This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Shan Jiang,$^a$ Zhaohui Ren,$^a$ Ming Li,$^a$ Siyu Gong,$^a$ Yifeng Yu,$^a$ Jingyuan Pei,$^b$ Xiao Wei,$^a$ Ge Shen$^a$ and Gaorong Han$^a$.

Single-crystal heterostructured PbTiO$_3$/CdS nanorods were fabricated by a hydrothermal process. In the composites, well-crystalline CdS nanoparticles grew on the surface of tetragonal perovskite PbTiO$_3$ nanorods and formed sharp PbTiO$_3$/CdS interfaces. It was revealed that the as-synthesized heterostructured PbTiO$_3$/CdS nanorods exhibited higher photocatalytic performance in degradation of MB under visible light irradiation over pristine PbTiO$_3$ nanorods and CdS nanoparticles. The enhanced performance is associated with the proper band alignment and promoted separation of photogenerated carriers by forming sharp interfaces between PbTiO$_3$ and CdS in the heterostructure. Our results suggest that the heterostructured PbTiO$_3$/CdS nanorods may be promising for high efficient visible-light-driven photocatalyst.

Introduction

In recent years, visible-light-driven photocatalysts have attracted much interest due to their high efficient photocatalytic activities using 46% of the incoming solar energy for water pollution treatment.$^{1,4}$ Among many approaches to developing novel photocatalysts, heterostructured design of semiconductor composites have been extensively studied because their physical and chemical properties can be largely optimised or modified by forming heterojunctions.$^{5-6}$ Due to its narrow band gap of 2.4eV,$^{7-8}$ high light harvesting efficiency in the visible region$^{9-10}$ and easy fabrication,$^{11}$ CdS becomes one kind of promising semiconductor building blocks for heterostructured visible-light-driven photocatalysts. Nevertheless, there are several issues that still limit their wide applications in environmental remediation and solar conversion.$^{12}$ For example, the CdS nanoparticles tend to aggregate, forming larger particles, which results in a reduced surface area and a higher recombination rate of photogenerated electron-holes.$^{13}$ In addition, CdS is easy to be corroded because the sulfide anion can be easily oxidized by photogenerated holes in aqueous media.$^{14}$ One way to prevent the self-oxidation of CdS is to couple the CdS nanoparticles with another semiconductor which have a lower but closely-lying conduction band (CB) and an appropriate valence band (VB), by forming heterostructured composite photocatalysts.$^{11}$ Up to now, several types of semiconductor nanomaterials, such as SnO$_2$,$^{15}$ TiO$_2$,$^{16}$ ZnO,$^{17}$ Fe$_2$O$_3$,$^{18}$ have been coupled with CdS to form heterostructured composites, which exhibited fascinating visible-light-driven photocatalytic performance. As the previous work discussed, the enhanced photocatalytic properties were ascribed to an effective separation of photogenerated electrons and holes via the heterostructured interfaces between CdS and other semiconductors,$^{19}$ where high quality interface with matched band alignment is desired to promoting charge carrier separation.$^{20}$

Owing to flexible structure adoption and fruitful physical-chemical properties, perovskite oxide nanomaterials have been widely exploited as model photocatalysts in many studies.$^{21-24}$ Recently, we designed and synthesized single-crystal TiO$_2$/PbTiO$_3$ composite by a hydrothermal route, which demonstrated high visible-light catalytic performance as a result of the large-scale of sharp interfaces between TiO$_2$ and PbTiO$_3$. However, the composite suffers low visible light absorption due to the wide band gap for TiO$_2$ and PbTiO$_3$, and the separation behaviour of photogenerated electron-hole pairs at the heterostructured interface is still unclear. Here, we further proposed the possible design of 1D heterostructured composite by forming well-crystallization sharp interfaces between PbTiO$_3$ nanorod and a narrow gap semiconductor nanomaterial, where proper band alignment, enhanced light harvesting and efficient separation of photogenerated carriers could be presumably achieved.

In this work, we used single-crystal perovskite PbTiO$_3$ nanorods as 1D nanoscale backbones for the secondary growth of CdS nanoparticles via a hydrothermal process. The composites demonstrate a superior photocatalytic activity for methylene blue compared to pure PbTiO$_3$ and CdS under...
visible irradiation. Such performance has been discussed in terms of the sharp well-crystalline interfaces between PbTiO$_3$ and CdS with the balance of matching band alignment and high visible light harvesting efficiency, as well as the improved separation for the photogenerated carriers.

