Synthesis of GO-modified Cu₂O nanosphere and the photocatalytic mechanism of water splitting for hydrogen production

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Abstract: A new one-step method for synthesizing cuprous oxide nanosphere without any additive surfactant in room temperature and atmospheric pressure was carried. The nanospheres with the diameters less than 100 nm were well-dispersed and formed the core-shell structure with the GO. The partial reduction of GO increases the atomic percentage of sp² carbon (graphene sheets). It was found that sp² carbon with better conductivity plays an important role in mitigating electron-hole recombination and enhancing electron transfer between Cu₂O and GO and thus enhance the photocatalytic activity. The highest hydrogen yields for GO-modified samples (118.3 μmol) were more than twice as large as that of bare Cu₂O nanosphere (44.6 μmol).

Key words: Cu₂O nanosphere, graphene oxide, photocatalyst, hydrogen, water splitting

1 Introduction

Solar energy has been caught much attention for global researchers because it is renewable, carbon-free and the largest source available among all the developing renewable energy sources [1]. The common way of utilizing solar energy is to convert it into electricity by photo-voltaic cells [2], while the other routine is to convert it into chemical energy, such as hydrogen [3], methanol [4], or carbon monoxide [5], directly by photocatalysts. Since the first photocatalyst, TiO₂, used for hydrogen production during the water splitting reaction was reported at 1972 [6], TiO₂ has been explored as a stable, efficient and nontoxic photocatalyst or support. However, its large band gap (3.2 eV) has constrained its further utilization as the commercial catalyst for photocatalytic hydrogen production.

The p-type semiconductor cuprous oxide (Cu₂O) with a direct band gaps of 1.9~2.2 eV [7-9] is a kind of widely-used photocatalyst for pollutant degradation [9-13], carbon dioxide reduction [5, 14-17] and water splitting for hydrogen production [2, 8, 18-21]. Its narrower band gap, higher visible light absorption and better electron-hole separation suggests it can be a more potential photocatalyst than TiO₂ [17, 21]. For further research in the morphology, Cu₂O sphere has larger specific surface area and higher photocatalytic performance than those of Cu₂O cubic or bulk [22-24]. Many reported methods to form Cu₂O spheres need various kinds of surfactant, such as Polyvinyl Pyrrolidone (PVP) and Cetyltrimethyl Ammonium Bromide (CTAB) during hydrothermal [2, 15, 25] or solvothermal treatment [11, 26]. Uniform shapes would be obtained in these methods, however, expensive surfactants and extended period would also be cost. Besides, all shapes of Cu₂O can be easily oxidized to CuO or other compounds and lost the ability to produce hydrogen. Thus, modified surface of Cu₂O and improved synthetic methods are needed.

Graphene oxide (GO) has been proved as the potential carbonaceous solid support or cocatalyst [2, 8, 18, 19, 27] to enhance the photocatalytic activities of Cu₂O. Graphene oxide (GO) is derived from extensive oxidation of graphite in chemical oxidation methods. The sheets of GO can be easily dispersed or exfoliated in aqueous solution because they contain hydrophilic oxygen functional groups on

constituting graphene sheets.[28] The photoelectronic properties of GO are related to the composition of oxygen bonding on graphene sheets and these sheets were able to grow on the surface of Cu₂O due to some oxygen composition. So the photoelectrons can be easily transfer from Cu₂O to GO sheets [29] and reduced electron-hole recombination by constructing heterojunctions [1].

Some similar works on Cu₂O/RGO photocatalysts for hydrogen production have been reported [30-32]. It was found that Cu₂O on RGO sheet can promote the separation of electrons and holes pairs by efficiently trapping the accumulated electrons [30]. The graphene sheets was utilized as an electron acceptor and formed a p-n junction with Cu₂O [31]. And it plays an important role in synergistically absorbing visible light, suppressing the charge recombination and enhancing the crystallinity [32]. However, the synergistic effect and the photocatalytic mechanism of GO-modified Cu₂O nanospheres have not be clearly discussed.

