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Graphical Abstract

The resultant ternary spherical Ag-Cu₂O/rGO composite with complex heterostructures exhibited excellent photocatalytic activity and higher stability.



Construction of Reduced Graphene Oxide-Supported Ag-Cu₂O composites with Hierarchical Structures for Enhanced Photocatalytic Activities and Recyclability

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Abstract

Ternary spherical Ag-Cu₂O/reduced graphene oxide (rGO) nanohybrids with excellent hierarchical structures are developed through a simple one-pot, two-stage reduction synthetic route at room temperature without any surfactants. In the resulted complex heterostructures, both Ag and rGO are in direct contact with Cu₂O, and Ag nanocrystals are mainly deposited on the surface of Cu₂O spheres. The resultant ternary spherical Ag-Cu₂O/rGO composite exhibits excellent photocatalytic activity in photocatalytic degradation of methyl orange (MO) under visible light irradiation, which is much higher than that of either the single component (Cu₂O) or two components systems spherical Cu₂O/rGO, and Ag-Cu₂O. In particular, the resultant ternary composites possess excellent stability and extend light absorption range. The PL spectrum results have demonstrated that not only Ag but also rGO could capture the photogenerated electrons from Cu₂O, thus leading to effective separation of electrons and holes. In particular, it is found that the direct junction and interaction between Ag and Cu₂O in the ternary composites is more beneficial for charge transportation than the direct contact between Ag and rGO (labeled as sample Ag-rGO-Cu₂O), and thereby the resultant Ag-Cu₂O/rGO composites with such complex heterostructures exhibit a better photoactivity than sample Ag-rGO-Cu₂O. This work provides an insight into designing and synthesizing new Cu₂O-based hybrid materials for effectively improving the photocatalytic performance.

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Keywords: ternary spherical Ag-Cu₂O/rGO composite, photocatalytic activity, recyclability, charge transportation

1 Introduction

Currently, among the semiconductor photocatalysts, metal oxide semiconductors have been widely investigated for degradation of organic pollutants due to its strong photocatalytic activity and photoelectrochemical stability in aqueous media.^{1,2} But, as we know, many metal oxide semiconductors are only functional in the UV region owing to their large band gaps, for instance, 3.0 eV for TiO₂³ and 3.2 eV for ZnO⁴, which severely limits their practical applications. Semiconductors with narrow band gaps would be more favorable for the utilization of visible light. Cu₂O is regarded as excellent candidates for visible-light photocatalysis because it is a p-type oxide semiconductor with a suitable band gap of 2.0-2.2 eV.^{5,6} In particular, it is inexpensive, ease in preparation, and good environmental acceptability. To date, various Cu₂O nanostructured materials such as hollow nanocubes.⁷ nanocubes.⁸ nanospheres, ⁹ octahedral, 26-facet polyhedral, ¹⁰ have been achieved and used for degradation of organic dyes. However, because of a short hole-diffusion length, there exists an easy recombination of photogenerated electron-hole pairs, which leads to a very low quantum efficiency and limits its promising applications in photocatalysis.^{11,12} Therefore, much effort now has been focused on the design and fabrication of suitable Cu₂O-based composite/hybrid materials with high charge separation efficiency for improving the photocatalytic activity.¹³⁻¹⁷

Constructing noble metal-semiconductor binary nanohybrids is one of the most effective methods for improving photocatalytic activity.^{12,18} Generally, it is believed that the formed Schottky barriers at the metal-semiconductor heterojunction interface can retard electron-hole pair recombination in photocatalysis.^{19,20} Therefore, this heterostucture exhibits enhanced photocatalytic activity compared with pure metal oxide semiconductors due to a decrease in the recombination rate of photogenerated electron-hole pairs. Several binary metal-Cu₂O composites with enhanced degradation properties now have been reported.¹³⁻¹⁵ For example, Wang *et al.* produced noble

metal/Cu₂O by depositing Ag or Au nanoparticles onto Cu₂O under the irradiation of visible light.¹² Zhu et al. synthesized Cu₂O-Au hierarchical heterostructures with a series of morphologies by controlling the amount of PVP and HAuCl₄.²¹ Mahmoud *et* al. reported that Cu₂O-Au nanoframes with different Cu₂O layer thickness and showed increasing of photodegradation rate of MB dye with the thickness of the Cu₂O frame increasing.²² In addition, several groups reported that noble-Cu₂O core-shell nanostructures with different core's shapes, such as nanorods, nanocubes, nanoplates, edge- and corner-truncated octahedral, icosahedral, octahedral, show enhanced photocatalytic activities.²³⁻²⁵ However, at present, there are still some fundamental issues hampering the application of noble metal/Cu₂O catalysts. First, for synthesizing noble-Cu₂O with controlled morphology, certain capping agents and surfactants, such PVP, SDS and CTAC are usually needed,^{21,24,25} which may affect the contact between reacting molecules and catalysts.²⁶ Additionally, particle aggregation in aqueous solution and structural morphology changes during the photocatalytic process could also lead to the serious reduction of their catalytic properties in reusing.²⁷ Therefore, stability is of great importance for Cu₂O as an effective catalyst in practical application.^{28,29}

More recently, graphene-semiconductor nanocomposites (NCs) have shown remarkable promising applications in the photocatalytic degradation of organic dyes.³⁰ It is widely recognized that the incorporation of graphene into semiconductor photocatalysts can effectively hinder the recombination of electron-hole pairs, and thus result in high performance of photocatalytic activity.^{31,32} Moreover, graphene sheets as a stabilizer can effectively prevent the particle aggregation and thereby improve their stability.³³ Based on this, there have been some reports on the synthesis of Cu₂O/graphene photocatalysts.^{16,17,34} Moreover, the as-synthesized Cu₂O/graphene hybrids are proven to be better photocatalyts than native Cu₂O. Beyond the aforementioned binary nanocomposites, most recently, ternary metal-semiconductor/graphene have shown enhanced photocatalytic activity towards the removal of organic pollutants compared to binary composites.³⁵ Some ternary graphene-base semiconductor nanocomposites have been synthesized so far, including

3

Au/rGO-TiO₂, ³⁶ Ag-ZnO/rGO, ³⁷ as well as Pd-ZnO-GO.³⁸ However, to the best of our knowledge, the studies on the noble metal-semiconductor/graphene ternary nanohybrids involved in photocatalysis have been scarcely reported at present. The main reason may be that the formation of a ternary graphene hybrid generally need the multiple-step synthesis procedure, which is much more complicated and not suitable for mass production.³⁸ In addition, requiring rapid heating processes or high reaction temperatures also limit their practical applications.^{36,37} Therefore, more efforts should be done to explore simple and efficient strategies for mass preparation of metal-Cu₂O/graphene ternary composites with better photocatalytic performance. Especially, among nobles, Ag is particularly attractive because of the relatively low cost and distinctive properties such as superior conductivity, chemical stability.³⁹ It is significant to prepare Ag-Cu₂O/graphene ternary composites with high activity and durability for visible-light photocatalysis.