Experimental

Synthetic procedures

The synthesis of single-crystal perovskite PbTiO$_3$ nanorods is described in our previous report.$^{26}$ A typical synthesis of heterostructured PbTiO$_3$/CdS nanorods was as follows: 0.2g PbTiO$_3$ nanorods were well-dispersed in deionized water(30mL) under magnetic stirring and then cadmium chloride (CdCl$_2$) (1~5mM) and thiourea (1~5mM) were added into the suspension. The resulting mixture was continually stirred for 30min at room temperature to ensure the reaction had gone to completion and then added into a 50ml Teflon-lined stainless steel autoclave. The autoclave was maintained at 160°C for 12h, followed by cooling naturally to room temperature. The as-prepared samples were washed with deionized water and ethanol for several times, and subsequently air-dried at 60°C for 24h. The mass ratio of CdS in heterostructured PbTiO$_3$/CdS nanorods was about 5wt%-25wt%.

CdS nanoparticles were also prepared separately as a control experiment: 30mL aqueous solution of cadmium chloride (CdCl$_2$) (5mM) and thiourea (5mM) in deionized water was added into a 50ml Teflon-lined stainless steel autoclave. After magnetic stirring for 30 min, the autoclave was maintained at 160°C for 12h, followed by cooling naturally to room temperature. The as-prepared samples were washed with deionized water and ethanol for several times, and subsequently air-dried at 60°C for 24h.

Characterization

The morphology and the crystalline structure of the as-prepared heterostructured PbTiO$_3$/CdS nanorods were characterized with a Hitachi field emission scanning electron microscope (FESEM) instrument Model SU-70 at 3 kV and a FEI Tecnai G2 F20 S-TWIN high-resolution transmission electron microscope (HR-TEM) rated at 200 kV. X-ray powder diffraction (XRD) patterns were obtained by Thermo ARL X'TRA powder diffractometer with Bragg–Brentano geometry by Cu K$_\alpha$ radiation (λ = 1.54056 Å) with 0.82 Å resolution. The specific surface area was determined according to the Brunauer–Emmett–Teller (BET) method using a Tristar II 3020 surface area and porosity analyser (Micrometrics). UV-visible absorption spectroscopy was recorded on UV-vis spectrophotometer (SHIMADZU UV-2550). The photoluminescence spectra were performed at room temperature using the 325 nm line of a continuous-wave He-Cd laser as the excitation source.

Photocatalytic Activity Measurement

In this study, we used the photocatalytic degradation of methylene blue (MB) under visible light to evaluate the photocatalytic activity of the as-prepared heterostructured PbTiO$_3$/CdS nanorods, as MB is a typical model pollutant. A 300W Xe lamp with a UV cut-off filter (λ>400nm) was used as the visible light source and kept 20cm away from the photocatalytic reactor during the photocatalytic activity measurement. In a typical run of measurement, as-prepared catalyst (0.1g) was added into 100ml of MB solution (1×10$^{-5}$ mol/L). Prior to the beginning of irradiation, the suspension was stirred for 40min to reach the adsorption-desorption equilibrium between the MB and the photocatalyst in dark. After that, the suspension was continuously stirred and exposed to light irradiation while the temperature of the suspension was kept at room temperature. Analytical samples were taken from the suspension every 0.5h and the photocatalyst powders were separated by centrifugation. The MB concentrations of the samples were measured by the UV-vis spectrophotometer and monitored by analysing the absorbance at 664nm. The PbTiO$_3$ nanorods and CdS nanoparticles were used in the control experiments.

Results and discussion

![SEM images](image-url)

Figure 1. SEM images of (a) PbTiO$_3$ nanorods, (b) CdS nanoparticles, heterostructured PbTiO$_3$/CdS nanorods with mass ratio of (c) 15wt% and (d) 25wt%.

The morphology of the pristine PbTiO$_3$ nanorods, CdS nanoparticles and the heterostructured PbTiO$_3$/CdS nanorods was investigated by SEM, respectively. As shown in Figure 1a, the diameter of PbTiO$_3$ nanorods is about 200nm and the surface of the nanorods is clean. As shown in Figure 1b, CdS nanoparticles clearly aggregated with irregular shape and a wide size distribution from 50nm to 1µm. However, Figure 1c
and 1d show smaller CdS nanoparticles grew uniformly and tightly on the surface of PbTiO$_3$ nanorods in the heterostructured composite. With the increase of mass ratio for CdS, the diameter of the coated CdS nanoparticles increased from 20nm to 80nm. 