In this paper, a one-step method for synthesise cuprous oxide nanosphere without any additive surfactant in room temperature and atmospheric pressure was proved to be an effective and low-cost method. The diameter of the nanosphere was less than 100 nm. In order to investigate the structure of GO-modified Cu₂O nanospheres synthesized in this method and the photocatalytic mechanism, XRD, Raman spectra, XPS, SEM, UV-Vis and PL were carried. It was found out that the GO sheets were well-dispersed and formed the core-shell structure with Cu₂O nanospheres. The positive conduction band edge potentials of all GO-modified sample were turning to negative potential region during irradiation, which is attributed to the partial reduction of GO sheets. Further research found that the increased atomic percentage of sp² carbon (graphene sheets) with better conductivity plays an important role in mitigating electron-hole recombination and enhancing electron transfer between Cu₂O and GO, which leads to the enhancement of photocatalytic activity. The highest hydrogen yields for GO-modified samples (118.3 μmol) were more than twice as large as that of bare Cu₂O nanosphere (44.6 μmol).

2 Experimental

2.1 Preparation of graphene oxide (GO)

GO was prepared using a modified Hummers method from graphite powders.[25, 33, 34] 0.5 g of graphite, 0.5 g of NaNO₃, and 23 mL of concentrated H₂SO₄ were stirred together in an ice water bath. Then, 3 g of KMnO₄ was added into the above mixture under 0 °C. The solution was the stirred for about 1.5 hours at 35 °C. After the main reaction was completed, 40 mL of deionized water was slowly dropped into the above solution while the temperature was raised to 90 °C. After stirring for 30 minutes, another 10 mL H₂O₂ and 40 mL of deionized water was dropped in, respectively, and the color of the mixture changed from brown to yellow. Then the mixture was centrifuged at 6000 rpm for 10 min. Then the obtained yellow transparent liquid was filtered by a microporous barrier filter, and the solid was washed repeatedly using 5% HCl solution until the sulfate could not be detected in the solution through standard barium chloride precipitation test. The above product was sequentially washed using distilled water until the pH value of washed water was approximated to 7. Finally, the solid GO was supersonic dispersed in deionized water.

2.2 Preparation of GO-modified Cu₂O nanosphere

The GO-modified Cu₂O nanosphere was synthesized under room temperature by using hydrazine hydrate as the reductive agent. 0.3 g of cupric citrate and 150 ml of deionized water were stirred for 15 minutes. Then GO dispersion was added to the above mixture and kept stirring for 2 hours. Then 1.43 ml of hydrazine hydrate (80 vol.%) was diluted to 100 ml aqueous solution and then slowly dropped to

above mixture and kept stirring for 40 minutes. Finally, after filtration, washing and vacuum drying, the dark green powder was prepared. The GO-modified samples with 0.1 wt.%, 0.5 wt.% and 1 wt.% of GO addition were denoted as GO/Cu₂O-0.1, GO/Cu₂O-0.5 and GO/Cu₂O-1, respectively. The bare Cu₂O nanosphere (denoted as Cu₂O-NS) was prepared without GO addition and the RGO synthesized for comparison was prepared without cupric citrate addition. In this method, no surfactant was added and the formation of nanosphere shape may be attributed to the clathration of Cu²⁺ and citrate.

Figure 1. Preparation of Cu₂O nanospheres and the GO-modified samples.

2.3 Characterization

X-ray diffraction (XRD) analysis was performed with the PANalytical X'Pert diffractometer (X'Pert PRO MPD, PW3040/60) within the 2-θ ranged from 5° to 80° by a speed of 6° per minute with Cu-Kα ($\lambda = 0.154060$ nm) radiation (40 kV, 40 mA). The crystallite size was calculated by the Scherrer equation from the XRD spectra. UV-vis spectroscopy in the 300 nm-800 nm was measured with a Lambda 750 Diffuse Reflectance Spectroscopy. X-Ray photoelectron spectroscopy (XPS) analysis were conducted through a thermo ESCALAB 250XI multifunctional imaging electron spectrometer (Thermo Fisher Scientific Inc.) equipped with an Al K radiation source. UV-vis spectroscopy in the region of 300 nm-800 nm was measured with a Lambda 750 Diffuse Reflectance Spectroscopy. Fluorescence spectra were obtained using a photoluminescence (PL) spectrometer (Perkin Elmer, LS-55). The concentration of methanol and ethanol were detected by a gas chromatograph (GC-7890II), equipped a flame ionization detector and a stainless steel packed column (PorapakQ, 2 mm×1 m).