On the basis of the above issues, this work provides an excellent method for fabricating hybrids of Ag-Cu₂O/rGO. Herein, the spherical Ag-Cu₂O/rGO composites with a unique nanostructure are successfully synthesized through a facile one-pot, two-stage reduction synthetic route at room temperature without adding any surfactants. In the resultant hierarchical structure, Ag nanocrystallties are mainly located on the surface of Cu₂O spheres and spherical Ag-Cu₂O heterostructures are attached on the rGO sheets. The photocatalysis experiment results demonstrate that the resultant ternary composites exhibit remarkably enhanced photocatalytic properties and stability towards decomposition of methyl orange (MO) compared with Cu₂O, Cu₂O/rGO and Ag-Cu₂O under visible light irradiation, mainly due to the effective separation between photoelectron/hole pairs. Notably, compared with Ag-Cu₂O, ternary Ag-Cu₂O/rGO exhibits more excellent photocatalytic cycling stability. In addition, it is noteworthy that the rGO-supported sphere-like Ag-Cu₂O nanohybrids exhibit higher photoactivity than the sample Ag-rGO-Cu₂O ternary composites (including more Ag nanoparticles in direct junction with rGO), indicating that the direct junction between Ag and Cu₂O can more effectively separate the photogenerated charges due to the Schottky effects at the metal-semiconductor

4

interface.

2 Experimental Sections

2.1 Raw Materials

The following chemicals were used: copper nitrate trihydrate ($Cu(NO_3)_2$ ·3H₂O), silver nitrate (AgNO₃), hydrazinium hydrate (N₂H₄·H₂O, 85%) and methyl orange (MO) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All of these reagents were of analytical grade and used without further purification. Graphite oxide (GO, powder) was supplied by Institute of Coal Chemistry, Chinese Academy of Sciences. We used distilled water as the solvent.

2.2 Preparation of Sphere-like Ag-Cu₂O/rGO NCs

Spherical Ag-Cu₂O/rGO nanocomposites (NCs) were prepared via a two-stage reduction process using N₂H₄·H₂O. This formation and evolution process mainly contain three stages: (1) the formation process of sphere-like Cu₂O/rGO; (2) mixing of the AgNO₃ and Cu₂O/rGO; (3) the formation process of sphere-like Ag-Cu₂O on rGO. In a typical synthesis, 50 mg of GO was dispersed into 100 mL of distilled water with sonication for 1 h to obtain uniform suspension of GO. Then, 0.05 g Cu(NO₃)₂·3H₂O was dissolved in 50 mL of water and mixed with aqueous solution of GO (0.5 mg/mL, 3 mL) under vigorous stirring. Next, N₂H₄·H₂O (1 mL, 0.5 M) was dropwised into the suspension with constant stirring. Two minutes later AgNO₃ (4 mL, 5 mM) was added into the above solution and stirred for 5 min. Finally, N₂H₄·H₂O (1.5 mL, 0.5 M) was dropwised into the result solution again for finishing reduction reaction. The solid products were separated by centrifugation and washed repeatedly with distilled water and absolute alcohol to remove residual ions and N₂H₄. In the end, the as-prepared solids were dried for 4 h in vacuum oven at 60 °C.

Preparation of the Ag-rGO-Cu₂O NCs. 0.05 g Cu(NO₃)₂·3H₂O was dissolved in 50 mL of water and mixed with aqueous solution of GO (0.5 mg/mL, 3 mL) under constant stirring. Different from spherical Ag-Cu₂O/rGO prepared via a two-stage reduction with N₂H₄ described above, the total dosage of hydrazine hydrate (2.5 mL)

Journal of Materials Chemistry A

was once added into an aqueous solution containing GO and Cu^{2+} . Then, AgNO₃ (4 mL, 5 mM) was added into the mixture and stirred for 5 min. This sample is marked by Ag-rGO-Cu₂O.

Preparation of the Ag-Cu₂O/rGO NCs Loading with Various Amount of rGO. The Ag-Cu₂O/rGO NCs with various rGO weight percentages (0.45, 0.90, 1.8, 5.2 and 8.4 wt %) were obtained by adjusting the concentration of the GO (0.025, 0.05, 0.1, 0.3, 0.5 mg/mL) and keeping the doses of Cu(NO₃)₂, AgNO₃ and N₂H₄ in the typical synthesis. This procedure produced five samples which were labeled as G1-0.45, G2-0.90, G3-1.8, G4-5.2 and G5-8.4, respectively.

Preparation of Ag-Cu₂O/rGO NCs with Various Amount of Ag. The Ag-Cu₂O/rGO NCs with loading of 6.4, 12 and 17 wt% Ag were prepared by controlling the volume of AgNO₃ (2, 4, 6 mL) under identical conditions. The samples were marked by Ag6.4-S1, Ag12-S2 and Ag17-S3.

For comparison, Cu_2O were synthesized according to our previous work with some modication.⁴⁰ Briefly, N₂H₄ (2.5 mL, 0.5 M) was added into 50 mL Cu(NO₃)₂ solution under the constant stirring. Cu₂O/rGO and Ag-Cu₂O were obtained by the similar procedure employed in the synthesis of G3-1.8 except for without adding AgNO₃ and GO, respectively.

2.3 Characterizations

The structure and composition of the as-synthesized nanoparticles were conducted by X-ray diffraction (XRD) using a German Bruker D8 X-ray diffractometer with the K_a radiation of Cu (λ =1.5418 Å). Fourier transform infrared (FT-IR) spectra of the products were acquired on FTS 135 FT-IR spectrophotometer; Raman Spectroscopy of the samples was recorded on a Horiba LabRAM HR800 Raman microspectrometer using the 514 nm excitation line from an Ar-ion laser with a power of about 5 mW. N₂ adsorption-desorption was tested on ASAP2020HD88 in nitrogen atmosphere. The microstructure of the obtained products was characterized by transmission electron microscopy (TEM) on JEM-1011 at an accelerating voltage of 100 kV and scanning electron microscopy (SEM) using Hitachi S4800 equipped with X-ray energy

dispersive spectroscopy (EDS) capabilities. A high-resolution TEM (HRTEM) was performed on a JEOL 2100. UV-vis diffuse reflectance adsorption spectra were measured by using a Tu1901 spectrophotometer. PL spectra were tested on F280 fluorescence spectrophotometer. X-ray photoelectron spectroscopy (XPS) spectrum were measured on ESCALAB 250 with a monochromatized Mg-Ka source and a resolution of 1.00 eV.

2.4 Photocatalysis Experiments

The photocatalytic activities of the samples were investigated by the degradation of the aqueous solution of methyl orange (MO) under visible-light irradiation at room temperature. The degradation reactions were conducted in an XPA-7 type photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China) equipped with 400 W metal-halide lamp and a cutoff filter (λ >420 nm). In detail, 10 mg of catalyst was dispersed into 50 mL aqueous solution of the MO dye (40 mg/L). Prior to irradiation, the suspension was magnetically stirred in the dark for 40 min to establish an adsorption-desorption equilibrium between the photocatalyst and MO. At given intervals, 5 mL suspension was sampled and centrifuged at 10,000 rpm. The absorbance of supernatant was monitored by a Hitachi U-4100 spectrophotometer.

For the purpose of comparing with other catalysts, the photocatalysis experiments were carried out using MO (32 mg/L) and kept other experimental conditions constant. In addition, the samples (G3-1.8 and Ag-Cu₂O) were washed with water several times and dried for durability test.

The degradation efficiency of the MO was calculated according to its initial and final concentrations of the solutions by eq:⁴¹

 $D\% = (c_0 - c)/c_0 \times 100\%$

Here, c_0 is the initial concentration of methyl orange and c is the temporal concentration.

