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## CuO/CuSCN valence state heterojunctions with visible light enhanced and ultraviolet light restrained photocatalytic activity<sup>†</sup>

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CuSCN is applied, for the first time, in a photocatalytic system to form CuO/CuSCN valence state heterojunctions, which exhibited enhanced visible light driven photocatalytic activity and, surprisingly, ultraviolet light restrained activity. Proper migration of photogenerated carriers is proposed to explain the photocatalytic process.

Due to the enormous potential of photocatalytic technology for practical applications in environmental treatment and new energy development,<sup>1</sup> photocatalytic systems have become a hot research topic worldwide. However, the rapid recombination of photogenerated charge carriers for single semiconductors has seriously impeded improvements in photocatalytic efficiency. Nanostructured heterojunctions offer the opportunity to design new high efficiency composite photocatalytic systems. Some examples, including AgI/ BiOI and AgCl/H<sub>2</sub>WO<sub>4</sub>·H<sub>2</sub>O<sup>2,3</sup> have been reported, which confirm that heterojunction photocatalysts are an effective way to expand the photo-absorption range and to facilitate charge separation. Generally, efforts have been focused on modifying traditional wide band gap photocatalysts via compositing suitable narrow band gap semiconductors based on semiconductor theory.<sup>4</sup> It is known that valence changes usually occur in photocatalytic reactions when the electrons and holes are generated by suitable light excitation.<sup>5</sup> Nevertheless, plenty of semiconductors cannot utilize these excited electrons and holes to achieve valence changes due to their high rate of recombination. Therefore, it is possible to obtain a series of photocatalysts by compositing two materials with different metallic element valence states to form valence state heterojunction photocatalysts, which could efficiently separate the photo-induced electrons and holes.

Copper based compounds possess significant advantages in photoconversion efficiency and the promotion of charge separation *via* an interfacial charge transfer between  $Cu^0$ ,  $Cu^+$ ,  $Cu^{2+}$  under light irradiation. CuSCN is a traditional wide band gap inorganic semiconductor, which has a p-type hole-conducting material, and is thought to be the most promising p-type window material for nanocrystalline solar cells due to its transparency in the visible light spectrum range, reasonable hole conductivity ( $\geq 5 \times 10^{-4} \text{ S cm}^{-1}$ ) and chemical stability.<sup>6</sup> The band gap of CuSCN is about 3.6 eV, which positions the conduction band and valence band at about -3.1 eV and +0.5 eV (NHE), respectively.<sup>7</sup> Although, CuSCN has a wide forbidden band, there is hardly any photocatalytic activity under UV light irradiation due to the high recombination of the photo-generated carriers. CuO is also an important p-type transition metal oxide with a narrow band gap of 1.7 eV, which is a potential field material, excellent catalyst and also has photoelectrochemical properties.8 However, pure CuO has limited photocatalytic activity under visible light irradiation.9 Most reports about CuO in photocatalytic systems discuss composite structures, such as CuO-TiO<sub>2</sub> and CuO-ZnO photocatalysts.<sup>10,11</sup> Therefore, CuO is an excellent candidate material to composite with other appropriate semiconductors to explore new photocatalytic systems.

In this paper, the valence state heterojunction photocatalyst CuO/ CuSCN has been successfully synthesized via a facile one-step method for the first time. The obtained CuO/CuSCN contains two copper valence states in which the photocatalytic activity is attributed to the suitable band structures of CuO and CuSCN and the valence change of Cu<sup>+</sup> and Cu<sup>2+</sup>. A photocatalytic mechanism of visible light enhanced and ultraviolet light restrained photocatalytic activity is also proposed. Visible light could excite the CuO semiconductor to generate electrons and holes, and the electrons would partially transfer to the valence band (VB) of the CuSCN semiconductor which is slightly more positive than the conduction band (CB) of CuO. The main construction in the VB of CuSCN is Cu 3d, which could become Cu<sup>0</sup> after accepting electrons and then revert back to Cu+ via reaction with dissolved oxygen. Thereby, the electron and hole have been separated efficiently, and the hole in the VB of CuO could oxidize methylene blue (MB) molecules. When the CuSCN semiconductor is also excited by UV light, the electrons in the CuSCN CB would transfer to the CuO CB, which could enhance the recombination of electron-hole pairs in the CuO semiconductor. Therefore, the photocatalytic activity has been limited.