The microstructure and morphology of the heterostructured PbTiO$_3$/CdS 25wt% nanorods were further investigated by TEM (Figure 3). As shown in Figure 3a, the CdS nanoparticles are about 80nm in diameter and growing on the surface of PbTiO$_3$ nanorods, which is consistent with SEM images. HRTEM image (Figure 3b) and the corresponding fast Fourier transform (FFT) (Figure 3c and d) of the interface region reveal the clear and sharp interface (dash line in the Fig 3b) with well-crystallization between PbTiO$_3$ and CdS. The lattice spacing of 0.276nm and 0.284nm for the nanorod could be indexed to the (110) and the (011) planes of tetragonal perovskite PbTiO$_3$. The lattice fringes of 0.336nm and 0.316nm are consistent with the spacing of (002) and (101) planes for the hexagonal greenockite CdS. TEM and HRTEM images further confirm the existence of crystalline CdS nanoparticles, which grew on the PbTiO$_3$ surface by forming unique sharp interface.

The phase and crystalline composition of the as-prepared samples were investigated by XRD. As shown in Figure 2a, all the peaks of the black curve can be indexed into the tetragonal perovskite structure of PbTiO$_3$ (JPCDS06-0452) and no other crystalline impurities were detected. The sharp diffraction peaks with a high intensity reveal high quality of crystallization for the samples. For the heterostructured PbTiO$_3$/CdS nanorods, the peaks marked by blue squares could be indexed into hexagonal greenockite CdS (JPCDS41-1049). The enhancement in the intensity of the peaks associated with different mass ratio of CdS can be ascribed to the improved crystallization and the increased amounts of CdS nanoparticles grown on the PbTiO$_3$ surface. Furthermore, the Raman spectra were collected to investigate the crystal phase and the microstructure of the heterostructured PbTiO$_3$/CdS nanorods. As shown in Figure S1, in the Raman spectrum of heterostructured PbTiO$_3$ nanorods, the peaks at 85, 151, 216, 287, 352, 437, 505, 651 and 750 cm$^{-1}$ can be identified as the E(1TO), E(1LO), E(2TO), B1+E, A1(2TO), E(2LO)+A1(2LO), E(3TO) and A1(3TO) of perovskite PbTiO$_3$.$^{27}$ As shown in Figure 2b, in the Raman spectra of as-synthesized heterostructured PbTiO$_3$/CdS nanorods, an additional peak at 301cm$^{-1}$ which can be ascribed to E(1LO) of CdS became stronger along with the increasing mass ratio of CdS.$^{28}$

In this work, the heterostructured PbTiO$_3$/CdS nanorods are utilized for the photocatalytic degradation of MB under visible light irradiation. As a comparison, the photocatalytic properties of the pristine PbTiO$_3$ nanorods and the CdS nanoparticles were also investigated. Figure 4a shows the UV-vis absorption spectra of the MB solution containing heterostructured PbTiO$_3$/CdS 25wt% nanorods as photocatalyst. [b] Photocatalytic performances of different samples under visible light irradiation: CdS nanoparticles, the PbTiO$_3$ nanorods and the heterostructured PbTiO$_3$/CdS nanorods with increasing mass ratio of CdS.

![Image](https://example.com/image1)

**Figure 3.** (a) TEM image of the heterostructured PbTiO$_3$/CdS 25wt% nanorod; the HRTEM image (b) and the corresponding fast Fourier transform (FFT) (c and d) of the heterostructured interface between PbTiO$_3$ and CdS.

**Figure 4.** [a] Absorption spectra of the MB solution exposed to visible light irradiation for different time in the presence of heterostructured PbTiO$_3$/CdS 25wt% nanorods as photocatalyst. [b] Photocatalytic performances of different samples under visible light irradiation: CdS nanoparticles, the PbTiO$_3$ nanorods and the heterostructured PbTiO$_3$/CdS nanorods with increasing mass ratio of CdS.

![Image](https://example.com/image2)
degraded after the same irradiation time for the solution containing pristine PbTiO₃ and CdS, respectively.

Table 1 lists the first-order reaction rates of different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>K (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.005</td>
</tr>
<tr>
<td>PbTiO₃</td>
<td>0.010</td>
</tr>
<tr>
<td>CdS</td>
<td>0.012</td>
</tr>
<tr>
<td>PbTiO₃/CdS 5wt%</td>
<td>0.011</td>
</tr>
<tr>
<td>PbTiO₃/CdS 15wt%</td>
<td>0.014</td>
</tr>
<tr>
<td>PbTiO₃/CdS 25wt%</td>
<td>0.017</td>
</tr>
</tbody>
</table>

In this equation, C₀ is the dye concentration at time=0, C the concentration of dye at a time of t, K is the apparent first-order reaction rate, and t is the visible light exposure time. As listed in table 1, MB solution without adding catalyst was denoted as “Blank”. And the first-order reaction rate of heterostructured PbTiO₃/CdS 25wt% nanorods shows a maximum of 0.017 min⁻¹, which is 1.4 times as that of CdS(0.012min⁻¹) and 1.7 times as that of pure PbTiO₃(0.010min⁻¹). The mechanism for the enhanced photocatalytic performance of heterostructured PbTiO₃/CdS nanorods can be discussed in terms of the following three aspects.

