

Cite this: *RSC Adv.*, 2017, 7, 50056

# The size controlled synthesis of Cu<sub>2</sub>S/P25 hetero junction solar-energy-materials and their applications in photocatalytic degradation of dyes

Hongqin Huang,<sup>a</sup> Fang Li,<sup>a</sup> Huigang Wang <sup>\*ab</sup> and Xuming Zheng<sup>ab</sup>

In this paper highly dispersed Cu<sub>2</sub>S nanocrystals loaded on commercially available TiO<sub>2</sub> form P25, denoted as Cu<sub>2</sub>S/P25, was firstly fabricated by a deposition–precipitation process, to establish close pn hetero junctions to improve the visible light activity and the stability of Cu<sub>2</sub>S on the catalyst surface. The catalysts were characterized by TEM, SEM, XRD, XPS, Raman, etc., the photocatalytic degradation kinetics of Cu<sub>2</sub>S-loaded TiO<sub>2</sub> nanoparticles on methylene blue was systematically investigated. The results show that a lower amount of loading of Cu<sub>2</sub>S on Cu<sub>2</sub>S/P25 led to a higher photocatalytic degradation performance under visible light irradiation. The Cu<sub>2</sub>S quantum size effects on the absorption band edge and photo induced catalytic performance were also investigated.

Received 30th June 2017  
Accepted 16th October 2017

DOI: 10.1039/c7ra07253h

rsc.li/rsc-advances

## 1. Introduction

Methods to harvest sunlight radiation with a higher conversion efficiency to chemical or electrical power are needed to satisfy the demands of clean and green energy.<sup>1–4</sup> For irradiation under light with a given wavelength, semiconductors with a specific band gap can resonate with the given light and produce electrons and holes, consequently generating active hydroxyl radicals in solution.<sup>5,6</sup> These active hydroxyl radicals can degrade organics and kill microorganisms by advanced oxidation processes.<sup>7,8</sup> Many semiconductors have been tested and TiO<sub>2</sub> is a proverbial semiconductor with the advantages of high photocatalysis activity, wide band gap (3.2 eV), high earth abundance, chemical stability and environmental friendliness.<sup>9–11</sup> Photodegradations based on TiO<sub>2</sub> and its hetero junction materials have attracted great attention in these decades due to their obvious advantages on the visible-light driven solar energy utilization.<sup>12,13</sup> Various nanostructured hetero junctions have been reported and their enhanced photocatalytic efficiency has been achieved. For example, composites of MoS<sub>2</sub>–TiO<sub>2</sub>,<sup>14</sup> SnO<sub>2</sub>–TiO<sub>2</sub>,<sup>15,16</sup> CeO<sub>2</sub>–Cu<sub>2</sub>O<sup>17</sup> and ZnO–TiO<sub>2</sub>,<sup>18–20</sup> etc. have been synthesized by coupling two semiconductors.

Chalcocite (Cu<sub>2</sub>S) is a p-type semiconductor for abundance in copper vacancies with a narrow bulk band gap of 1.2 eV.<sup>21–23</sup> Further combining with n-type TiO<sub>2</sub> by forming hetero-structured nanocrystals would therefore be interesting in regard

to achieving special properties, especially in photo degradation applications.<sup>12,13</sup> In addition, the bandgap of Cu<sub>2</sub>S semiconductors and its characteristic absorption spectrum in the visible wavelength region make it highly desirable for use as sensitizers when they are combined with the TiO<sub>2</sub> nanocrystals. On the other hand semiconductors with band gaps capable of harvesting visible incident wavelength energy (0.9 to 2.3 eV) usually suffer from UV induced photocorrosion, the stability of Cu<sub>2</sub>S under solar spectrum incidence thereof could be significantly enhanced by the formation of hetero junctions that could rapidly remove the photon-generated electrons and holes from the cuprous sulfide.<sup>24–26</sup> Enhanced chemical stability, improved charge separation and increased photocatalytic efficiency of such composite nanostructures have been extensively studied by our group.<sup>6,27–31</sup> In recent years of particular interest are the size dependent properties such as size quantization effects in semiconductor nanoparticles. Due to the quantum-confinement and surface effects, nanometer-sized semiconductors possess unique size-dependent physiochemical properties that one does not see in the corresponding bulk solids.<sup>32,33</sup> The ability to synthetically tune these nanocrystal sizes provides the opportunity to study and understand the relationship between spectrum character, photo degradation performance and quantum effects that occur uniquely at the nanoscale. In addition, these nanocrystal dots open up new ways to utilize hot electrons or generate multiple electron–hole pairs with a single photon.<sup>34–36</sup> Multiple electron–hole pairs generation in PbS nanocrystals–TiO<sub>2</sub> single crystals has shown that photocurrents with quantum yields greater than one electron per photon can be achieved with a single high-energy photon.<sup>37</sup>

The purpose of this work was to know how and what the extent the quantum confinement of Cu<sub>2</sub>S effect on the visible

<sup>a</sup>Department of Chemistry, State Key Laboratory of Advanced Textiles Materials and Manufacture Technology, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, China. E-mail: zdwhg@163.com; huigangwang@uni-osnabrueck.de; Fax: +86-571-8684-3627; Tel: +86-571-8684-3627

<sup>b</sup>Zhejiang Provincial Top Key Academic Discipline of Chemical Engineering and Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China



light catalytic performance when it is coated onto the surface of  $\text{TiO}_2$  particles. In the present work, a series of different  $\text{Cu}_2\text{S}$  size were achieved precipitated on P25 by deposition-precipitation process and their size effect on the absorption band edge and the catalytic performance were systematically investigated. By change the P25 quantity the  $\text{Cu}_2\text{S}$  loading amount effects on the morphology and photocatalytic performance were also investigated. The photocatalytic degradation performance of the hetero structure catalysts was evaluated using methylene blue (MB) as a model pollutant. This dye is non-biodegradable and commonly used in the textile industry. As a result, this molecule is widely used for testing photocatalytic activity.