Fig. 1A shows the X-ray powder diffraction patterns of the as-prepared CuO/CuSCN, pure alpha-CuSCN, and CuO. It clearly displays that the peaks of the CuO/CuSCN sample (Fig. 1B) coincide

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Fig. 1 (A) XRD patterns of pure CuSCN, CuO/CuSCN, and pure CuO crystals and (B) UV-vis diffuse reflectance spectra of the samples.

with those of the standard orthorhombic alpha-CuSCN (JCPDS No. 29-582) and CuO phases (JCPDS No. 89-2531). The peaks in Fig. 1A a and c match those of pure CuSCN and CuO. The as-prepared CuO/CuSCN (Fig. 1A b) displays both the peaks of CuO, and pure alpha-CuSCN crystals, and no other peaks were found, which indicates that the as-prepared samples are the CuO/CuSCN composite of high purity.

XRD patterns of CuO/CuSCN synthesized *via* different molar ratios of raw materials are given (Fig. S1, ESI<sup>†</sup>). We observed CuO peaks when the molar ratio of Cu(NO<sub>3</sub>)<sub>2</sub> and NaSCN were about 1:1 and 1:2 (Fig. S1A and B, ESI<sup>†</sup>) and no CuO peaks were observed when the molar ratio of Cu(NO<sub>3</sub>)<sub>2</sub> and NaSCN increased to 1:3 or 1:4 (Fig. S1C and D, ESI<sup>†</sup>). Although CuO could not be detected by XRD the colours of the samples are fuscous, which could reflect the DRS (UV-vis diffuse reflectance spectra) results (Fig. 1B). When the molar ratio of Cu(NO<sub>3</sub>)<sub>2</sub> and NaSCN was 1:1, the as-prepared sample had the strongest absorption in the visible light region among the four different molar ratio samples. The absorbency of the four samples in the visible light region decreased when the molar ratio of NaSCN increased, which resulted from the different amounts of CuO nanocrystals formed on the surface of the CuSCN microcrystals.

The formation of the CuO/CuSCN composite is described in the schematic diagram (Fig. S2, ESI<sup> $\dagger$ </sup>). [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ions could be generated after excess NH3 H2O was added into the Cu(NO3)2 solution, and CuSCN and CuO were gradually formed during the evaporation process at 80 °C. The mixed solution could release NH<sub>3</sub> slowly during the heating process, which could restrict the release speed of Cu<sup>2+</sup> ions in solution. Due to the vastly different solubility between CuSCN and CuO, an abundance of CuO nanocrystals could form at the start of the heating reaction, and then the SCN<sup>-</sup> ions can consume the Cu<sup>2+</sup> ions in the CuO nanocrystals to generate CuSCN microcrystals. During oxidation-reduction reactions between Cu<sup>2+</sup> and SCN<sup>-</sup> ions, there was also some (SCN)<sub>2</sub> gas that escaped into the air with heating at 80 °C, which offered an opportunity for the residual CuO nanocrystals to form on the surface of CuSCN microcrystals. As the amount of SCN- ions increased fewer CuO nanocrystals formed, which caused the colours of the obtained samples that to become lighter.