3 Results and Discussion

3.1 Characterization of Ag-Cu₂O/rGO Nanocomposites

Fig. 1A shows the X-ray diffraction (XRD) patterns of GO, Cu₂O/rGO, Ag-Cu₂O and Ag-Cu₂O/rGO. For GO, a sharp peak around 12.4° is observed, which corresponds the characteristic peak of the (001) plane (Fig. 1A-a).⁴² In the pattern of Cu₂O (Fig. 1A-b), all the diffraction peaks are readily indexed to cubic Cu₂O (JCPDS 65-3288). In the case of Fig. 1A-c, in addition to the diffraction peaks of Cu₂O, the extra weak diffraction peaks at 20 values of 38.1°, 44.3°, 64.4° and 77.4° can be indexed to the (111), (200), (220) and (311) faces of the Ag, respectively, confirming the formation of Ag-Cu₂O composites (JCPDS 65-2871). Moreover, the intensities of Ag peaks are weaker than those of the Cu₂O, indicating low loading of Ag in the composite. In the as-synthesized ternary composite, there are no significant changes observed in the XRD pattern compared with the XRD spectra of Ag-Cu₂O sample, and no typical diffraction peak of graphene (002) is observed, accompanied with the disappearance of the peak at 12.4° for the GO. This is probably because that the quantity of rGO is too low and the rGO might completely be shielded due to the loading of Cu₂O and Ag on the graphene sheets. According to the TGA curve in Fig. S1, the mass content of rGO in the Ag-Cu₂O/rGO composites was calculated to be about 8.4%.

The effective reduction of GO to rGO and the formation process of Ag-Cu₂O/rGO can be further demonstrated by the Fourier-transform infrared (FT-IR) spectra and Raman spectra. Fig. 2A shows the FTIR spectra of the as-synthesized GO and Ag-Cu₂O/rGO. Clearly, GO exhibits abundant oxygen-containing groups. The peaks at 3444, 1731, and 1622 cm⁻¹ are assigned to the stretching vibration of the O-H groups, the C=O carbonyl stretching, and the skeletal vibrations of graphitic domains, respectively. In addition, the stretching vibration band C-O of epoxy is located at 1226 cm⁻¹.^{31,43} However, in the case of Ag-Cu₂O/rGO, the carboxylic acid vibration band (v_{C=O} at 1731 cm⁻¹) disappears, and the intensity of other oxygen-containing functional groups decreases dramatically. More significantly, a new peak appears at 626 cm⁻¹, which corresponds to the Cu-O stretching vibration in the Cu₂O phase.⁴⁴ The above observations indicate that most of the oxygen-containing groups of GO, particularly carboxyl groups, have been removed by the reducing reaction and the

presence of Cu₂O in the composite.

Raman spectroscopic measurement is used to further characterize the presence of rGO in the ternary hybrid sample. Fig. 2B shows the Raman spectra of the as-synthesized GO and Ag-Cu₂O/rGO, respectively. In the Raman spectrum of Ag-Cu₂O/rGO, two characteristic bands at 1368 cm⁻¹ (D band) and 1584 cm⁻¹ (G band) for graphitized structures are observed.^{42,45} Clearly, the intensity ratio of I_D/I_G for the Ag-Cu₂O/rGO (~0.90) is higher than that for GO (0.77), indicating that the amount of oxygen-containing functional groups for the Ag-Cu₂O/rGO sample decreases after adding hydrazine, and the conjugated graphene networks are re-established.⁴⁵ Meanwhile, it is also observed that the peak for G band (1603 cm⁻¹) of GO, probably due to the recovery of hexagonal network of carbon atoms with defects.⁴⁶ In addition, for the ternary hybrids, three new peaks at around 150, 212 and 634 cm⁻¹ appear, which are associated with the Cu₂O.⁴⁷

X-Ray photoelectron spectroscopy (XPS) measurement was performed to further estimate the reduction degree of rGO in the Ag-Cu₂O/rGO NCs. The XPS spectrum of the C 1s of the GO (Fig.S2a) indicates that the five peaks centered at 284.5, 285.6, 286.7,287.8 and 288.8 eV can be assigned to sp^2C , sp^3C , -C-O, -C=O and -COO groups, respectively.⁴⁸ In comparison with the GO spectrum, the intensities of the oxygen containing groups obviously decrease, and the content of them is reduced by 21% in the Ag-Cu₂O/rGO NCs (Fig.S2b).⁴⁹ This result is in good agreement with the IR and Raman. On the other hand, compared with the spectrum of the sample Ag-Cu₂O, it is found that the binding energies of Cu 2p (932.6 and 952.5 eV) in the Ag-Cu₂O/rGO NCs are slightly higher than that in Ag-Cu₂O, implying that rGO interacts strongly with the Cu₂O, which is beneficial to the transfer of photogenerated electrons Cu₂O during the photocatalytic process (Fig. S2c-e).^{50,21}

The morphology and microstructure of the Ag-Cu₂O/rGO composites are characterized with TEM and SEM. From Fig. 3, we can see that the rGO sheets exhibit a typical rippled and crumpled structure and some spherical Ag-Cu₂O hybrids are entirely or partially enwrapped by rGO sheets. Meanwhile, it is observed that most

of small Ag nanoparticles are directly deposited on the surface of Cu₂O with a sphere-like shape and few "free" Ag particles exist on the rGO sheets. The average size of Cu₂O spheres is calculated to be about 250 nm in diameter and that of Ag is about 40 nm. Moreover, it should be noted that after a long duration of sonication during the preparation of the TEM specimen, these spherical Ag-Cu₂O hybrids are still loaded on the rGO sheets, indicating an intimate interfacial contact between the rGO and Ag-Cu₂O hybrids. A HRTEM image taken from the selected area of the Ag-Cu₂O/rGO composites is shown in Fig. 4b and 4c. The observed interplanar spacing of 0.24 nm and 0.25 nm corresponds to (111) lattice plane of Ag and (111) lattice planes of Cu₂O, respectively, which further reveals that Ag nanocrystals are deposited on the surfaces of Cu₂O. The stacking width is calculated to be 0.37 nm for rGO layers corresponding to the spacing of the (002) lattice planes.⁵¹ It is evident that Ag-Cu₂O hybrids have been successfully synthesized and anchored on the surface of rGO. To further confirm the composition and observe distribution of various elements, the elemental distribution of Ag-Cu₂O/rGO composites was determined by EDS elemental mapping. Fig. 5 shows representative SEM images of Ag-Cu₂O/rGO composites along with the corresponding elemental maps for O, Cu, Ag and C. It can be seen the Cu and O element mappings of the composite exhibit sphere-like distribution and the C signals cover the entire sample area, suggesting that they are mainly from the rGO. It is also observed that Ag nanoparticles are mainly dispersed on the surface of Cu₂O sphere in the composites. Combining the results of XRD, FTIR, Raman spectra, SEM, and TEM, it can be concluded that the ternary spherical Ag-Cu₂O/rGO hybrids have been successfully prepared. Additionally, TEM images of bare sphere-like Cu₂O, Cu₂O/rGO and Ag-Cu₂O composite are shown in Fig. S3. As can be seen from the picture, the introduction of rGO has no effect on the morphology of Cu₂O. And it is found that without rGO, the obtained Ag-Cu₂O have a slightly larger average size of about 300-450 nm. Therefore, rGO has an influence on growth of Ag-Cu₂O. The decrease in Ag-Cu₂O particle size might be attributed to the existence of GO nanosheets as the dispersing agent, inhibiting Cu₂O particles aggregation into bigger spheres.⁴¹