## 2. Experimental sections

### 2.1 Synthesis of $\text{Cu}_2\text{S}$ /P25 composites with deposition-precipitation method

To systematically investigate the synthesis condition and the relationship with the photocatalysis performance, the reactant amounts were varied, which are listed in Table 1. In a typical synthesis of  $\text{Cu}_2\text{S}$ /P25 composites,  $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$  (0.2 g, 1 mmol) and 0.72 g P25 were added to the mixture of dodecanethiol and 1-octadecene (30 mL) in a three-necked flash under  $\text{N}_2$  atmosphere. Then it was heated to 220 °C and maintained at that temperature for 30 min after reaction, it was cooled to room temperature naturally. The product was precipitated by introducing ethanol and centrifuging at 9000 rpm. The precipitate was washed several times with ethanol and was dried under vacuum at a temperature of 60 °C for 12 h.

### 2.2 Characterization

The morphologies of  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{S}$ /P25 were examined by a field-emission scanning electron microscope (FE-SEM, Hitachi S4800) and a transmission electron microscope (TEM, JEM 2100). The crystalline structure of samples was measured by X-ray diffraction (DX-2700). UV-visible diffuse reflectance spectra (DRS) of samples were recorded using a UV-vis NIR spectrophotometer (Varian Cary 5000). X-ray photoelectron spectroscopy (XPS) measurements were examined on Kratos AXIS Ultra DLD (Al K $\alpha$  monochromatic source). Adventitious C 1s peak (284.6 eV) was used as binding energies reference. The 488 nm laser excited Raman spectra were measured on a quartz sheet equipped with triplemonochromator (TriVista TR557, Princeton

Instruments) and an argon ion laser (approximately 30 mW on the sample). The CCD chip active area covers a wavenumber of 1089  $\text{cm}^{-1}$  and the spectral resolution boasts for 2.5  $\text{cm}^{-1}$ .

### 2.3 Photocatalytic activity measurements

The photocatalytic activity of  $\text{Cu}_2\text{S}$ /P25 samples was evaluated by the degradation rate of methylene blue under visible-light irradiation. The experimental set up placed in a black box consisted of a 200 mL beaker irradiated by a 300 W, 220 V xenon lamp (CEL-HXUV300, Beijing Au Light). The distance between the lamp and the solution is 15 cm. The temperature inside the reactor was maintained at ca. 25 °C by means of a continuous circulation of water surrounding the reactor. 100 mL methylene blue (MB) aqueous solution (10  $\text{mg L}^{-1}$ ) was mixed with 50.0 mg photocatalyst powder in the above 200 mL beaker. Before irradiation, the suspension was stirred in the black box for about 30 min till to reach the adsorption-desorption equilibrium. After the photoreaction runs, samples of 3 mL were withdrawn from the suspension at regular time intervals during the irradiation, and then centrifuged to separate the photocatalysts. The quantitative determination of remnant MB was conducted by measuring its maximum absorption at 665 nm with a Shimadzu UV-2501 PC spectrophotometer. For comparison, the MB photodegradation experiment was conducted under the same conditions.

## 3. Results and discussion

The morphology of as-prepared  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{S}$ /P25 composites were investigated by FE-SEM, EDS spectrum and high magnification TEM. Fig. 1A and B comparatively shows the FE-SEM of P25 and  $\text{Cu}_2\text{S}$ /P25 composites respectively. Fig. 1A shows the typical P25 morphology, the uniform particles spread over the picture. Fig. 1B shows the entry S5 morphology of  $\text{Cu}_2\text{S}$ /P25, with the help of P25 image we could see that there are many tiny nanoparticles anchored over the surface of P25. Red circled area shows that the nanoparticles are uniformly in size and could be assigned to the  $\text{Cu}_2\text{S}$  nanocrystals, the particle size of  $\text{Cu}_2\text{S}$  is around 15 nm. To clearer present the location of  $\text{Cu}_2\text{S}$  nanocrystals, SEM-EDS mapping were applied and the images were shown in Fig. 1C and D. Fig. 1C indicated that the element Cu were not confined in a specific space; they were evenly distributed throughout the entire matrix. The EDS profile shows correct stoichiometry of  $\text{Cu}_2\text{S}$  to  $\text{TiO}_2$  in the nanocomposite structure. The atomic ratio of Cu and Ti in the nanocomposite structure was 3.0 at% : 33.5 at% obtained from the SEM-EDS spectrum as shown in Fig. 1D.

Quantum confinement of carriers and enhanced surface effects at nanodimensions are well known to result in large modifications in the structural, optical, and electronic properties of nanoparticles.<sup>38,39</sup> Balamurugan B. has reported the size-dependent changes in  $\text{Cu}_2\text{O}$  nanoparticles, result in conductivity type inversion on reduction of nanoparticle size.<sup>40–42</sup> So it is necessarily to know how and what is the extent the quantum confinement of  $\text{Cu}_2\text{S}$  effect on the visible light catalytic performance. In the present work, a series of different  $\text{Cu}_2\text{S}$  size were

**Table 1** The entry label and the corresponding reactant amounts used in the preparation of  $\text{Cu}_2\text{S}$ /P25 composites

Sample	Copper acetate/g	P25/g	Dodecanethiol (mL)	1-Octadecene (mL)
S1	0.2	0.40	30.00	0
S2	0.2	0.72	30.00	0
S3	0.2	1.12	30.00	0
S4	0.2	2.56	30.00	0
S5	0.2	0.72	15.00	15.00
S6	0.2	0.72	5.00	25.00
S7	0.2	0.72	0.75	29.25



