilising effect of TiO_2 on the formation of PbS nanoparticles. Experiments showed that it was difficult to prepare a PbS colloidal solution at pH 3 in the absence of TiO_2. This means that there may be an interaction between the TiO_2 and PbS nanoparticles. In addition, IR experiments showed that the S–H band at 2567 cm^{-1} in the spectrum of $SHCH_2CO_2H$ had disappeared completely in the IR spectrum of the coupled semiconductors, while the band of C=O at 1717 cm^{-1} in the spectrum of $SHCH_2CO_2H$ acid shifted to 1600 cm^{-1}. These results implied that $SHCH_2CO_2H$ interacted with both TiO_2 and PbS nanoparticles,[8] and that two types of particles were linked *via* the bifunctional molecules.

In our experiment, the Ti : Pb molar ratio was 10 : 1. This means that PbS nanoparticle can only occupy part of the surface of TiO_2 nanoparticles, leaving the rest exposed to the interface with the solution, which can be induced to be positively charged at pH < 4. Therefore we envisaged the substitution of TiO_2/PbS coupled semiconductors for polycationic compounds. By alternating deposited TiO_2/PbS with polyanionic compounds, we succeeded in fabricating a new type of coupled semiconductor nanoparticle monolayer.

The fabrication process of the TiO_2/PbS monolayer is shown schematically in Fig. 1. A freshly cleaned quartz slide (or Formvar-covered, 200 mesh copper grid) was first immersed in 0.5 vol%, aqueous cationic poly(ethyleneimine) (PEI) solution for 20 min. After rinsing with Milli-Q water, the substrate was transferred into a solution containing 5 mg of poly(styrene-4-sulfonate) (PSS) in 10 ml H_2O (pH 4) for 20 min to obtain a negatively charged surface. The resulting substrate was then dipped into the TiO_2/PbS colloidal solution for 40 min at 5 °C to absorb one layer of coupled semiconductor nanoparticles. In the above process, pretreatment of the substrates with PEI solution promoted adhesion of the films to a variety of surfaces,[9] thus providing a wide range of choices for fabrication of ultrathin films for different purposes. Fig. 2 shows the UV–VIS spectra of the monolayer films. Comparison of Fig. 2(*a*) and (*c*) shows obvious absorption into the visible region when the coupled semiconductor was adsorbed onto the film, which would be contributed by PbS particles, while little absorption was found in the same region for a pure TiO_2 monolayer. This means that PbS together with TiO_2 was adsorbed onto the film, rather than only one type of particle. In addition, a small absorption peak was found at 250 nm in the TiO_2/PbS monolayer. The same peak was also present in a pure TiO_2 monolayer, but was absent in the casting film of the coupled semiconductor. It is proposed that the interaction between PSS and TiO_2 may contribute to this absorption peak.

Transmission electron micrographs (TEM) were taken to give a direct view of the morphology of the coupled semiconductor. Two kinds of particles of different size are clearly

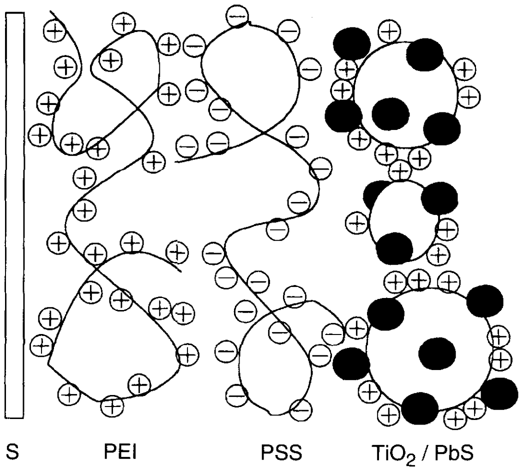


Fig. 1 Schematic drawing illustrating the build-up of a TiO_2/PbS monolayer. S, PEI, PSS refer to substrate, poly(ethylenimine) and poly(styrene-4-sulfonate), respectively. Filled circles refer to PbS and open circles to TiO_2.

seen in Fig. 3(*a*). The larger particles, believed to be TiO_2, have an average diameter of 20 nm. The smaller particles, distributed more or less homogeneously on the surface of the larger particles, have an average diameter of 3 nm, and are believed to be PbS particles. Both types of nanoparticle are roughly spherical. Thus the direct association of two semiconductor colloids is confirmed. The coupled semiconductor aggregates in some regions. A possible reason might be that the bifunctional $SHCH_2CO_2H$ acts as a cross-linking agent which directs this aggregation.