3.2 Formation of Ag-Cu₂O/rGO composites

To better understand the formation process of the spherical Ag-Cu₂O/rGO composites, two control experiments are carried out. First, we changed the order of adding GO. In the first step, spherical Cu₂O were synthesized, and then these particles were mixed with a mixture of GO and Ag precursor solution, followed by reduction with hydrazine. Fig. S4a shows the morphology of the obtained sample. It can be seen that some sphere-like Cu₂O nanoparticles scattered out of the rGO sheet and some Ag particles directly grew onto the rGO. Second, different from spherical Ag-Cu₂O/rGO prepared via the two-stage reduction with hydrazine hydrate, the total dosage of hydrazine hydrate (2.5 mL) was once added into a aqueous solution containing GO and Cu²⁺ to produce hybrid composites instead of two times, which is marked by Ag-rGO-Cu₂O. It can be seen that Ag nanoparticles can not well grow on the surface of sphere-like Cu₂O and many Ag nanoparticles are directly deposited on the rGO sheets (Fig. S4b). The above results demonstrate that two-stage reduction with N₂H₄ is the key to the formation of the present sphere-like "Ag-Cu₂O nanojunction" on rGO sheets.

Based on the experimental results, the synthetic route for the preparation of Ag-Cu₂O/rGO composites is summarized in Scheme 1 (Supporting Information). In the first stage, Cu²⁺ ions were anchored on the surface of GO sheets due to the electrostatic interactions. With adding 1.0 mL hydrazine hydrate, Cu²⁺ was reduced quickly to Cu₂O nanoparticles accompanied with the reduction of GO to rGO. The produced Cu₂O nanoparticles with small sizes self-aggregate into sphere shape driven by thermodynamics because of the high surface energy, and deposit on the rGO sheets.⁵² In the second stage, with adding of another 1.5mL N₂H₄, the exposed surfaces of Cu₂O, resulting in the formation of Ag-Cu₂O/rGO hybrid structure. Two-stage reduction with N₂H₄ would be beneficial to control the growth rate of Ag nanoparticles. A slow reduction process could facilitate Ag nanoparticles deposited on the surface of Cu₂O. For easy observation of the morphological evolution of Cu₂O, representative TEM images of Ag-Cu₂O/rGO NCs prepared at different stages are

taken and shown in Fig. S5.

3.3 Optical properties

Optical properties of the prepared samples are tested using UV-vis diffuse reflectance spectroscopy. For comparison, the UV-vis diffuse reflectance spectra (DRS) of Cu₂O, Cu₂O/rGO, Ag-Cu₂O and Ag-Cu₂O/rGO are displayed in Fig. 6(a). The band gap can be estimated from the intercepts of the tangents to the $(\alpha hv)^2$ vs. photon energy (hv) plots, shown in Fig. 6(b). The roughly estimated band gap energies of these samples are about 2.04, 1.95, 1.70 and 1.60 eV for Cu₂O, Cu₂O/rGO, Ag-Cu₂O and Ag-Cu₂O/rGO, respectively. The absorption edge of Cu₂O exists at around 650 nm, which is consistent with previous reports.53 Compared with the unmodified sphere-like Cu₂O, all the modified Cu₂O composites display red-shifted absorption edges. Notably, Ag-Cu₂O/rGO and Ag-Cu₂O show a more red-shift. Therefore, these two complex photocatalysts are expected to have better abilities to utilize sunlight and have improved photocatalytic ability. As for Ag-Cu₂O/rGO, the absorption edge appears to be at about 780 nm, and the band gap Eg exhibits a significant reduction as compared to bare Cu₂O, implying that the Ag-Cu₂O/rGO nanohybrids can absorb nearly in the full visible-light region. This red shift may be mainly attributed to the Schottky effects between Ag and Cu₂O.²⁹ In addition, the interface coupling interaction between Ag-Cu₂O and rGO in ternary composite further narrows the band gap of Cu₂O.³⁴ The same phenomenon can be also observed for other GR-based semiconductor nanocomposites.⁵⁴

In addition, in order to investigate the surface plasmon resonance (SPR) effect of Ag in the composite, the UV-vis absorption spectra of Cu₂O, Ag-Cu₂O, Ag-Cu₂O/rGO are displayed in Fig. S6. Clearly, bare Cu₂O nanospheres have a broad absorption peak at about 600 nm.¹² The absorption spectra of Ag-Cu₂O and Ag-Cu₂O/rGO also show the absorption peak of Cu₂O at about 600 nm, while the extremely weak surface plasmon resonance (SPR) absorption band of the Ag nanoparticles located at 400-500 nm can be observed only in sample Ag-Cu₂O.^{12,55} Therefore, it is concluded that the plasmonic effect has no great contribution to the

improved photocatalysis process.

3.4 Photocatalytic Activities properties of the Ag-Cu₂O/rGO composites

Firstly, we evaluated the effect of the Ag loading amounts on the photocatalytic activity of spherical Ag-Cu₂O/rGO composites by photocatalytic degradation of MO (40 mg/L) aqueous solution under visible-light irradiation. The temporal changes in the concentration of MO were monitored by examining the variations in the maximal absorption in UV-vis spectra at 464 nm. Ag-Cu₂O/rGO hybrids with different Ag loading amounts (6.4 wt%, 12 wt% and 17 wt%) could be synthesized by adjusting the Ag⁺ amount added in the solution at fixed concentration of GO. It can be seen from Fig. S7 that the number of Ag nanoparticles deposited on the surfaces of Cu₂O spheres shows a slight increase with increasing of the amount of Ag from 6.4% to 17%. The degradation percentage of MO follows an order of 12Ag-S2 (76.6%) > 17Ag-S3 (70.6%) > 6.4Ag-S1 (64.2%), as shown in Fig. 7a. Clearly, the photocatalytic activities of the Ag-Cu₂O/rGO hybrids decrease slightly after the Ag loading amount reached to 17%. 12% is the optimal loading content of Ag, and the higher content of silver could be detrimental to the photocatalytic efficiency. As is reported in the literature, Ag nanoparticles attached onto Cu₂O can act as electron sinks to prevent the recombination of the photogenerated electrons and holes, therefore achieving better activity.⁵⁶ However, relatively higher Ag content may act as a new recombination center between electrons and holes, thus lowering the photocatalytic activity of photocatalyst.⁵⁶

Next, we further investigated the photocatalytic activities of the Ag-Cu₂O/rGO samples with different rGO weight percentages under visible-light irradiation, shown in Fig. 7b. The Ag-Cu₂O/rGO composites with various rGO weight percentages (0.45%, 0.9%, 1.8%, 5.2%, 8.4%) can be achieved by adjusting the GO amount added in the mixtures at fixed concentration of Ag and the samples are labeled as G1-0.45, G2-0.9, G3-1.8, G4-5.2 and G5-8.4. It can be seen that degradation percentage of MO follows an order of 87% (G3-1.8) \approx 85% (G2-0.9) > 78% (G4-5.2) \approx 77% (G5-8.4) > 71% (G1-0.45) in an hour. Clearly, G3-1.8 and G2-0.9 shows almost the same

catalytic activities and the degradation efficiency of G3-1.8 is a little higher than that of G2-0.9, while the photocatalytic activities of the sample G5-8.4 shows decrease with increasing amounts of rGO. Hence, the optimum amount of rGO is about 0.9~1.8 wt% for the present Ag-Cu₂O/rGO composite photocatalytic system. A further increase in the amount of rGO leads to a reduction of the activity, in agreement with the previous report.⁴¹ It is known that graphene in the Cu₂O/rGO system can promote the charge separation, and restrain the hole-electron recombination of Cu₂O, which results in an enhanced photocatalytic activity.¹⁶ The decreased activity of the photocatalyst with more rGO in the system may be attributed to a blocking effect of rGO.⁵⁷ Some active sites on the surface of Cu₂O could be unfortunately shielded in more rGO.