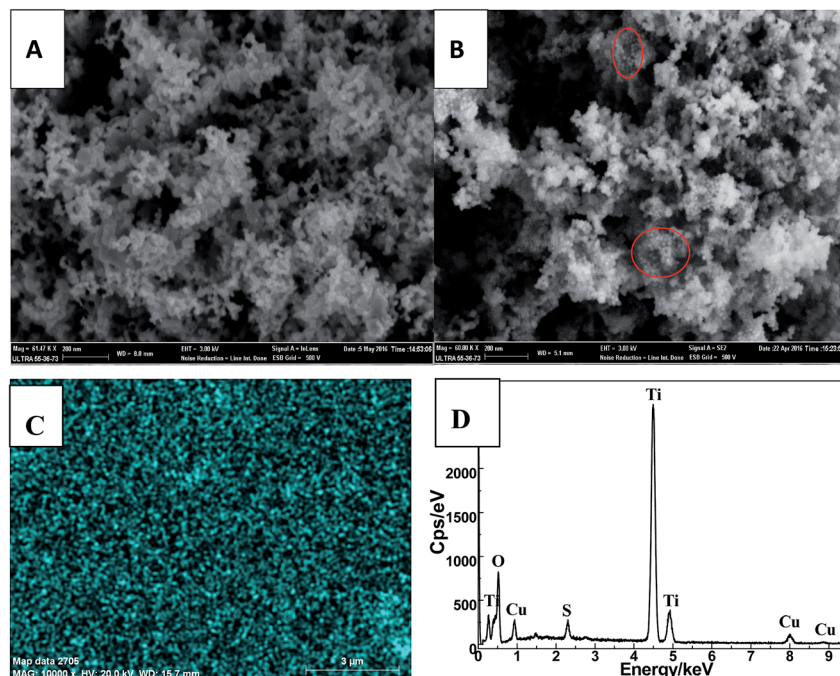


Fig. 1 FE-SEM images of the P25 (A),  $\text{Cu}_2\text{S}/\text{P25}$  (B). SEM-EDS mapping of Cu (C) and SEM-EDS spectrum (D) of  $\text{Cu}_2\text{S}/\text{P25}$ .

achieved in entry S5 to S7 by controlling the volume ratio of dodecanethiol to 1-octadecene. Fig. 2A–C shows the TEM of  $\text{Cu}_2\text{S}$  nanocrystals corresponding to the volume ratio of dodecanethiol to 1-octadecene 1 : 1, 1 : 5 and 1 : 39, respectively, as is shown in Table 1 sample entry S5, S6 and S7. All the  $\text{Cu}_2\text{S}$  nanocrystals are uniformly formed and the average diameter is 15 nm, 8 nm and 4 nm respectively. It shows that, with the relative content of dodecanethiol to 1-octadecene decrease, the diameter of  $\text{Cu}_2\text{S}$  decrease from 15 nm to 4 nm. The final size is almost one quarter of the original. This provide

us perfect opportunities for the investigation the size effect on all kind of properties vary from light absorption to photocatalytic performance.

The TEM image in Fig. 2D shows the unique  $\text{Cu}_2\text{S}/\text{P25}$  composites prepared following the entry S5, confirming that the  $\text{Cu}_2\text{S}$  nanocrystals distributed uniformly on the P25 nanoparticles. The  $\text{Cu}_2\text{S}$  crystals are uniformly in spherical shape and their diameter are 15 nm while the P25 particles are in irregular shape with their diameter approximately of 21 nm. The HRTEM image in Fig. 2E show well resolved {011} lattice

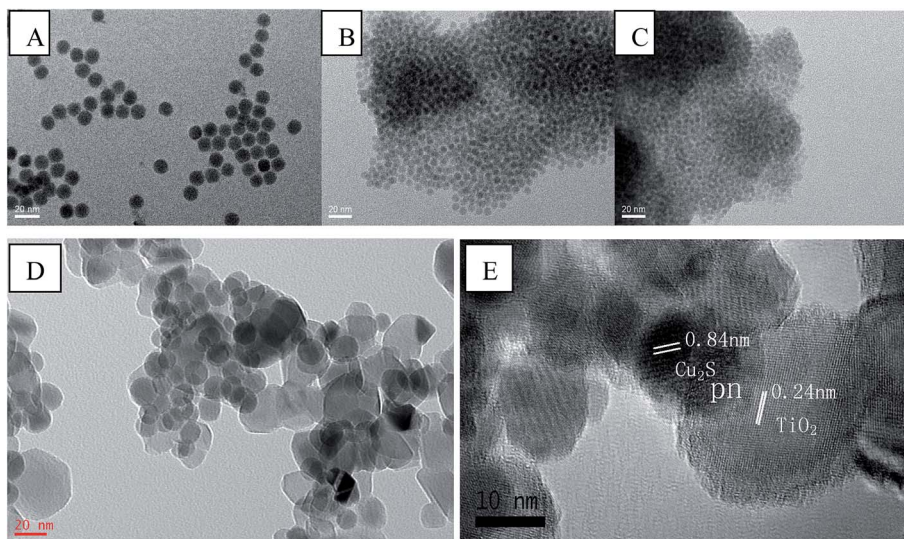


Fig. 2 The morphology of  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{S}/\text{P25}$ . TEM images of  $\text{Cu}_2\text{S}$  nanocrystals synthesized at the temperature of 220 °C with 1 mmol  $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$  and (A) 15 ml dodecanethiol and 15 mL 1-octadecene, (B) 5 ml dodecanethiol and 20 mL 1-octadecene, (C) 0.75 ml dodecanethiol and 29.25 mL 1-octadecene. HRTEM image of the  $\text{Cu}_2\text{S}/\text{P25}$  heterostructures (D, E).





fringes (interplanar distance  $d = 0.84$  nm) of  $\text{Cu}_2\text{S}$  chalcocite-M crystalline structure (JCPDS 33-0490). Distance  $d = 0.24$  nm in Fig. 2E is the indication of a highly crystalline  $\text{TiO}_2$  anatase framework corresponding to the  $\{103\}$  crystal planes (JCPDS 88-0866). These exposed facets are clear indicative of the coexistence of  $\text{Cu}_2\text{S}$  and  $\text{TiO}_2$  components, the overlap part of  $\text{Cu}_2\text{S}$  and  $\text{TiO}_2$  indicating that  $\text{Cu}_2\text{S}/\text{P25}$  composites pn hetero junctions were formed.

### 3.1 Phase composition

XRD was carried out to investigate the crystal identity of  $\text{Cu}_2\text{S}$  and the effect of  $\text{Cu}_2\text{S}$  on the crystal structure of  $\text{TiO}_2$ . Fig. 3 shows the XRD pattern of  $\text{Cu}_2\text{S}/\text{P25}$  p-n heterostructure composite materials and the starting material P25 nanoparticles. The P25 powder contains 20% rutile and 80% anatase. The diffraction peaks at  $2\theta = 25.3, 37.8, 48.0, 53.1, 55.4, 62.7, 68.8$  in P25 corresponds to the (101), (004), (200), (105), (211),

(204), and (116) planes of anatase  $\text{TiO}_2$  (JCPDS no. 84-1286). While the peak at  $27.4^\circ, 36.1^\circ$  and  $41.5^\circ$  are also present, indicating there coexists the rutile phase (JCPDS no. 88-1175). The dashed lines in Fig. 1 indicate the correlation of anatase crystal planes of  $\text{Cu}_2\text{S}/\text{P25}$  prepared with different reactant amounts. Clearly, the XRD pattern obtained at different ratio exhibit no difference in XRD pattern with P25. The comparison of XRD pattern of  $\text{Cu}_2\text{S}$ , P25 and  $\text{Cu}_2\text{S}/\text{P25}$  indicate that the interposition of  $\text{Cu}_2\text{S}$  in the P25 has no effect on the crystal structure of P25 powders, the main structure is preserved.