2.4 Photocatalytic reaction testing

Photocatalytic reactions for overall water splitting were carried out in a 15 mL quartz cell with a 25 mm×25 mm window for light transmission at room temperature under visible light irradiation ($\lambda > 400$ nm, ≈ 0.1 W/cm²). The catalyst powder (30 mg) was suspended in 10 vol. % methanol aqueous solution (15 mL) by magnetic stirring. In this paper, methanol plays a role as the sacrifice agent to scavenge photo-generated holes. The evolved gases were determined with a gas chromatograph equipped with a TCD detector.

3 Results and Discussion

3.1 Characterization of GO/Cu₂O

Figure 2. XRD patterns (A) of Cu_2O -NS and the GO-modified samples and Raman patterns (B) of GO and the GO-modified samples

The XRD patterns of Cu_2O -NS and the GO-modified samples are shown in Figure 2(A). Five strong peaks belong to cubic phase of Cu_2O (Reference code: 03-065-3288) are corresponding respectively to (110), (111), (200), (220) and (311) planes. It indicates the crystallization of Cu_2O -NS did not restrain by the strong reducibility of hydrazine. However, the XRD patterns of the GO-modified samples are much more complicated, because not only Cu_2O and CuO peaks were detected, but also many indistinguishable peaks were found from 10 to 30 degree. It may be attributed to the groups on the surface of graphene oxide and some other copper compound. Among the XRD patterns of the GO-modified samples, no graphite peaks (26.6° , 002) and metal copper peaks (43.38° , 111; 50.50° , 200)[35] are observed, and the weak peaks at around $2\theta=10.6^\circ$ corresponds to the reflection (001) plane of GO[25].

Figure 2(B) shows two characteristic bands arising from GO and the GO-modified samples. The D band ($\sim 1350\text{ cm}^{-1}$) and the G band ($\sim 1590\text{ cm}^{-1}$), identical to the bare GO nano-sheets. The D band results from disorder in the symmetrical hexagonal graphitic lattice, while the G band originates from the in-plane stretching motion of symmetric sp^2 C-C bonds.[25] The intensity of D and G bands for GO-modified samples are weak because of the small amount of GO addition. The D/G intensity ratios for GO, GO/ Cu_2O -0.1, GO/ Cu_2O -0.5 and GO/ Cu_2O -1 are 0.98, 0.93, 1.05 and 1.17, respectively. The ratios for the GO-modified samples are close to that of GO, it suggests that little of the doped GO are reduced. The ratios for GO/ Cu_2O -0.5 and GO/ Cu_2O -1 are slightly larger than that of GO. It indicates the GO were partly reduced to graphene or some other carbon species [36]. The D/G intensity ratio increases with the increasing of the GO addition, which may be attributed to the formation of GO shell and Cu_2O core structure because the GO shell will prevent further reduction of Cu_2O core and then consume larger part of hydrazine during synthesis. The cover of GO also results in the incomplete reduction of Cu (II) and forms CuO for all the GO-modified samples.

Table 1-Texture properties of Cu_2O nanosphere and the GO-modified samples.

Sample	BET surface area (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3g^{-1})	The crystallite size of Cu_2O (nm)
Cu_2O -NS	23.8	6.22	0.16	7.22
GO/ Cu_2O -0.1	14.1	3.45	0.08	9.93
GO/ Cu_2O -0.5	19.3	3.07	0.11	22.71
GO/ Cu_2O -1	14.2	3.06	0.08	19.87

Figure 3. Pore size distribution curve (A) and nitrogen adsorption isotherms (B) of Cu₂O nanosphere and the GO-modified samples.

Table 3 shows the texture properties of Cu₂O nanosphere and the GO-modified samples, including BET surface area, average pore diameter, total pore volume and the crystallite sizes of Cu₂O calculated by Debye-Scherrer equation. After doping GO, the BET surface areas, average pore diameter and total pore volume decrease sharply while the crystallite size of Cu₂O increase from 7.22 to 22.71 nm. The groups on the surface of GO sheets may obstruct the clathration of Cu²⁺ and citrate, which leads to agglomeration of copper oxides particles and cover of mesoporous. However, the pore size distribution curve (Figure 3 (A)) shows that the pore distribution of mesoporous were similar, and both of the order of the mesoporous amounts (dV(logd) value) and the order of nitrogen adsorption volumes (Figure 3 (B)) were Cu₂O-NS > GO/Cu₂O-0.5 > GO/Cu₂O-0.1 > GO/Cu₂O-1. The mesoporous amounts and nitrogen absorption volumes of the GO-modified samples were less than those of Cu₂O-NS, which indicates that GO was cover on the surface of Cu₂O nanospheres and it might be formed a kind of core-shell structure. Besides, GO/Cu₂O-0.5 has the largest surface area and total pore volume and the smallest average pore diameter among all GO-modified samples, and its expected photocatalytic activity might be the best of all.