To further evaluate the photocatalytic activity of the resultant Ag-Cu₂O/rGO composites (G3-18), a series of the MO (40 mg/L) photocatalytic degradation experiments with the Ag-Cu₂O/rGO NCs, pure sphere Cu₂O, Cu₂O/rGO, Ag-Cu₂O, as the photocatalysts are carried out under identical conditions. Fig. 7c shows the time-dependent UV-vis absorption spectra of MO aqueous solution in the presence of the Cu₂O-Ag/rGO sample under visible-light. The intensity of the main absorption peak of MO at about 464 nm decreased gradually as the daylight-irradiation time increases and the absorption peak of MO solution has almost vanished after 1h visible-light irradiation. Fig. 7d displays photocatalytic degradation of MO solution under visible-light irradiation with all the photocatalyst samples (10 mg), respectively. As can be seen, there is no evident photodegradation of MO in the absence of catalyst. In contrast, all the as-prepared photocatalysts exhibit high photocatalytic performances. Especially, spherical Ag-Cu₂O/rGO composite exhibits the best efficiency and more than 87% of the initial dyes are decomposed by the composite in 1 h. However, nearly 41% of the initial dye still cannot be decomposed in the solution after the same time for using the as-prepared pure Cu₂O nanospheres as a photocatalyst. The as-prepared Ag-Cu₂O and Cu₂O/rGO also show much higher photocatalytic activity than pure Cu₂O nanospheres. The removal efficiency of Ag-Cu₂O and Cu₂O/rGO are up to 78% and 69%, respectively. The order of

degradation rate of MO (40 mg/L) is as follows: Ag-Cu₂O/rGO (G3-1.8) > Ag-Cu₂O > Cu₂O/rGO > Cu₂O. Herein, it is worth mentioning that the degradation efficiency of Ag-Cu₂O is higher than that of Cu₂O/rGO, indicating that the spherical Ag-Cu₂O composite is more efficient for increasing the photoactivity.

What's more, for purpose of meaningful comparing our result with other photocatalysts as reported in the literatures,^{58,59} we carried out another experiment as follows: 10 mg Ag-Cu₂O/rGO was added into 32 mg/L of MO solution. It is seen that after irradiation under visible light for 1 h, the MO degradation efficiency reaches about 95%, which is higher than the catalysts reported in the references, such as $Cu_2O/PA/rGO$,¹⁷ Cu_2O -Au,²¹ Cu_2O/Ag ,⁵⁸ $Fe_3O_4@C@Cu_2O$ composites (see cycle 1 of Ag-Cu₂O/rGO in Fig.8a and Table S2).⁵⁹

Besides the activity of photocatalysts, the stability is significant to their practical applications.^{28,29} Because of higher photocatalytic activity of Ag-Cu₂O/rGO and Ag-Cu₂O, we selected them for recycling degradation experiments of MO (32 mg/L). As can be seen in Fig. 8, Ag-Cu₂O/rGO maintains a high and stable photocatalytic activity even after three cycles. By contrast, the Ag-Cu₂O shows a significant reduction in its photocatalytic degradation activity, which is already decreased by 40% in the third cycling. Obviously, photocatalytic stability is remarkably enhanced due to introduction of rGO. To further study the stability of the Ag-Cu₂O/rGO composite, we collected it at the end of the recycling experiment and characterized it with XRD. The result indicates that the position and the ratio of peaks after the third recycle experiment are almost same to that of the fresh sample (Fig. S8), clearly indicating that the composite possesses higher stability and less photocorrosion during the photocatalytic reaction. One possible reason for the great improvement of the photocatalytic stability is that the photocorrosion of Ag-Cu₂O may be restrained due to the presence of rGO. Spherical Ag-Cu₂O composite is attached on rGO or encapsulated with rGO, which can greatly protect composite from dissolution and the structural changes. Furthermore, the presence of the rGO layer also slows the oxidation of Cu₂O.³⁴

In addition, we also evaluate the photocatalytic activity of the sample named as

15

Ag-rGO-Cu₂O with 8.4% rGO and 12% Ag content (Fig. S4b). In the case of the sample Ag-rGO-Cu₂O, more Ag nanoparticles are directly attached on rGO sheets rather than on the surface of Cu₂O in comparison to the sample Ag-Cu₂O/rGO composite. Obviously, the sample Ag-rGO-Cu₂O exhibits lower photocatalytic degradation than the resultant Ag-Cu₂O/rGO with the same rGO (8.4%) and Ag (12%) content (shown in Fig. S9). This demonstrates that the direct junction between Ag and Cu₂O in ternary composites (Ag-Cu₂O/rGO) is more favorable for promoting electron-hole pair separation and improving the photocatalytic activity than the junction between Ag and rGO (Ag-rGO-Cu₂O), which is further evidenced by the following PL spectra.

3.5 Photocatalytic mechanism for Ag-rGO/Cu₂O

There are many factors that influence photocatalytic activity. Firstly, as mentioned above, due to the band gap narrowing of the hybrid material, the Ag-Cu₂O/rGO photocatalyst is expected to achieve more efficient utilization of the solar spectrum and shows improved photocatalytic ability. Secondly, as is well known, photocatalysts with high specific surface areas and large pore volumes are helpful for the enhancement of photocatalytic performance because large surface area provides more surface sites for the adsorption of reactants molecules, which is a requisite for good photocatalytic activity.⁶⁰ We measured the surface areas of all the samples (Fig. S10), and the corresponding parameters including the BET surface areas and the pore size are listed in Table S1. Evidently, the corresponding pore size distribution curve calculated from desorption branch by the Barrett-Joyner-Halenda (BJH) method displays the formation of large mesopores and macropores for the samples Cu₂O, Cu₂O/rGO, Ag-Cu₂O, Ag-Cu₂O/rGO.⁶¹ The BET surface areas of Ag-Cu₂O/rGO (14.41 m² g⁻¹) and Ag-Cu₂O (13.25 m² g⁻¹) are higher than that of Cu₂O (8.80 m² g⁻¹) and Cu_2O/rGO (9.16 m² g⁻¹). A further observation shows that the BET surface areas of Cu₂O/rGO (9.16 m² g⁻¹) and Cu₂O (8.80 m² g⁻¹) are almost same. The same situation occurs for the Ag-Cu₂O/rGO and Ag-Cu₂O. Therefore, the contribution from graphene to the specific surface area is negligible, and the introduction of Ag

nanoparticles is an important contributing factor for achieving higher BET surface area, which is similar to findings of previous reports.⁵⁸ Moreover, it is found that the pore size of Ag-Cu₂O/rGO (18.3 nm) shows a slight decrease compared with that of Ag-Cu₂O (23.5 nm), which may be that the rGO blocked some mesopores and micropores.⁶² As displayed in Fig. S11, the amounts of MO adsorbed onto Ag-Cu₂O/rGO and Ag-Cu₂O after equilibrium in the dark for 40 min are about 51% and 42%, respectively, which are higher than those of Cu₂O/rGO and Cu₂O. Obviously, as-prepared Ag-Cu₂O/rGO and Ag-Cu₂O/rGO and