XPS studies were conducted over  $\text{Cu}_2\text{S}/\text{P25}$  in order to understand the chemical state and chemical environment of the Cu element on P25 (Fig. 4). As shown in Fig. 4a, the wide-scan survey spectra of  $\text{Cu}_2\text{S}/\text{P25}$  contain O, Ti, C, Cu and S elements; the emergence of the C element can be attributed to residual carbon from the sample and adventitious hydrocarbon from the XPS instrument itself. The Cu 2p core level spectrum, shown in Fig. 4b, is composed of two peaks at the binding energies of 932.48 eV and 951.88 eV, assigned to Cu ( $2p_{3/2}$ ) and Cu ( $2p_{1/2}$ ) respectively, which are in good agreement with the reported values of  $\text{Cu}_2\text{S}$  (i.e., the characteristic peaks of Cu  $2p_{3/2}$  for Cu(0), Cu(I), and Cu(II) are at 932 eV, 932.7 eV, and 933.6 eV, respectively). As is known that Cu(II) have the characteristic shake up peaks of  $2p_{3/2}$  around 940 eV and 957 eV which have not been detected in our experiment. All in all, no Cu or  $\text{CuS}$  are presented in our sample. The plausible reason maybe could be found in the experiment treatment. In our reaction system,  $\text{Cu}_2\text{S}/\text{P25}$  were prepared under an  $\text{N}_2$  protection atmosphere at  $220^\circ\text{C}$  with the dodecanethiol as reductant, and the reductant is excessive to ensure the complete reduce of  $\text{Cu}^{2+}$ . The Ti 2p XPS spectrum is shown in Fig. 4c, which was composed by two peaks, the Ti  $2p_{3/2}$  located at 458.68 eV and the  $2p_{1/2}$  located at 464.5 eV, respectively, suggesting the presence of Ti(IV) species.

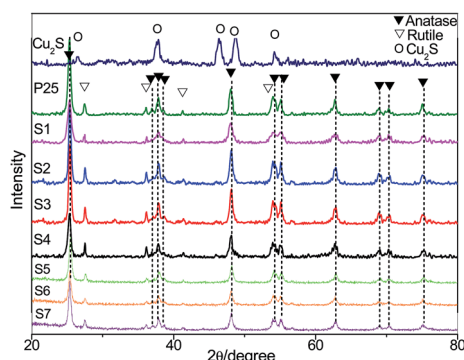


Fig. 3 XRD pattern of  $\text{Cu}_2\text{S}$  nanocrystal, P25 and  $\text{Cu}_2\text{S}/\text{P25}$  heterostructures.

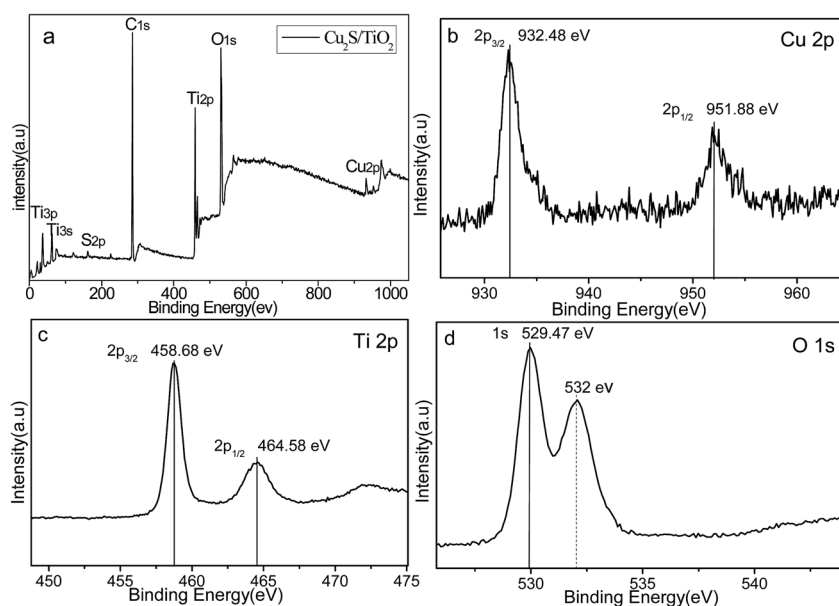


Fig. 4 (a) Wide-scan XPS survey spectra for the  $\text{Cu}_2\text{S}/\text{P25}$  composites. (b) High-resolution XPS spectrum of (b) Cu 2p, (c) Ti 2p and (d) O 1s for the sample of  $\text{Cu}_2\text{S}/\text{P25}$ .



They are in fairly well agreement with the literature data of  $\text{TiO}_2$ . The Ti 2p XPS spectrum (Fig. 4c) indicates the incorporation of  $\text{Cu}^+$  induces no significant changes of the  $\text{Ti}^{4+}$  2p electron density. Meanwhile, the XPS spectra of O 1s (Fig. 4d) split as two peaks at 529.47 eV and 532.00 eV respectively after the deposition of  $\text{Cu}_2\text{S}$  NPs, owing to the generation of surface oxygen vacancies. [M. Xing, J. Zhang, F. Chen and B. Tian, *Chem. Commun.*, 2011, 47, 4947–4949] The surface oxygen vacancies is expected to prohibit the recombination of electron-hole pairs and enhanced the visible light absorption efficiency. The results of XPS indicate that  $\text{Cu}_2\text{S}/\text{P25}$  composites have been formed.