The morphologies of the samples prepared by different molar ratios of  $Cu(NO_3)_2$  and NaSCN were investigated by SEM as shown (Fig. S3A–D, ESI<sup>†</sup>). In the obtained composites, the morphological structures of the CuSCN crystals are microrods, which are surrounded by CuO nanosheets. With increasing molar ratio of NaSCN, the amount of CuO gradually decreased, which can be clearly observed (Fig. S3A–D, ESI<sup>†</sup>). When the molar ratio between  $Cu(NO_3)_2$  and NaSCN is 1:4, the CuO in the obtained samples could not be



Fig. 2 XPS results of the Cu 2p (A) and O 1s (B) in the CuO/CuSCN composite.

observed in the SEM images (Fig. S3D, ESI<sup>†</sup>). The morphologies of pure CuSCN and CuO are microrods and nanosheets, respectively, which is confirmed by the SEM images as shown (Fig. S3E and F, ESI<sup>†</sup>). The microstructure of the CuO/CuSCN composite can also be confirmed by the TEM image (Fig. S6, ESI<sup>†</sup>).

The elemental composition and chemical status of the asprepared samples (Cu(NO<sub>3</sub>)<sub>2</sub>:NaSCN = 1:2) were also examined by X-ray photoelectron spectroscopy (XPS). XPS spectra of Cu 2p and O 1s in CuO/CuSCN are given in Fig. 2. The Cu 2p spectra of CuO/ CuSCN consists of two individual peaks at about 931.5 eV and 951.5 eV which can be attributed to Cu 2p3/2 and Cu 2p1/2 and also with a peak separation of 20 eV, indicating that the valence state of the Cu ion is +1.12 The Cu 2p peaks could be further divided into two different peaks at Cu2+ that feature a Cu 2p3/2 binding energy at 933.6 eV and Cu 2p1/2 binding energy at 953.4 eV. There is also a satellite pattern of 943 eV in the Cu 2p<sub>3/2</sub> XPS spectra.<sup>13</sup> The molar ratio of Cu<sup>+</sup>/Cu<sup>2+</sup> is about 5.38 in the sample based on the XPS results of Cu 2p. The spectrum of O 1s consists of peaks situated at binding energies of 529.0 eV, 530.8 eV and 533.0 eV. It is well recognized that 529.0 eV is assigned to the CuO lattice oxygen.14 The peak at 530.8 eV is the binding energy of O atoms on adsorption, and the binding energy 533.0 eV has been assigned in the literature to the presence of water.<sup>15</sup> Therefore, Cu<sup>2+</sup> ions exist in the form of CuO, and the CuO/ CuSCN composite is obtained.

The photocatalytic activity of CuO/CuSCN was estimated by the degradation of methylene blue (MB) under visible light irradiation. Fig. 3 shows the photo-degradation activity of MB dye as a function of irradiation time over different photocatalysts or light sources. MB dye could be decomposed completely over the CuO/CuSCN composite photocatalyst under visible light irradiation in 60 minutes (Fig. 3a). As shown in Fig. 3b, the photocatalytic activities of CuO, CuSCN and mechanically mixed CuO/CuSCN (molar ratio 1:5) are also measured for comparison and do not exhibit photocatalytic activity under visible light irradiation. The photocatalytic activities of the same sample (raw material molar ratio 1:2) are evaluated under different light source irradiation as shown in Fig. 3d. CuO/CuSCN has higher photocatalytic efficiency under irradiation by visible light than under irradiation by UV + Vis light and the possible reasons will be presented in the following section.

Photocatalytic activities of the samples that were synthesized with different raw material molar ratios are shown in Fig. S4 (ESI<sup>†</sup>). When the molar ratio of Cu(NO<sub>3</sub>)<sub>2</sub> and NaSCN is 1:2, the obtained sample possesses the greatest photocatalytic activity. Based on the experimental results above, the molar ratio of raw materials could control the amount of CuO nanocrystals on the surface of the CuSCN microcrystals. Therefore, CuO nanocrystals not only enhance



**Fig. 3** Photodegradation of MB dye as a function of irradiation time. (a) Photocatalytic activity of the CuO/CuSCN (1:2) composite under visible light irradiation. (b) Comparative photocatalytic results of different samples. (c) Photocatalytic activity of the CuO/CuSCN (1:2) composite under UV-vis light irradiation. (d) Photocatalytic activities (1:2) comparison of the results of UV + Vis and Vis light irradiation.

absorption in the visible light region, but also tune the photocatalytic activities of the CuO/CuSCN composites.