Beyond the above mentioned, in a photocatalysis process, efficient charge separation and transportation is of importance in improvement in the photoactivity.²⁸ The photoluminescence (PL) technique is an effective way to study the efficiency of charge carrier trapping, immigration and transfer. A lower PL intensity usually implies lower electron-hole recombination rate and higher photocatalytic activity.⁶³ Fig. 9 shows the measured PL emission spectra of the as-prepared structures at the excitation wavelength of 325 nm, which is higher than the band gap of Cu₂O. It is clearly observed that the as-prepared pure Cu₂O nanospheres display a strong PL intensity at around 650 cm⁻¹ (1.9 eV), which should be the near band emission of Cu₂O.⁶⁴ After the rGO is combined with the Cu₂O, the PL signal shows a apparent decrease, indicating that the recombination of the excitons in Cu₂O is efficiently hampered. In the case of Ag-Cu₂O/rGO, evidently PL intensity is further reduced compared to Cu₂O/rGO, suggesting that most of the photogenerated electrons are trapped by Ag and rGO, thereby resulting in the observed PL quenching. Moreover, it is noted that the PL intensity of Ag-Cu₂O/rGO is also lower than Ag-Cu₂O. Based on the above results, it is concluded that not only Ag but also rGO can capture the photoinduced electrons of Cu₂O to suppress the recombination of the hole-electron pairs and thereby the ternary Ag-Cu₂O/rGO show more effective charge separation due to the cooperative effect of Ag and rGO. In addition, it is also observed that the as-prepared Ag-Cu₂O exhibited a lower intensity than Cu₂O/rGO, indicating the higher charge separation in Ag-Cu₂O than Cu₂O/rGO. As displayed in Fig. 9, the PL

Journal of Materials Chemistry A

intensity follows an order: Ag-Cu₂O/rGO < Ag-Cu₂O < Cu₂O/rGO < Cu₂O, which is greatly consistent with the photocatalytic result.

In addition, Fig. S12 presents PL signal of the sample Ag-Cu₂O/rGO and Ag-rGO-Cu₂O with the same rGO content (8.4%) and Ag content (12%). It can clearly be seen that the PL intensity of the sample Ag-rGO-Cu₂O composites is higher than that of Ag-Cu₂O/rGO, demonstrating that charge separation in Ag-Cu₂O/rGO is more effective than Ag-rGO-Cu₂O. As a consequence, the Ag-Cu₂O/rGO composite exhibits a better photoactivity than the sample Ag-rGO-Cu₂O.

Based on the characterization and experimental data discussed above, we propose a possible photocatalysis mechanism for the spherical Ag-Cu₂O/rGO NCs, as illustrated in Fig. 10. As is well known, because the work function of Ag (4.26 eV) is lower than Cu₂O (~5.0 eV), the electrons will transfer from Ag to Cu₂O until the energy thermodynamic equilibrium level is established.^{12,65} This leads to an upward shift of the Cu₂O Fermi level and downward shift of Ag Fermi level. Under visible light irradiation, the electrons in the conduction band of Cu₂O can easily flow into Ag because the newly equilibrium lower Fermi level of metallic silver facilitated the migration of photo-excited electrons to the surface of Ag nanoparticles.⁶⁶ Therefore, the formation of heterostructured junctions between Ag and Cu₂O can effectively drive the separation and transportation of the electron-hole pairs. On the other hand, because the Fermi level of rGO (-4.42~4.48 eV)^{55,67} is below the potential of the conduction band of Cu₂O, it is possible that graphene also acts as an electronic acceptor. Thus both Ag and rGO could serve as acceptors of the photogenerated electrons from Cu₂O, as shown in Fig. 10. This efficient exciton separation could prolong recombination time of electron-hole pairs and leave more charge carriers to form reactive species. The photogenerated electrons with longer lifetime can be captured by O_2 to form superoxide anion radicals ($\cdot O_2^{-}$), in turn, the $\cdot O_2^{-}$ further reacts with H_2O to produce hydrogen peroxide (H_2O_2) and hydroxyl radical ('OH), which are strong oxidizing agents to decompose the organic dye.64,68 Meanwhile, the photogenerated holes accumulated in the valence band (about 1.92 eV vs NHE) of Cu₂O are also available to directly oxidize the pollutants (MO about 1.48 eV vs

NHE).^{18,68,69} As the decomposition of dyes, the adsorption equilibrium broke and more MO molecules would be decomposed into CO₂, H₂O through a series of redox reactions. As a result of minimal recombination of photogenerated charges, the ternary Ag-Cu₂O/rGO exhibited obviously enhanced photicatalytic activity. It is worth noting that rGO plays two roles in the composite. First, rGO acts as an acceptor of the photogenerated electrons from Cu₂O and thus enhances the photoactivity. At the same time, rGO could play another role as a stabilizer, which can protect Cu₂O-Ag composite from dissolution and the structural changes, and thereby improving the stability of the photocatalyst.⁵⁰

However, in the case of sample Ag-rGO-Cu₂O system, probably due to the work function of Ag lower than rGO, the electrons captured by rGO could not move to Ag nanoparticles in contact with rGO,^{67,70} thus causing a decrease in the light harvesting efficiency of Cu₂O. Thereby, sample Ag-rGO-Cu₂O exhibited a relatively strong PL intensity compared to Ag-Cu₂O/rGO under the same experimental conditions. This demonstrates that the direct junction between Ag and Cu₂O facilitates more efficient charge separation, and results in a better photocatalytic performance under visible light illumination.

4 Conclusions

In this work, we obtain an excellent composite structure of rGO-supported spherical Ag-Cu₂O nanohybrids via a simple one-pot, two-step reduction synthetic route at room temperature, which possesses extended light absorption range, good adsorption capacity and the minimal recombination of photogenerated charges. More importantly, the resultant Ag-Cu₂O/rGO composites show a superior stability according to the cycling tests, mainly due to introduction of rGO into Ag-Cu₂O system. Notably, it is found based on the experimental data that the direct junction between Ag and Cu₂O in the ternary Ag-Cu₂O/rGO is more favorable for charge transportation than the direct contact between Ag and rGO, thus resulting higher photocatalytic activity of Ag-Cu₂O/rGO than that of Ag-rGO-Cu₂O. This work provides new ideas for constructing highly efficient and stable supported Cu₂O based catalysts for practical

applications.

Supporting Information

Schematic graph of the formation process of Ag-Cu₂O/rGO, further characterization of the different samples, the curves of adsorption and photodegradation of MO under visible light irradiation at 25°C with different catalysts: Cu₂O, Cu₂O/rGO, Ag-Cu₂O and Ag-Cu₂O/rGO (G3-1.8), respectively; the BET surface area, pore volume, average pore size and band gap energy of Cu₂O, Cu₂O/rGO, Ag-Cu₂O and Ag-Cu₂O/rGO. This material is available free of charge via the Internet at http://pubs.rsc.org.