Figure 4. SEM images of Cu_2O nanosphere (a), $\text{GO/Cu}_2\text{O}$ -0.1 (b), $\text{GO/Cu}_2\text{O}$ -0.5 (c) and $\text{GO/Cu}_2\text{O}$ -1 (d), along with the TEM image of $\text{GO/Cu}_2\text{O}$ -0.5 (e).

The SEM images of the nanosphere-shapes for all the samples are shown in Figure 4(a-d). The particle diameter of Cu_2O nanospheres (Figure 4(a)) is under 100 nm and the nanospheres are aggregated into clusters in order to minimize the surface energy. The aggregation was occurred during the reduction reaction of Cu^{2+} and hydrazine. However, for the GO-modified samples, the sizes and the dispersity of nanospheres increase with the increasing of the additive amount of GO, which indicates hydrophilic oxygen functional groups on the surface of GO sheets [28] play a role in the formation of larger and dispersive nanospheres. These groups provide the sites for the growth and separation of newly formed Cu_2O nanospheres by the aggregating the reactant, like Cu^{2+} , OH^- , hydrazine and etc. So too much of these groups leads to excessive aggregation of the ions and excessive growth of nanospheres, and thus the diameters increase from less than 100 nm (Figure 4(a)) to around 200 nm (Figure 4(d)) and the particle size of Cu_2O was too big to be covered by GO sheets. On the contrary, too little of these groups makes clusters or excessively aggregated particles as $\text{GO/Cu}_2\text{O}$ -0.1 (Figure 4(b)) and the bare Cu_2O nanospheres because of the unrestraint of growing positions. 0.5 wt.% of GO addition may be a proper amount which can lead to the formation of core-shell structure, like $\text{Cu}_2\text{O}@GO$ (Figure 4(c)) and it was further revealed through TEM (Figure 4(e)). The Cu_2O cores with the diameter at around 30 nm were covered by and effectively linked through the GO nano-sheets. The GO shell exhibited wrinkled and rough texture due to the flexible and extremely thin nature of the GO nano-sheets [25, 37]. These large wrinkled GO sheets covering numerous small Cu_2O cores may enhance the separation and transfer of charges.

In order to investigate the species on the surface of Cu_2O that enhance the visible light absorption, atomic

compositions analysis from the Cu 2p, O 1s and C 1s spectra were performed (Table 2). Atomic compositions of Cu (I) and O-Cu for Cu₂O-NS have the stoichiometric ratio approximates to 2:1 and neither metal copper nor Cu (II) was detected, which means the additive amount of hydrazine is appropriate for the reduction. However, for all GO-modified samples, the formation of Cu (II) may be attributed to 1) GO sheets cover the particles of Cu oxides and prevent the further reduction for CuO particle or 2) GO/GO has higher oxidation-reduction potential than Cu⁺/Cu²⁺, which leads to easier reduction of GO sheets than Cu²⁺. Further discussion is performed in section 3.2. Neither amounts of Cu (I) nor amounts of Cu (II) sharply decreased with the increasing of GO addition, which suggests that GO was formed on the surface rather than being mixed with the lattices of copper oxides. Meanwhile, both the atomic amount of sp² and sp³ carbon for GO/Cu₂O-0.5 were the largest among all, which suggests that GO sheets covered the larger surface area for GO/Cu₂O-0.5 than that of GO/Cu₂O-0.1 or GO/Cu₂O-1 and the core-shell structure was possibly formed on the surface of GO/Cu₂O-0.5. This result is in line with the sharp peaks on the XRD patterns and nanosphere-structure of SEM images. Beside, a large amount of oxygen-carbon compositions (O-C, O=C, C-O and O-C=O) were detected on the GO-modified samples while no such compositions were detected on Cu₂O-NS, which indicates the oxygen-carbon compositions come from the groups on the surface of GO.

Table 2- Atomic compositions (%) measured for the chemical species from the Cu 2p, O 1s and C 1s spectra.