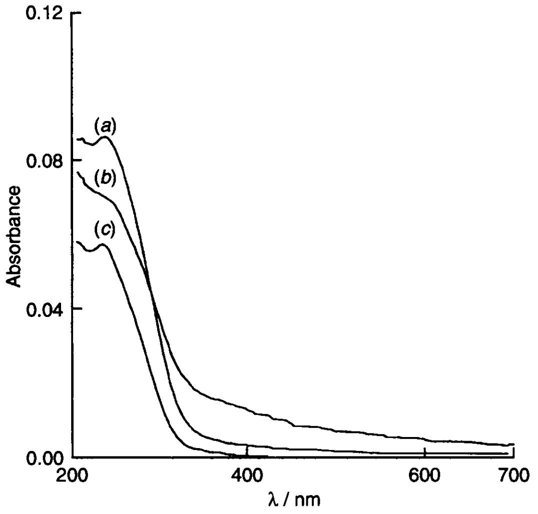
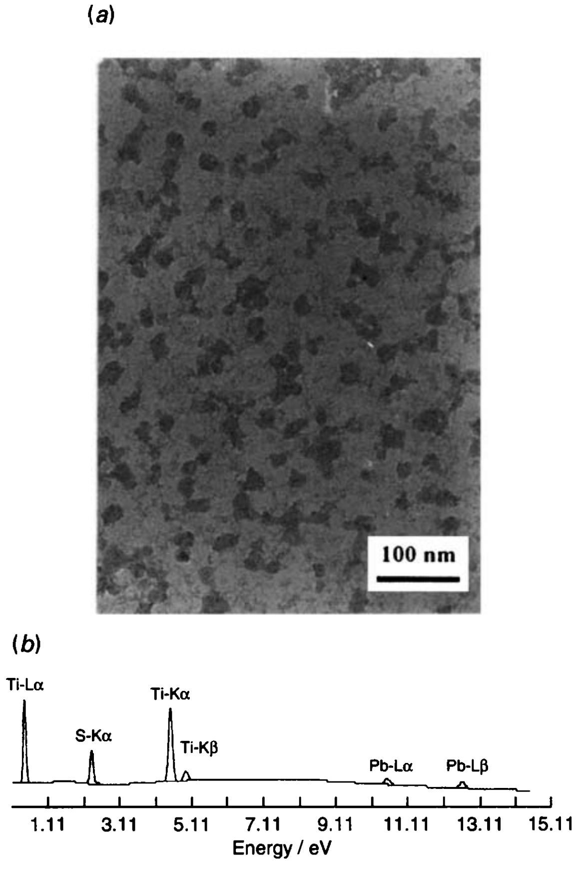


Fig. 2 UV–VIS spectra of (*a*) a coupled semiconductor nanoparticle TiO_2/PbS monolayer, (*b*) a coupled semiconductor nanoparticle TiO_2/PbS casting film and (*c*) a TiO_2 nanoparticle monolayer



Element	Mass %	Atom %
S	15.02	27.99
Ti	49.55	61.80
Pb	35.42	10.21
Total	100.00	100.00

Fig. 3 TEM micrograph (*a*) and EDS spectrum (*b*) of a coupled semiconductor nanoparticle TiO_2/PbS monolayer prepared on a Formvar-covered, 200 mesh copper grid. The magnification is 135000.

The coexistence of TiO_2 and PbS particles in the film was also confirmed by energy dispersive X-ray spectroscopy (EDS) [Fig. 3(*b*)], which can give a quantitative analysis for very thin samples. Since our sample is composed of only three monolayers, < 100 nm in overall depth, we can calculate the molar ratio of Ti : Pb : S accurately. The results of the analysis show that the molar ratio of Ti : Pb is roughly 6 : 1, which is relatively reasonable considering the ratio used in preparation of the coupled semiconductor (10 : 1). In addition, since the sulfur arises from three components; the PbS nanoparticles, $SHCH_2CO_2H$ and PSS, the molar ratio of S : Pb is a little less than 2. Ti, Pb and S are identified in the films, which means that the coupled semiconductor nanoparticles are successfully fabricated into a monolayer film.

The coupled semiconductor nanoparticle monolayer was finally characterized by X-ray photoemission spectroscopy (XPS), which indicated the presence of both titanium at 458.7 eV (Ti $2p_{3/2}$) and lead at 138.2 eV (Pb $4f_{7/2}$). The S 2p spectrum could be deconvoluted into two major peaks, one centred at 163 eV and the other at 168 eV. The former originates from a metal sulfide species, while the latter originates from the co-contribution of a surface sulfate species and PSS. The presence of a metal sulfide peak at 163 eV in conjunction with the Pb $4f_{7/2}$ peak confirmed the coexistence of PbS with TiO_2.[10]

In conclusion, a new kind of coupled semiconductor nanoparticle has been prepared and fabricated into a monolayer as a result of electrostatic interactions. Owing to the simple fabrication and the anticipated properties of the coupled semiconductor, this new self-assembled film and general method are anticipated to have a wide range of applications in designing molecular devices and integrated chemical systems for solar energy conversion.[11]

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