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References

(a) B. Li, T. Liu, L. Hu and Y. Wang, J. Phys. Chem. Solids, 2013, 74, 635-640; (b)
 S. Ahmed, M. G. Rasul, R. Brown and M. A. Hashib, J. Environ. Manage., 2011, 92, 311-330.

2 H. Wang, Y. Hu, Y. Jiang, L. Qiu, H. Wu, B. Guo, Y. Shen, Y. Wang, L. Zhu and A. Xie, *Dalton Trans.*, 2013, **42**, 4915-4921.

3 Y. Yu, L. Zhang, J. Wang, Z. Yang, M. Long, N. Hu and Y. Zhang, *Nanoscale Res. Lett.*, 2012, **7**, 347.

4 H. A. N. Dharmagunawardhane, W. R. Woerner, Q. Wu, H. Huang, X. Chen, A. Orlov, P. G. Khalifah and J. B. Parise, *J. Mater. Chem. A*, 2014, **2**, 19247-19252.

5 H. Yang, J. Ouyang, A. Tang, Y. Xiao, X. Li, X. Dong and Y. Yu, *Mater. Res. Bull.*, 2006, **41**, 1310-1318.

6 M. D. Susman, Y. Feldman, A. Vaskevich and I. Rubinstein, ACS Nano, 2014, 8, 162-174.

7 Z. Wang, H. Wang, L. Wang and L. Pan, J. Phys. Chem. Solids, 2009, 70, 719-722.

8 C. H. Kuo, C. H. Chen and M. H. Huang, Adv. Funct. Mater., 2007, 17, 3773-3780.

9 S. Sun, X. Zhang, X. Song, S. Liang, L. Wang and Z. Yang, *CrystEngComm*, 2012, 14, 3545.

10 Y. Zhang, B. Deng, T. Zhang, D. Gao and A. W. Xu, J. Phys. Chem. C, 2010, **114**, 5073-5079.

11 B. Zhou, Z. Liu, H. Wang, Y. Yang and W. Su, Catal. Lett., 2009, 132, 75-80.

12 Z. Wang, S. Zhao, S. Zhu, Y. Sun and M. Fang, CrystEngComm, 2011, 13, 2262.

13 D. Jiang, W. Zhou, X. Zhong, Y. Zhang and X. Li, ACS Appl. Mater. Interfaces, 2014, 6, 10958-10962.

14 J. Xiong, Z. Li, J. Chen, S. Zhang, L. Wang and S. Dou, ACS Appl. Mater. Interfaces, 2014, 6, 15716-15725.

15 X. Lin, R. Zhou, J. Zhang and S. Fei, Appl. Surf. Sci., 2009, 256, 889-893.

16 A. Wang, X. Li, Y. Zhao, W. Wu, J. Chen and H. Meng, *Powder Technol.*, 2014, 261, 42-48.

17 M. Wang, J. Huang, Z. Tong, W. Li and J. Chen, J. Alloys Compd., 2013, 568, 26-35.

18 X. Hu, X. Zhou, R. Wang, C. Hu and J. Qu, *Appl. Catal. B: Environ*, 2014, **154-155**, 44-50.

19 X. Z. Li and F. B. Li, Environ. Sci. Technol., 2001, 35, 2381-2387.

20 F. Yan, Y. Wang, J. Zhang, Z. Lin, J. Zheng, F. Huang, *ChemSusChem*, 2014, 7, 101-104.

21 H. Zhu, M. Du, D. Yu, Y. Wang, L. Wang, M. Zou, M. Zhang and Y. Fu, *J. Mater. Chem. A*, 2013, **1**, 919.

22 M. A. Mahmoud, W. Qian and M. A. El-Sayed, Nano Lett., 2011, 11, 3285-3289.

23 N. Meir, I. Jen-La Plante, K. Flomin, E. Chockler, B. Moshofsky, M. Diab, M. Volokh and T. Mokari, *J. Mater. Chem. A*, 2013, **1**, 1763.

24 W.-C. Wang, L.-M. Lyu and M. H. Huang, Chem. Mater., 2011, 23, 2677-2684.

25 (a) L. Kong, W. Chen, D. Ma, Y. Yang, S. Liu and S. Huang, *J. Mater. Chem.*, 2012,
22, 719; (b) C. H. Kuo, Y. C. Yang, S. Gwo and M. H. Huang, *J. Am. Chem. Soc.*,
2011, 133, 1052-1057.

26 T. Y. Zhang, X. Q. Li, S. Z. Kang, L. X. Qin, G. D. Li and J. Mu, *J. Mater. Chem. A*, 2014, **2**, 2952.

27 C. Hong, X. Jin, J. Totleben, J. Lohrman, E. Harak, B. Subramaniam, R. V. Chaudhari and S. Ren, *J. Mater. Chem. A*, 2014, **2**, 7147.

28 Y. Qu and X. Duan, Chem. Soc. Rev., 2013, 42, 2568-2580.

- 29 H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu and X. Wang, *Chem. Soc. Rev.*, 2014, **43**, 5234-5244.
- 30 X. An and J. C. Yu, RSC Adv., 2011, 1, 1426.
- 31 J. Wang, S. Liang, L. Ma, S. Ding, X. Yu, L. Zhou and Q. Wang, *CrystEngComm*, 2014, **16**, 399.
- 32 Q. Xiang, J. Yu and M. Jaroniec, Chem. Soc. Rev., 2012, 41, 782-796.

33 (a) C. Xu, X. Wang, L. Yang and Y. Wu, J. Solid State Chem., 2009, 182, 2486-2490; (b) G. Zhou, D.-W. Wang, F. Li, L. Zhang, N. Li, Z.-S. Wu, L. Wen, G. Q. Lu and H.-M. Cheng, Chem. Mater., 2010, 22, 5306-5313.

- 34 X. An, K. Li and J. Tang, ChemSusChem, 2014, 7, 1086-1093.
- 35 W. Gao, M. Wang, C. Ran, X. Yao, H. Yang, J. Liu, D. He and J. Bai, *Nanoscale*, 2014, **6**, 5498-5508.
- 36 Y. Wang, J. Yu, W. Xiao and Q. Li, J. Mater. Chem. A, 2014, 2, 3847.
- 37 S. Sarkar and D. Basak, CrystEngComm, 2013, 15, 7606.
- 38 L. Zhang, L. Du, X. Yu, S. Tan, X. Cai, P. Yang, Y. Gu and W. Mai, *ACS Appl. Mater. Interfaces*, 2014, **6**, 3623-3629.
- 39 T. Liang, W. Guo, Y. Yan and C. Tang, Int. J. Adhes. Adhes., 2007, 28, 55-58.
- 40 S. Xu, S. Sun, G. Chen and X. Song, J. Cryst. Growth, 2009, 311, 2742-2745.
- 41 Y. Feng, N. Feng, G. Zhang and G. Du, CrystEngComm, 2014, 16, 214.