Species Samples	Cu (I)	Cu (II)	O			C			
			O-Cu	O-C	O=C	C sp ²	C sp ³	C-O	O-C=O
Cu ₂ O-NS	72.96	0	27.04	0	0	0	0	0	0
GO/Cu ₂ O-0.1	23.4	9.26	19.8	1.06	1.4	7.03	4.7	4.88	28.47
GO/Cu ₂ O-0.5	10	7.44	12.44	14.46	2.87	10.22	11.84	8.01	22.72
GO/Cu ₂ O-1	9.55	4.9	9.36	25.69	7.74	6.59	6.99	9.84	19.34

Figure 5. UV-vis absorption spectra of Cu₂O nanosphere and the GO-modified samples.

The GO can distinctly change the absorption region of Cu₂O nanosphere as showed in Figure 5. The doping of GO on the surface Cu₂O nanosphere can slightly reduce the visible light absorption (400-500 nm) because of the reflection of GO sheets. The spectrum of GO in the visible light region is flat (around

0.6 a.u.) and the absorbances are much lower than those of the GO-modified samples. The red shift of the absorbance for the GO-modified samples were increasing obviously with the increasing of GO doping, which indicates the sample can enlarge the region of visible light absorption. It may be attributed to the easier transfer of electrons between Cu₂O and GO than on Cu₂O surfaces under irradiation instead of the enhancement of light absorption caused by GO addition.

Band gap, conduction band edge and valence band edge are three important parameters for semiconductor photocatalysts, and they can be calculation form the UV-vis absorption spectra. The values of band gaps for Cu₂O nanosphere and the GO-modified samples are estimated from the plot of the $(\alpha h\nu)^2$ versus photon energy ($h\nu$) [4, 38] as shown in Table 3. The band gap of Cu₂O-NS was estimated to be 1.90 eV, which was in the reported band gap region of Cu₂O (1.9~2.2 eV) [7, 8]. The band gaps of the GO-modified samples was narrowed from 1.02 eV to 0.52 eV with the increasing of GO addition. In order to investigate the band edges of Cu₂O nanosphere and the GO-modified samples, two widely-used equations for band edge calculation are showed below:

$$E_{CB} = \chi - E_c - \frac{1}{2}E_g \quad (\text{Equation 1})$$

$$E_{VB} = E_g + E_{CB} \quad (\text{Equation 2})$$

E_{CB} is the conduction band edge of a semiconductor at the point of zero charge. χ is the absolute electronegativity[39] of the semiconductor, expressed as the geometric mean of the absolute electronegativity of the constituent atoms, which is defined as the arithmetic mean of the atomic electron affinity and the first ionization energy. E_c is the energy of free electrons on the hydrogen scale (~4.5 eV). E_g is the band gap of the semiconductor [4, 38]. χ values for Cu₂O-NS, GO/Cu₂O-0.1, GO/Cu₂O-0.5 and GO/Cu₂O-1, which were calculated according to the measured atomic compositions (Table 2), are 5.16, 5.85, 6.25 and 6.46. Their conduction band edges and valence band edges were also shown in Table 3. The conduction and valence band edge of the Cu₂O nanosphere are -0.29 eV and 1.61 eV, which are approximated to the experimental and theoretical[40] results. Although the band gaps of all samples are avail to absorb visible light, the potentials of conduction band edges of the GO-modified samples are too positive to reduce H⁺, which suggests that GO-modified samples are not fit for catalyzing the water splitting reaction and their original structures must be change during irradiation.

Table 3-Band gaps, conduction band edges and valence band edges of Cu₂O- NS and the GO-modified samples.

Sample	Band gaps (eV)	Conduction band edge (eV)	Valence band edge (eV)
Cu ₂ O-NS	1.90	-0.29	+1.61
GO/Cu ₂ O-0.1	1.47	+0.62	+2.09
GO/Cu ₂ O-0.5	1.38	+1.06	+2.44
GO/Cu ₂ O-1	1.26	+1.33	+2.59
Cu ₂ O (theoretical, [40])	2.20	-0.28	+1.92

Figure 6. Photocatalytic performance of Cu₂O- NS, GO and the GO-modified samples.