It is known that photocatalytic activity is greatly affected by the recombination of the photo-generated electrons and holes which could decrease the quantum yield. Photoluminescence emission spectroscopy is an effective approach to understanding the separation capacity of the photo-generated carriers because of the direct result of the recombination of the free carriers. Herein, 320 nm is chosen as the excitation wavelength, the PL spectra of CuO/CuSCN, pure CuSCN and CuO are displayed in Fig. S5 (ESI†). It can be observed that pure CuSCN and CuO (Fig. S5B, ESI†) have strong emission peaks, deriving from the direct electron-hole recombination of the band transition while the CuO/CuSCN composites have lower peaks, suggesting that the photo-induced carriers can migrate easily between the CuO and CuSCN crystals and that recombination of the charges can be greatly limited.

On the basis of the experimental and theoretical results, a schematic diagram of the band levels of CuO/CuSCN and the possible photocatalytic reaction mechanism are given. Fig. 4A shows the band-edge of CuSCN and CuO. Neither CuSCN nor CuO possess photocatalytic activity under suitable light irradiation which might be due to the fast recombination of electrons and holes according to the PL results above. The photocatalytic activity results reveals that the CuO/CuSCN valence state heterojunction photocatalyst has much greater activity under visible light irradiation than under irradiation by UV + Vis light. We know that visible light only excites the CuO semiconductor to generate electrons and holes (Fig. 4C), and that the electrons could migrate to the VB of CuSCN, which is mainly a hybrid of Cu 3d. The electron can be accepted by Cu<sup>+</sup> in the CuSCN VB to become Cu<sup>0</sup>, and then can react with dissolved O<sub>2</sub> to revert back to Cu<sup>+</sup> ions in the CuSCN microcrystals.16 The Cu0 could be detected by XPS spectra of Cu LMM after photocatalytic reaction in N2 (Fig. S8, ESI<sup>+</sup>). So, the electrons and holes have been successfully separated, and the holes remaining in the VB of CuO could degrade pollutants in solution. A prominent contribution to the degradation of MB molecules is attributed to •OH radicals that could be obtained via oxidizing the OH<sup>-</sup> groups by holes.<sup>17</sup> Fig. 4B shows the mechanism of electron migration under UV + Vis light irradiation which could excite both the CuSCN and CuO semiconductors. The electrons in



**Fig. 4** Schematic diagram of the band structures of CuO/CuSCN valence state heterojunctions and the possible photocatalytic mechanism. (A) Band structure of the CuSCN and CuO semiconductor. (B) and (C) show the electron migration mechanism of photoinduced carriers under UV + Vis or visible light irradiation, respectively.

the CuO CB migrate to the CuSCN VB and combine with holes in the CuSCN VB. The stimulated electrons in the CuSCN CB can also transfer to the CB of CuO, and then recombine with holes in the CuO VB. Therefore, restricting the photocatalytic activity.

A CuO/CuSCN valence state heterojunction photocatalyst was synthesized by a facile one-step low temperature chemical bath method. While the pure CuSCN and CuO do not have photocatalytic activity, the as-prepared CuO/CuSCN heterojunction photocatalyst exhibited strong visible light absorption and photocatalytic activity against MB. The photocatalytic activity could also be controlled by adjusting the molar ratio of raw materials, and the sample with the most powerful photocatalytic activity is obtained when the molar ratio of Cu(NO3)2 and NaSCN is 1:2. Meanwhile, visible light enhanced and, surprisingly, ultraviolet light restrained photocatalytic activity is displayed by the CuO/CuSCN valence state heterojunction photocatalyst. Based on our systematic analysis, proper migration of photo-generated carriers is proposed to explain the visible light enhanced and ultraviolet light restrained photocatalytic processes. At the same time, this valence state heterojunction photocatalyst can extend the scope of photocatalytic development which will lead to more potential applications.

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