42 B. Li, H. Cao, G. Yin, Y. Lu and J. Yin, J. Mater. Chem. 2011, 21, 10645.

- 43 Z. Gao, J. Liu, F. Xu, D. Wu, Z. Wu and K. Jiang, *Solid State Sci.*, 2012, **14**, 276-280.
- 44 S. Deng, V. Tjoa, H. M. Fan, H. R. Tan, D. C. Sayle, M. Olivo, S. Mhaisalkar, J. Wei and C. H. Sow, *J. Am. Chem. Soc.*, 2012, **134**, 4905-4917.
- 45 J. Li and C.-y. Liu, Eur. J. Inorg. Chem., 2010, 2010, 1244-1248.

46 K. Krishnamoorthy, G. S. Kim and S. J. Kim, *Ultrason. Sonochem.*, 2013, 20, 644-649.

47 L. Yang, J. Lv, Y. Sui, W. Fu, X. Zhou, J. Ma, S. Su, W. Zhang, P. Lv, D. Wu, Y. Mu and H. Yang, *CrystEngComm*, 2014, **16**, 2298.

48 Y. Ping, J. Yan, Z. Wang, H. Wang and Q. Jiang, J. Mater. Chem. A, 2013, 1, 12188.

49 J. Zhou, G. Tian, Y. Chen, X. Meng, Y. Shi, X. Cao, K. Pan and H. Fu, *Chem. Commun.*, 2013, **49**, 2237.

50 (a) Y. Chen, G. Tian, Z. Ren, K. Pan, Y. Shi, J. Wang and H. Fu, *ACS Appl. Mater*. *Interfaces*, 2014, **6**, 13841; (b) X. Cao, G. Tian, Y. Chen, J. Zhou, W. Zhou, C. Tian and H. Fu, *J. Mater. Chem. A*, 2014, **2**, 4366.

51 G. Wang, X. Shen, J. Yao and J. Park, Carbon, 2009, 47, 2049-2053.

52 K. Chen and D. Xue, CrystEngComm, 2013, 15, 1739.

53 R. Li, X. Yan, L. Yu, Z. Zhang, Q. Tang and Y. Pan, *CrystEngComm*, 2013, 15, 10049.

54 Z. Wang, Y. Liu, B. Huang, Y. Dai, Z. Lou, G. Wang, X. Zhang and X. Qin, *Phys. Chem. Chem. Phys.*, 2014, **16**, 2758-2574.

55 S. K. Bhunia and N. R. Jana, ACS Appl. Mater. Interfaces, 2014, 6, 20085.

56 W. Lu, S. Gao and J. Wang, J. Phys. Chem. C, 2008, 112, 16792-16800.

57 Z. Chen, N. Zhang and Y.-J. Xu, CrystEngComm, 2013, 15, 3022.

58 W. Zhang, X. Yang, Q. Zhu, K. Wang, J. Lu, M. Chen and Z. Yang, *Ind. Eng. Chem. Res.*, 2014, **53**, 16316-16323.

59 S.K. Li, F.Z. Huang, Y. Wang, Y.H. Shen, L.G. Qiu, A.J. Xie and S.J. Xu, *J. Mater. Chem.*, 2011, **21**, 7459.

60 H. Zhang, X. Lv, Y. Li, Y. Wang and J. Li, ACS Nano, 2010, 4, 380-386.

61 J. Yu and J. Ran, Energy Environ. Sci., 2011, 4, 1364.

62 S. Han, L. Hu, Z. Liang, S. Wageh, A. A. Al-Ghamdi, Y. Chen and X. Fang, *Adv. Funct. Mater.*, 2014, **24**, 5719-5727.

63 L. Jing, Y. Qu, B. Wang, S. Li, B. Jiang, L. Yang, W. Fu, H. Fu and J. Sun, *Sol. Energ. Mat. Sol. C.*, 2006, **90**, 1773-1787.

64 Y. Wang, S. Li, H. Shi and K. Yu, Nanoscale, 2012, 4, 7817-7824.

65 (a) S. Lee, C. Liang and L. W. Martin, *ACS Nano*, 2011, 5, 3736-3743; (b) T. Minami, H. Tanaka, T. Shimakawa, T. Miyata and H. Sato, *Jpn. J. Appl. Phys.*, 2004, 43, 917-919.

- 66 Q. Li, C. Zhang, J. Ma, G. Wang and D. H. L. Ng, *ChemCatChem*, 2014, 6, 1392-1400.
- 67 J. Zhang, Z. Xiong and X. S. Zhao, J. Mater. Chem., 2011, 21, 3634.
- 68 G. He, M. Qian, X. Sun, Q. Chen, X. Wang and H. Chen, *Powder Technol.*, 2013, **246**, 278-283.
- 69 S. C. Yan, Z. S. Li and Z. G. Zou, Langmuir, 2010, 26, 3894-3901.
- 70 Y. Chen, Y. Tang, S. Luo, C. Liu and Y. Li, J. Alloys Compd., 2013, 578, 242-248.



Fig. 1 X-Ray diffraction patterns of (a) GO, (b) Cu₂O, (c) Ag-Cu₂O and (d)Ag-Cu₂O/rGO



Fig. 2 (A) FTIR spectra of (a) GO and (b) Ag-Cu₂O/rGO, (B) The Raman spectra of (a) GO and (b) Ag-Cu₂O/rGO.



Fig. 3 (a) and (b) TEM images of the resultant Ag-Cu₂O/rGO, (c) and (d) SEM images of Ag-Cu₂O/rGO.



Fig. 4 (a) TEM image of the obtained Ag-Cu₂O/rGO composites; (b) and (c) HRTEM images of Ag and Cu₂O taken from the Ag-Cu₂O/rGO composites, respectively.



Fig. 5 (a) Representative SEM image of the Ag-Cu₂O/rGO NCs, (b-e) EDAX mapping of the hybrids using O Ka, Cu Ka, Ag La and C Ka.



Fig. 6 (a) UV-vis diffuse reflectance adsorption spectra of pure Cu₂O, Cu₂O/rGO, Ag-Cu₂O and Ag-Cu₂O/rGO (G3-1.8); (b) plots of $(\alpha hv)^2$ vs. photon energy (hv).



Fig. 7 Photocatalytic degradation of MO (40 mg/L) under visible light irradiation at 25° C with different catalysts: (a) Ag-Cu₂O/rGO: 6.4Ag-S1, 12Ag-S2 and 17Ag-S. (b) Ag-Cu₂O/rGO: G1-0.45, G2-0.9, G3-1.8, G4-5.4 and G5-8.4. (c) Absorption spectrum of MO with irradiation time in presence of Ag-Cu₂O/rGO (G3-1.8). (d) Photocatalytic degradation of MO with Cu₂O, Cu₂O/rGO, Ag-Cu₂O and Ag-Cu₂O/rGO (G3-1.8).



Fig. 8 The curves of adsorption and photodegradation of MO by the Ag-Cu₂O and Ag-Cu₂O/rGO (G3-1.8), respectively.



Fig. 9 PL spectra of Cu₂O, Cu₂O/rGO, Ag-Cu₂O and Ag-Cu₂O/rGO (G3-1.8) nanoparticles with the excitation wavelength of 325 nm



Fig. 10 (A) Band diagram analysis of (a) individual Cu_2O and Ag, (b) Cu_2O and Ag in contact, and (c) Cu_2O , Ag and rGO in contact under visible light irradiation. All these values are for standard conditions, under the experimental conditions these values may vary slightly. (B) Proposed mechanism for the photocatalytic degradation of MO over Ag-Cu₂O/rGO nanocomposite under visible light irradiation.