Figure 6 shows the photocatalytic performance of Cu₂O- NS and the GO-modified samples. During more than 5000 minutes irradiation by visible light, hydrogen yields of all samples increase steadily without inactivation. GO/Cu₂O-0.5 and GO/Cu₂O-1 have higher hydrogen yields than that of Cu₂O-NS after 1000 and 3000 minutes' irradiation, respectively. At the 5387th minute, the hydrogen yields of GO/Cu₂O-0.5 and GO/Cu₂O-1 were 89.3 and 96.0 μmol, respectively, which were 2.0 and 2.2 times as large as that of Cu₂O-NS (44.6 μmol). However, the hydrogen yield of GO/Cu₂O-0.1 was even worse than that of the Cu₂O-NS. It may be attributed to pore cover and surface area reduce. For GO/Cu₂O-0.5 and GO/Cu₂O-1, their hydrogen yields were also less than Cu₂O-NS before 1000 and 3000 minutes' irradiation, respectively. It suggests that the structures change during irradiation, which will be discussed in the section 3.2. Besides, bare GO with poor light absorption have no hydrogen production, which indicates that GO plays a role as the co-catalyst to provide carbon sheets for core-shell structure forming.

3.2 Photocatalytic mechanism analysis

In order to investigate how the structure change and the effect on photocatalytic mechanism, SEM, XPS, UV-vis absorption analysis and photoluminescence (PL) for Cu₂O-NS and GO/Cu₂O-0.5 after irradiation were carried out. They were denoted as Cu₂O-NS-af and GO/Cu₂O-0.5-af, respectively.

Figure 7 is the XPS spectra for Cu 2p and C 1s of GO/Cu₂O-0.5 before and after irradiation. It shows that the Cu²⁺ species, such as Cu²⁺ 2p_{1/2} and Cu²⁺ 2p_{3/2}, take a large proportion with three strong satellite peaks before irradiation (Figure 7(A)). However, the Cu²⁺ species can hardly be detected after irradiation and only two strong peaks referred to Cu⁺ 2p_{1/2} and Cu⁺ 2p_{3/2} were detected, which indicate that the copper dioxide particles may be reduced by the photo-generated electrons. Figure 7(B) shows that the peaks for C=O and C-O of GO/Cu₂O-0.5 are much larger than the C sp² and C sp³, and the atomic percentages of C sp² and C sp³ are almost the same (Table 2). For GO/Cu₂O-0.5-af, the contents of C=O and C-O species decrease sharply because some organic groups like carboxyl and carbonyl can be degraded to carbon dioxide or other dissociative composition during visible light irradiation [41], and this decrease also enlarges the atomic percentages of C sp² and C sp³. But the percentages of C sp² are much larger than that of C sp³. By comparing the atomic compositions for GO/Cu₂O-0.5 and GO/Cu₂O-0.5-af (Table S1), it was found that the ratio of C sp² to C sp³ increase from 0.86 to 1.22 while a part of covered GO was desquamated (Figure 7(D)) and the GO shell was thinner and more smooth

(Figure 7(E)), which suggests that a part of sp^3 carbon was degraded during irradiation. In the Cu 2p spectrum of Cu_2O -NS (Figure 7(C)), it shows that Cu (II) species appeared. The valence band edge potential of Cu_2O -NS (1.61 eV) is more positive than $\mu_{Cu^+/Cu^{2+}}$ (0.18 eV) and μ_{O_2/H_2O} (1.23 eV), which indicates that a part of Cu (I) species of was oxidized to Cu (II) by the photo-generated holes or generated oxygen from the water splitting reaction.

Figure 7. XPS spectra for Cu 2p (A) and C 1s (B) of GO/Cu₂O-0.5 and Cu 2p (C) of Cu₂O-NS before and after irradiation along with SEM (D) and TEM (E) image of GO/Cu₂O-0.5-af.

For more details of the semiconductor properties of Cu₂O-NS-af and GO/Cu₂O-0.5-af, such as band gap, conduction band edge and valence band edge, were calculated (Table S2) according to the UV-Vis absorption spectra and XPS analysis. The conduction band edge (-0.10 eV) and valence band edge (1.80 eV) potentials of Cu₂O-NS-af shifted towards positive region compared to those of Cu₂O-NS (Table 3), because the increase of oxygen atomic percentage leads to the increase of the absolute electronegativity (χ values) according to equation 1 and 2. For all GO-modified samples, both CuO and