Raman spectroscopy is a sensitive tool for investigation the changes on the electrons and molecular structure information. To further identify the doped structure and crystalline of the samples, Raman studies were performed in the range of 120–700  $\text{cm}^{-1}$  that is shown in Fig. 5. All the spectra shown in Fig. 5 share the same Raman peaks at 143, 394, 513, and 636  $\text{cm}^{-1}$ , they could be assigned to the Raman-active modes of anatase with symmetries  $E_g$  (O–Ti–O symmetric stretching),  $B_{1g}$  (O–Ti–O wag),  $A_{1g}$  (O–Ti–O symmetric wag), and  $E_g$  (O–Ti–O asymmetric stretching), respectively.<sup>41</sup> No characteristic Rutile or Brookite phase Raman peaks was found, indicating the composition of pure anatase phase. After doping with  $\text{Cu}_2\text{S}$ , the  $\text{Cu}_2\text{S}/\text{P25}$  heterostructure shows additional weak peak at 268  $\text{cm}^{-1}$ , this could be assigned to the  $\text{Cu}_2\text{S}$  characteristic peaks.

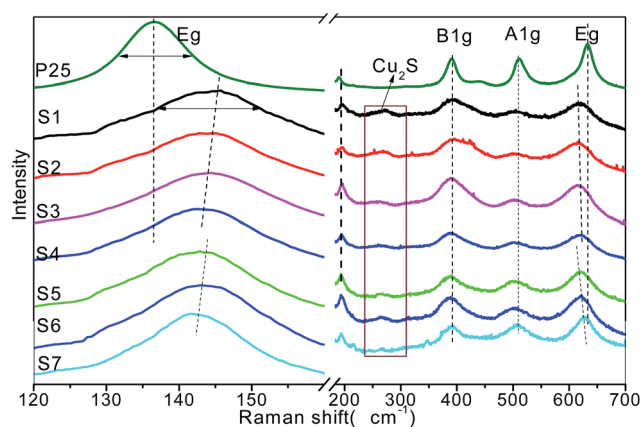


Fig. 5 Raman spectra of P25 and  $\text{Cu}_2\text{S}/\text{P25}$  with various  $\text{Cu}_2\text{S}$  loadings (S1 to S4) and various  $\text{Cu}_2\text{S}$  nanocrystal size (S5 to S7).

It is interesting to observe that the  $E_g$  peaks are sensitive to the composition change of the  $\text{Cu}_2\text{S}/\text{P25}$  hetero structure while the  $B_{1g}$  and  $A_{1g}$  are inert, the  $E_g$  peak at 145.7  $\text{cm}^{-1}$  gradually shifted downward to 142.3  $\text{cm}^{-1}$  as the P25 content increased from S1 to S4, extremely to 136.5  $\text{cm}^{-1}$  for pure P25; however, the  $E_g$  peak at 636  $\text{cm}^{-1}$  shifted to the opposite direction. Meanwhile the FWHM narrowed down as the  $\text{Cu}^+$  disappeared. This indicates that there was an interaction between the Cu and  $\text{TiO}_2$ , S1 contains the highest content of  $\text{Cu}^+$  and the frequency difference between P25 and  $\text{Cu}_2\text{S}/\text{P25}$  also reaches the highest (9.2  $\text{cm}^{-1}$ ) amongst all the prepared  $\text{Cu}_2\text{S}/\text{P25}$  hetero structure. The  $\text{Cu}^+$  creates crystalline defects in the lattice structure of  $\text{TiO}_2$  nanocrystals and the defects increase with the increase of Cu content. The crystalline defects affect the characteristic vibrational frequency of the anatase  $\text{TiO}_2$ ; it can act as a trap to capture photoelectrons, which makes a contribution to inhibiting the charge recombination. The  $E_g$  peaks are also sensitive to the  $\text{Cu}_2\text{S}$  particle size change of the  $\text{Cu}_2\text{S}/\text{P25}$  hetero structure. As is shown in Fig. 5 S5 to S7, when the particle size of  $\text{Cu}_2\text{S}$  increase from 4 nm to 15 nm, the  $E_g$  peak at 142.8  $\text{cm}^{-1}$  shift downward to 141.7  $\text{cm}^{-1}$ . And again, the  $E_g$  peak at 636  $\text{cm}^{-1}$  shift to the upward wavenumber. The smaller  $\text{Cu}_2\text{S}$  nanocrystal deposited on  $\text{Cu}_2\text{S}/\text{P25}$  hetero structure, the more crystalline defects were created. Thus, the XRD and Raman characterization of  $\text{TiO}_2$  and  $\text{Cu}_2\text{S}/\text{P25}$  demonstrate the high crystallinity of the titania materials and the presence of anatase phase.

To investigate the optical behavior of the as-prepared  $\text{Cu}_2\text{S}/\text{P25}$  and the size effect of  $\text{Cu}_2\text{S}$  on the optical property of  $\text{Cu}_2\text{S}/\text{P25}$ , the UV-vis diffuse reflectance spectra (DRS) were collected and were shown in Fig. 6. Clearly, the largest absorption edge of blank-P25 shown in Fig. 6a was at approximately 370 nm (3.3 eV), whereas the  $\text{Cu}_2\text{S}/\text{P25}$  composites show prominence absorption in the visible light region from 400 nm to 800 nm. The absorbance above 400 nm light region was enhanced by the introduction of  $\text{Cu}_2\text{S}$  nanocrystals. The composite of  $\text{Cu}_2\text{S}$  into the matrix of P25 has a significant effect on the optical property for the  $\text{Cu}_2\text{S}/\text{P25}$  composites.