Secondly, the heterostructured PbTiO₃/CdS nanorods have larger surface area than those of PbTiO₃ nanorods and CdS nanoparticles. The BET surface areas of PbTiO₃ nanorods, CdS nanoparticles and heterostructured PbTiO₃/CdS 25wt% nanorods were calculated from the N₂ adsorption-desorption isotherms (Figure 6). CdS nanoparticles has been determined to have a low surface area of 0.5973m²/g, due to the agglomerate of the CdS nanoparticles through the hydrothermal process (Figure 1b). In contrast, the heterostructured PbTiO₃/CdS nanorods has a surface area of 4.0684m²/g, 42.8% higher than that of PbTiO₃ nanorods. The increase in the surface area could be ascribed to large scale of the heterostructured interfaces, and the rough surface of the heterostructured nanorods could provide more reaction sites for the photocatalytic activity.
At last, the efficient separation of the photogenerated carriers at the heterostructured interface of the composite is another crucial factor to improve the photocatalytic activity. This could be confirmed by the photoluminescence (PL) spectra of the PbTiO$_3$ nanorods, CdS nanoparticles and heterostructured PbTiO$_3$/CdS 25wt% nanorods, as shown in Figure 7. In the PL spectrum of the PbTiO$_3$ nanorods, no emission peak could be observed, which may indicate the low content of surface defects in the pristine PbTiO$_3$._31 As for to the PL spectrum of CdS, a band edge emission can be found at 516nm. Significant quenching of the band edge emission for CdS was observed after CdS nanoparticles were being combined to PbTiO$_3$ nanorods by forming sharp heterostructured interfaces, which implied that most of the photogenerated electro-hole pairs could be separated efficiently before the recombination process at the interface. The drastic quenching is reasonable, which could be ascribed to the proper band alignment between PbTiO$_3$ and CdS. Furthermore, the formation of well-crystalline heterostructured interface would facilitate the charge transfer and promote the photogenerated carriers separation at the interface._15

The schematic illustration for separation of the photogenerated carriers at the interface of the heterostructured PbTiO$_3$/CdS nanorods under visible light irradiation is shown in Figure 8. The calculated band edge ($E_{cb}$) for PbTiO$_3$ (-4.23eV) and CdS (-3.98eV) with respect to the absolute vacuum scale (AVS) is reported in previous study._9,23 PbTiO$_3$ has a 0.25eV electric potential difference in the CB matching well with CdS, which is favourable for charge separation at the heterostructured interface. As shown in Figure 8, once the electrons in the VB of PbTiO$_3$ and CdS are excited to the CB under visible irradiation, the photo-induced electrons on the CB of CdS would transfer to the CB of PbTiO$_3$ while the photo-induced holes on the VB of the PbTiO$_3$ would transfer to the VB of CdS. Thus, the photogenerated electro-hole pairs could be separated more efficiently at the interface of the heterostructure and their recombination should be suppressed. In addition, the transportation of the photogenerated carriers through the heterostructured interface would be accelerated with the existence of electric potential difference._32,33 On the other hand, the reducing size of CdS nanoparticles when forming heterostructured interface may shorten the diffusion pathway of the photogenerated charge carriers, which could facilitate the photocatalytic reaction in the PbTiO$_3$/CdS heterostructured nanorods._19 Compared to single-phase photocatalysts, such heterostructure containing large scale of well-crystallization sharp interfaces possesses significant advantages in promoting the separation and transfer of the photogenerated carrier, eventually leading to an improvement in the photocatalytic performance.

Conclusions

Single-crystal PbTiO$_3$/CdS heterostructured nanorods were synthesized by a hydrothermal approach. With the size range of 20-80nm, the well-crystallized CdS nanoparticles grew on the single-crystal perovskite PbTiO$_3$ nanorods and formed large scale of sharp interfaces. The heterostructured PbTiO$_3$/CdS 25wt% nanorods demonstrated highest photocatalytic activity for the degradation of methylene blue (MB) under visible light irradiation, which could be attributed to the enhanced visible light harvesting efficiency, the larger surface areas of the heterostructures, large content of well-crystalline heterostructured interfaces, proper alignment of the band structure and efficient separation of the photogenerated carriers. These results show that the heterostructured PbTiO$_3$/CdS nanorods could be promising for high-performance visible-light-driven photocatalyst, and the findings may provide useful insights into the design of novel heterostructured photocatalyst.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No.51232006, 51472218). This work was financially supported by the Fundamental Research Funds for the Central Universities under Grant Nos. 2014XZZX005

Notes and references