Cu₂O can be detected with weak XRD reflection and strong XPS signal on the GO-modified samples, it indicates that CuO and Cu₂O particles are conjugated instead of being mixed up or highly separated with each other which leads to the electrons flowed from Cu₂O with a lower χ values of 5.33 eV to CuO with a higher χ values of 5.81 eV until the chemical potential become equal [39]. The potential of this photo-generated electron flow formed by excitation of Cu₂O was calculated to be -0.27 eV, which is more negative than that of μ_{Cu^{2+}/Cu^+} (-0.18 eV) and may lead to the reduction of Cu (II) oxide and the composition of oxygen bonding on the surface. Table S2 also shows that conduction band edge of GO/Cu₂O-0.5-af was calculated to be -0.02 eV, which is much negative than that of GO/Cu₂O-0.5 and negative enough to reduce H⁺ to hydrogen during photocatalysis. It also suggest that a part of photoenergy had to be used to reduce Cu (II) oxide and GO instead of producing hydrogen at the beginning of photocatalysis.

Figure 8 shows the hydrogen production rate of Cu₂O-NS and the GO-modified samples. The hydrogen production rate of Cu₂O-NS was reducing from the top rate of 1.6 $\mu\text{mol/h}$ to around 0.5 $\mu\text{mol/h}$, and the reduction of production rate was predicted by the XPS analysis and the semiconductor properties calculation from UV-Vis absorption spectra. It also indicates the Cu₂O nanosphere was a kind of active photocatalysts with poor stability. After being modified by GO, GO/Cu₂O-0.1, GO/Cu₂O-0.5 and GO/Cu₂O-1 have enhance stability of hydrogen production rate. Although GO/Cu₂O-1 had higher rate than GO/Cu₂O-0.5, its stability performed worse. It may be attributed to the oxidation of Cu₂O nanosphere because the nanospheres were only grown on the surface of GO (Figure 4(d)). Hydrogen production rate of GO/Cu₂O-0.5 was gently increasing and it reached the highest point and become stable at the 3100th minutes. It is the core-shell structure that leads to the gentle reduction of CuO and GO.

Figure 8. Hydrogen production rate of Cu₂O-NS and the GO-modified samples.

The high electronegativity of oxygen atoms on carbon sheets causes the charge flow that exerts p-type semiconductivity to GO.[28, 42] In order to investigate the relationship between this charge flow on the surface and the structure change during irradiation, photoluminescence spectra (PL) of were carried out. Figure 9 shows the PL spectra of GO/Cu₂O-0.5 before, after 1000 minutes and 2000 minutes irradiation (denoted as “0 min”, “1000 min” and “2000 min”, respectively) with an excitation wavelength of 350 nm. The extremely reduced PL intensity indicates the mitigated charge recombination in comparison to Cu₂O [14] caused by the faster electrons transfer between Cu₂O and GO. From the above discussion of the XPS

spectra (Figure 7), it suggests that it is the new-forming sp^2 carbon leads to this mitigated electron-hole recombination.

Figure 9. Photoluminescence spectra of GO/Cu₂O-0.5 before, after 1000 minutes and 2000 minutes irradiation (denoted as “0 min”, “1000 min” and “2000 min”, respectively) with an excitation wavelength of 350 nm.

In summary, the photocatalytic mechanism of GO-modified Cu₂O can be described as the follow steps: (a) CuO was reduced gradually by the photo-generated electrons from the conduction band edge of Cu₂O, which leads to negative removing of conduction band edge potentials of catalyst. (b) A part of GO was reduced and the amount of sp^2 carbon increased, which leads to the increase of electroconductibility and enhancement of charge transfer. (c) Hydrogen was evolved on the surface of Cu₂O catalysts while the photo-generated electrons from Cu₂O cores were transferred through the newly formed sp^2 carbon.

4 Conclusion

The one-step method for synthesizing cuprous oxide nanosphere without any additive surfactant in room temperature and atmospheric pressure was examined to be an easy and efficient method that the diameter of the nanospheres was less than 100 nm. The Cu₂O nanospheres were well-dispersed and formed the core-shell structure with 5 wt.% GO. The partial reduction of GO leads to the increase of atomic percentage of sp^2 carbon (graphene sheets). Its better conductivity plays an important role in mitigating electron-hole recombination and enhancing electron transfer between Cu₂O and GO and thus enhance the photocatalytic activity. The highest hydrogen yields for GO-modified samples (118.3 μ mol) were more than twice as large as that of bare Cu₂O nanosphere (44.6 μ mol).

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