With the increase of  $\text{Cu}_2\text{S}$  content (S4 to S1), the absorbance curve becomes relatively flat in the visible light region for  $\text{Cu}_2\text{S}/\text{P25}$  while the light absorption feature of  $\text{Cu}_2\text{S}/\text{P25}$  nanocomposite in the UV region (particularly at the wavelength of 300 nm) is the same as that of blank-P25. After the addition of  $\text{Cu}_2\text{S}$ , the absorption edge is red-shifted to the lower energy

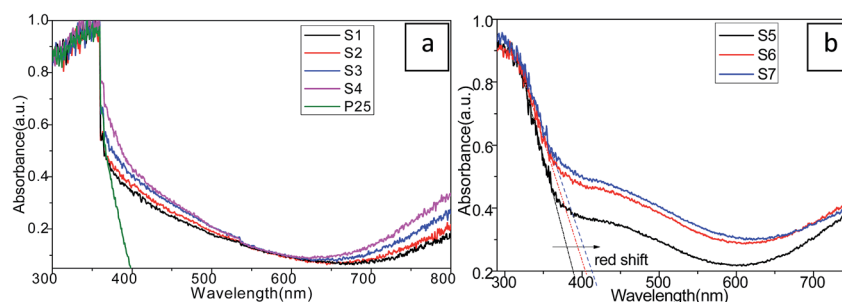


Fig. 6 UV-vis absorption spectra of P25 and  $\text{Cu}_2\text{S}/\text{P25}$  with various  $\text{Cu}_2\text{S}$  loadings (a) and various  $\text{Cu}_2\text{S}$  nanocrystal size (b).



value with enhanced absorbance intensity in the whole visible light range. The results of DRS indicate that Cu<sub>2</sub>S/P25 nanocomposites have the significantly enhanced visible light absorption property and they are able to be “band-gap” photo-excited by visible light irradiation. Electron-hole pairs can be generated by visible light excitation and thus the improved photoexcited performance can be expected.

The Cu<sub>2</sub>S nanocrystal size effects on the electron excitation transition properties can be referred to Fig. 6b. Fig. 6b S5, S6 and S7, corresponds to the Cu<sub>2</sub>S nanocrystal size of 15 nm, 8 nm and 4 nm, shows that when the crystal size decrease the absorption edge red shifts to the lower energy and the visible light region absorption enhances accordingly. The smaller, the better visible light absorption efficiency should be expected.

### 3.2 Photocatalytic activity of as-synthesized Cu<sub>2</sub>S/P25

It is well known that the photocatalysis activity depends on the photo response efficiency, the catalysts crystallinity, and the phase of the materials. In this work, the visible light induced photocatalytic activities of the as-synthesized Cu<sub>2</sub>S/P25 were evaluated by photocatalytic degradation of MB under visible light irradiation. For comparison, the photocatalytic activity of every sample was tested under identical conditions. Before irradiation, the suspension was stirred in the black box for about 30 min to ensure the equilibrium have been reached for the MB adsorption-desorption process on the catalysts. The final equivalent absorbance concentrations, *i.e.*, the initial photodegradation concentration of MB, were normalized for different samples. As shown in Fig. 7a, The Cu<sub>2</sub>S/P25 can efficiently photo degrades MB under visible light irradiation, five different catalysts (S1, S2, P25, S3 and S4) showed 60.8%, 65.3%, 69.1%, 71.4% and 80.1% MB decolorization rates ( $1 - c_t/c_0$ ), respectively, under xenon lamp illumination after 240 min. The MB self photodegradation was also included in the figure and it reached 28.0% degradation rate in 240 min.

On the basis of a simplified Langmuir-Hinshelwood model, the linear relationship of  $\ln(C/C_0)$  versus time (see Fig. 7b) upon visible light irradiation indicates that MB degradation follows pseudo first order kinetics; the apparent rate constant ( $k$ ) shown in Fig. 7b was calculated from the plot of  $\ln(C/C_0)$  vs. time. The highest apparent rate constant, obtained for S4, is  $6.0 \times 10^{-3} \text{ min}^{-1}$ , which decrease with the increase of relative Cu<sub>2</sub>S

content in the Cu<sub>2</sub>S/P25 nanocomposite. The high efficiency performance could be ascribed to its unique cooperative effects and low band gap energy. The photocatalytic activity is in agreement with the rule of visible light region absorption. Generally, the photocatalytic activity is proportional to  $(I_\alpha \phi)^n$  ( $n = 1$  for low light intensity and  $n = 1/2$  for high light intensity), where  $I_\alpha$  is the photo numbers absorbed by photocatalyst per second and  $\phi$  is the efficiency of the band gap transition. The enhancement of the photo activity with Cu<sub>2</sub>S doping can be partly explained in terms of an increase in  $I_\alpha \phi$  resulting from intensive absorbance in the visible region. Cu<sub>2</sub>S doping expands the wavelength response range of P25 into the visible region and increased the number of photo-generated electrons and holes to participate in the photocatalytic reaction.

In order to investigate the particle size effect on the photo induced catalytic performance, a series of different Cu<sub>2</sub>S size were achieved precipitated on P25. As shown in Fig. 8a, the photocatalytic performances of the Cu<sub>2</sub>S/P25 hetero structures with difference in Cu<sub>2</sub>S nanocrystal size were tested under visible light irradiation. It is found that their photocatalytic activities are varying with the Cu<sub>2</sub>S size alternation. The apparent rate constant, obtained for S7 (4 nm), is the highest among them reach to  $9.4 \times 10^{-3} \text{ min}^{-1}$ , which decrease with the increase of Cu<sub>2</sub>S crystal size in the Cu<sub>2</sub>S/P25 nanocomposite. Smaller Cu<sub>2</sub>S crystal size shows the higher photocatalytic activity, which is in agreement with our anticipation from the DRS characterization in Fig. 6b.

The stability of a photocatalyst is very important for practical applications; thus, a durability test was performed to confirm the stability of the S7 photocatalyst, which achieved the highest performance. According to Fig. 8b, the MB photodegradation efficiency changed very slightly after 5 cycles of the experiment under identical conditions, indicating that the photocatalyst has superior photocatalytic stability.

The Mechanism for the Photocatalytic activity of Cu<sub>2</sub>S/P25 under visible light excitation could be described as pn hetero-structure which is shown in Fig. 9. As is demonstrated from HRTEM and XPS that Cu<sub>2</sub>S and P25 forms a pn hetero junction and the p-type semiconductor Cu<sub>2</sub>S acts as the anode ( $E_g = 1.22 \text{ eV}$ ), and n-type P25 acts as the cathode ( $E_g = 3.2 \text{ eV}$ ). Under visible light irradiation, meso TiO<sub>2</sub> exhibited low photocatalytic ability due to its weak absorption “tail”. Once Cu<sub>2</sub>S are

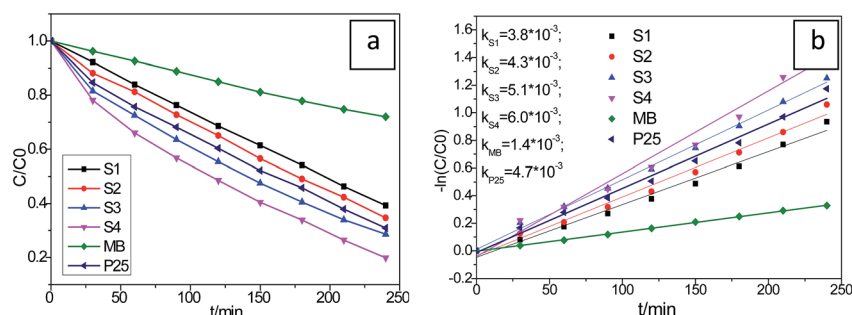


Fig. 7 Photodegradation of MB over various samples upon visible light irradiation (a). Kinetic linear fitting curves and the apparent rate constant for liquid-phase photocatalytic degradation of MB over different samples under visible light irradiation (b).



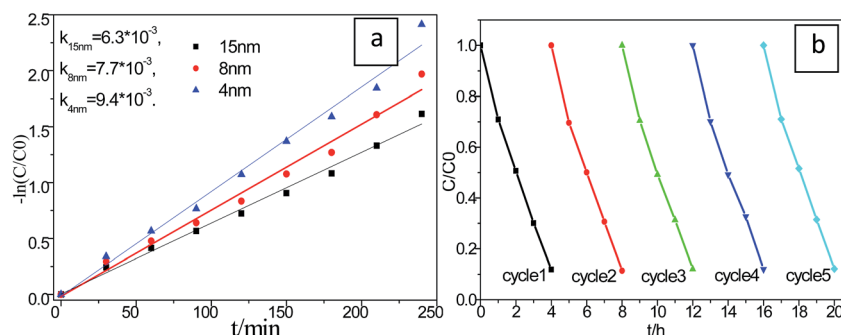


Fig. 8 Kinetic linear fitting and the apparent rate constant for photocatalytic degradation of MB over different  $\text{Cu}_2\text{S}$  nanocrystal size of  $\text{Cu}_2\text{S}/\text{P25}$  hetero structures under visible light irradiation (a). Durability study over  $\text{Cu}_2\text{S}/\text{P25}$  hetero structures for MB photodegradation under visible light irradiation (b).

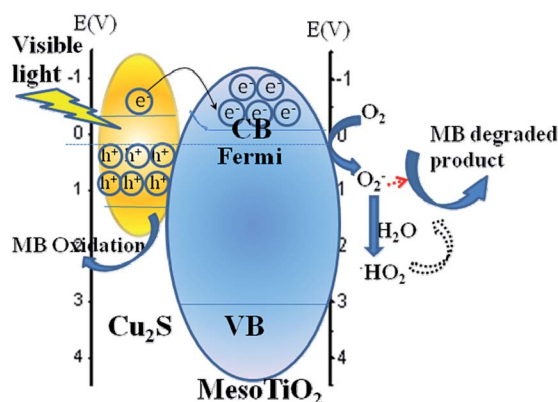


Fig. 9 Proposed mechanisms for the photocatalytic activity of  $\text{Cu}_2\text{S}/\text{P25}$  under visible light excitation.

incorporated into P25, the  $\text{Cu}_2\text{S}/\text{P25}$  hetero junction catalysts shows enhanced visible region absorption efficiency, upon visible light irradiation the valence band electron resonant with incident photon and excited to conduction band and generate the hot electrons on the  $\text{Cu}_2\text{S}/\text{P25}$  surface, significantly increasing the yield of interfacial “hot electrons” with a higher potential energy than P25, and the position of the Fermi level will be shifted closer to the CB of P25. Subsequently, the “hot electrons” transferred to the CB of P25. The pn hetero junction at the interface also helps the transferred “hot” electrons accumulate in the  $\text{TiO}_2$  CB, preventing them from traveling back to the  $\text{Cu}_2\text{S}$  nanocrystals. Since no holes are generated in the valence band (VB) of  $\text{TiO}_2$ , the transferred “hot electrons” in the  $\text{TiO}_2$  CB should have much longer lifetimes, offering more probability to reduce the  $\text{O}_2$  adsorbed on the P25 surface and the consequent sequence MB degradation.

## 4. Conclusions

$\text{Cu}_2\text{S}/\text{P25}$  composites were prepared. SEM shows  $\text{Cu}_2\text{S}$  nanoparticles were uniformly formed and distributed on the  $\text{TiO}_2$  nanoparticles, the average diameter of  $\text{Cu}_2\text{S}$  can be tailored from 4 nm to 16 nm and the diameter of P25 was 21 nm. The doping of  $\text{Cu}_2\text{S}$  in the P25 shows an enhanced light absorbance

in the visible light region. Notably, a lower amount of  $\text{Cu}_2\text{S}$  nanocrystals doping on  $\text{TiO}_2$  nanoparticles exhibited the higher photocatalytic degradation efficiency under visible light irradiation. Size effect shows that the smaller  $\text{Cu}_2\text{S}$  crystal size owns the longer absorption wavelength and stronger visible light absorption intensity, and the visible light photodegradation experiment shows the better performance is reached accordingly. The as prepared photocatalysts has superior photocatalytic stability in the degradation of MB experiment.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by grants from National Natural Science Foundation of China (No. 21473161 and 21271155), Zhejiang Provincial Natural Science Foundation of China (LZ17B030001), Alexander von Humboldt Foundation (No.1141172) and Zhejiang SCI-TECH University for 521 distinguished scholar's scheme.

## References

- 1 D. M. Bierman, A. Lenert, W. R. Chan, B. Bhatia, I. Celanovic, M. Soljagic and E. N. Wang, *Nat. Energy*, 2016, **1**, 16068.
- 2 S. F. H. Correia, P. P. Lima, P. S. Andre, R. A. S. Ferreira and L. D. Carlos, *Sol. Energy Mater. Sol. Cells*, 2015, **138**, 51–57.
- 3 P. A. Bharad, K. Sivarajani and C. S. Gopinath, *Nanoscale*, 2015, **7**, 11206–11215.
- 4 A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diao, C.-Y. Yeh, S. M. Zakeeruddin and M. Graetzel, *Science*, 2011, **334**, 629–634.
- 5 J. M. Luther, P. K. Jain, T. Ewers and A. P. Alivisatos, *Nat. Mater.*, 2011, **10**, 361–366.
- 6 T. Han, H. Wang and X. Zheng, *RSC Adv.*, 2016, **6**, 7829–7837.
- 7 M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang and Y. Liu, *Chem. Eng. J.*, 2016, **284**, 582–598.
- 8 S. Esplugas, D. M. Bila, L. G. T. Krause and M. Dezotti, *J. Hazard. Mater.*, 2007, **149**, 631–642.





- 9 J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo and D. W. Bahnemann, *Chem. Rev.*, 2014, **114**, 9919–9986.
- 10 X. Chen, L. Liu, P. Y. Yu and S. S. Mao, *Science*, 2011, **331**, 746–750.
- 11 A. Fujishima, X. Zhang and D. A. Tryk, *Surf. Sci. Rep.*, 2008, **63**, 515–582.
- 12 Z. Zhang, Y. Huang, K. Liu, L. Guo, Q. Yuan and B. Dong, *Adv. Mater.*, 2015, **27**, 5906–5914.
- 13 Y. He, Y. Wang, L. Zhang, B. Teng and M. Fan, *Appl. Catal., B*, 2015, **168**, 1–8.
- 14 H. Fu, K. Yu, H. Li, J. Li, B. Guo, Y. Tan, C. Song and Z. Zhu, *Dalton Trans.*, 2015, **44**, 1664–1672.
- 15 I. M. A. Mohamed, V.-D. Dao, A. S. Yasin, H. M. Mousa, H. O. Mohamed, H.-S. Choi, M. K. Hassan and N. A. M. Barakat, *Chem. Eng. J.*, 2016, **304**, 48–60.
- 16 V. R. de Mendonca, C. J. Dalmaschio, E. R. Leite, M. Niederberger and C. Ribeiro, *J. Mater. Chem. A*, 2015, **3**, 2216–2225.
- 17 D. Sharma, V. R. Satsangi, R. Shrivastava, U. V. Waghmare and S. Dass, *Int. J. Hydrogen Energy*, 2016, **41**, 18339–18350.
- 18 F. Liao, B. T. W. Lo and E. Tsang, *Eur. J. Inorg. Chem.*, 2016, 1924–1938, DOI: 10.1002/ejic.201501213.
- 19 B. M. Rajbongshi, S. K. Samdarshi and B. Boro, *J. Mater. Sci.: Mater. Electron.*, 2015, **26**, 377–384.
- 20 K. Shen, K. Wu and D. Wang, *Mater. Res. Bull.*, 2014, **51**, 141–144.
- 21 L. Xiao, D. Yuan, P. Li, L. Huang, B.-W. Mao and D. Zhan, *Sci. China: Chem.*, 2015, **58**, 1039–1043.
- 22 G. Mondal, P. Bera, A. Santra, S. Jana, T. N. Mandal, A. Mondal, S. Il Seok and P. Bera, *New J. Chem.*, 2014, **38**, 4774–4782.
- 23 J. Li, H. Zhao, X. Chen, H. Jia and Z. Zheng, *Mater. Res. Bull.*, 2013, **48**, 2940–2943.
- 24 L. Yang, W. Duan, H. Jiang, S. Luo and Y. Luo, *Mater. Res. Bull.*, 2015, **70**, 129–136.
- 25 T. Wang and J. Gong, *Angew. Chem., Int. Ed.*, 2015, **54**, 10718–10732.
- 26 O. E. Rayevska, G. Y. Grodzyuk, V. M. Dzhanan, O. L. Stroyuk, S. Y. Kuchmiy, V. F. Plyusnin, V. P. Grivin and M. Y. Valakh, *J. Phys. Chem. C*, 2010, **114**, 22478–22486.
- 27 F. Li, T. Han, H. Wang, X. Zheng, J. Wan and B. Ni, *J. Mater. Res.*, 2017, **32**, 1563–1572.
- 28 T. Han, D. Zhou and H. Wang, *Powder Technol.*, 2016, **301**, 959–965.
- 29 H. Wang, Y. Fu, T. Han, J. Wan and X. Zheng, *RSC Adv.*, 2015, **5**, 33570–33578.
- 30 H. Wang, D. Zhou, Z. Wu, J. Wan, X. Zheng, L. Yu and D. L. Phillips, *Mater. Res. Bull.*, 2014, **57**, 311–319.
- 31 H. Wang, D. Zhou, S. Shen, J. Wan, X. Zheng, L. Yu and D. L. Phillips, *RSC Adv.*, 2014, **4**, 28978–28986.
- 32 T. Hanrath, *J. Vac. Sci. Technol., A*, 2012, **30**, 030802.
- 33 P. V. Kamat, *J. Phys. Chem. C*, 2008, **112**, 18737–18753.
- 34 H. Eshet, R. Baer, D. Neuhauser and E. Rabani, *Nat. Commun.*, 2016, **7**, 13178.
- 35 S. Akhavan, A. F. Cihan, A. Yeltik, B. Bozok, V. Lesnyak, N. Gaponik, A. Eychmueller and H. V. Demir, *Nano Energy*, 2016, **26**, 324–331.
- 36 M. C. Beard, J. M. Luther, O. E. Semonin and A. J. Nozik, *Acc. Chem. Res.*, 2013, **46**, 1252–1260.
- 37 J. B. Sambur, T. Novet and B. A. Parkinson, *Science*, 2010, **330**, 63–66.
- 38 D. Debellis, G. Gigli, S. ten Brinck, I. Infante and C. Giansante, *Nano Lett.*, 2017, **17**, 1248–1254.
- 39 A. Sanchez-Soares and J. C. Greer, *Nano Lett.*, 2016, **16**, 7639–7644.
- 40 R. Skomski, B. Balamurugan, P. Manchanda, M. Chipara and D. J. Sellmyer, *IEEE Trans. Magn.*, 2017, **53**, 2300307.
- 41 B. Balamurugan and T. Maruyama, *J. Appl. Phys.*, 2007, **102**, 034306.
- 42 P. Kumar, A. Kashyap, B. Balamurugan, J. E. Shield, D. J. Sellmyer and R. Skomski, *J. Phys.: Condens. Matter*, 2014, **26**, 064209.

