Research Article

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Photocatalytic reduction of graphene oxide with cuprous oxide film under UV-vis irradiation

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Abstract: We have grown Cu_2O films by different routes including self-oxidation and metal-organic deposition (MOD). The reduction efficiency of Cu_2O films on graphene oxide (GO) synthesized by modified Hummer's method has been studied. Surface morphology and chemical state of as-prepared Cu_2O film and GO sheets reduced at different conditions have also been investigated using atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS). Results show that self-oxidation Cu_2O film is more effective on photocatalytic reduction of GO than MOD- Cu_2O film. Moreover, reduction effect of self-oxidation Cu_2O film to GO is comparable to that of environmental-friendly reducing agent of vitamin C. The present results offer a potentially eco-friendly and low-cost approach for the manufacture of reduced graphene oxide (RGO) by photocatalytic reduction.

Keywords: graphene oxide, Cu_2O , MOD, photocatalyst

1 Introduction

Graphene as a two dimensional carbon material has gathered much more attention with its application prospect in various fields, such as energy storage, radiator, sensors, aviation and space, anti-bacterial, due to its high electric conductivity, good thermal conductivity, large specific surface area, and high mechanical strength, antibacterial activity [1–6]. Because of this, the synthesis method of graphene has become a hot topic. Various methods have been developed to fabricate graphene, including mechanical exfoliation, microwave-assistant exfoliation, chemical vapor deposition (CVD), epitaxial growth, electrochemical reduction and chemical oxidation-reduction method [6–

10]. Among these synthesis ways for graphene, CVD is mainly used in producing graphene film due to its application potential in flexible display field [11, 12]. However, modified Hummer's method, a chemical oxidation-reduction method, offers lower processing costs and more simple operation than other synthesis methods. And this chemical synthesis method is promising for mass production of GO and RGO because it is easy for scale-up [10, 13, 14]. It should be pointed out that hydrazine hydrate explosively used to be as a reductant is highly toxic and it is not suitable to be in large-scale implementation [15]. Therefore, it becomes very significant to explore an efficient and environmentally friendly technique to prepare reduced graphene oxide. At present, several new reductants including vitamin C, hydrohalic acids, Sodium borohydride, grape seed extract, and new reduction routes, such as hydrothermal, photocatalytic reduction, photothermally reduced, flash reduction have been developed [15–18]. Among all the strategies developed, photocatalytic reduction has attracted more attention because of its many advantages, such as safety, eco-friendly, easy-operation and high efficiency. In addition, a lot of photocatalysts, which used in the reduction of GO, have been developed at present. Choobtashani and Akhavan [18] found out that tungsten oxide film synthesized by various routes showed significant differences in photocatalytic reduction efficiency of the GO platelets especially after exposure to visible light of the environment [18]. In addition, he thought that the ZnO nanoparticles in the ZnO/GO composite could be applied in a gradual chemical reduction and consequently tuning the electrical conductivity of the GO platelets by variation of UV irradiation time in a photocatalytic process [19]. G. Williams found out that the direct interaction between TiO_2 particles and graphene sheets hinders the collapse of exfoliated sheets of graphene while GO undergoes reduction by accepting electrons from UV-irradiated TiO_2 [20].

In fact, transition metal oxides have been extensively applied in many fields, such as catalysts, supercapacitors, and superconductors due to their special physical properties and good stability [21–26]. To explore efficient and environmentally friendly technique to prepare reduced

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graphene oxide, we choose transition metal oxide Cu_2O as a model material. Compared with other common photocatalysts, Cu_2O has a low band gap energy (2.2 eV) [27–30]. Thus Cu_2O can absorb visible light at a wavelength of about 400–800 nanometers along with the excitation of electron–hole pair. And it has been widely investigated for photocatalyst reaction under visible light irradiation [21–23, 31]. Thus Cu_2O is considered to be a promising visible light active photocatalyst to produce graphene [23]. In addition, photocatalysis reduction efficiency of Cu_2O is reported to be related to its morphology [32, 33]. In this paper, GO has been reported to be fabricated by modified Hummer's method. Then we have explored the photocatalytic reduction effect of Cu_2O film prepared by different methods on GO sheets. And we have also discussed the influence of visible light in the environment on the photocatalytic reduction of GO. In addition, a comparative study of the photocatalytic reduction efficiency and eco-friendly reducing agent vitamin C to GO has been done.

2 Experimental procedures

2.1 Synthesis of GO

GO was synthesized using natural flake graphite powder (from Qingdao Tianheda graphite Co., LTD) by a modified Hummers' method. The pre-oxidation of graphite was initially carried out by reacting powdered flake graphite with $\text{K}_2\text{S}_2\text{O}_8$ and P_2O_5 in sulfuric acid with continuous stirring in an oil heating bath at 80°C . Then the suspension was filtered, followed by washing and vacuum drying treatment resulting in dark grey powder. Graphite oxide was synthesized by stirring pre-oxidized graphite and KMnO_4 in sulfuric acid. The reaction system went through three steps including the ice-bath, room-temperature reaction and high-temperature reaction process. Then the sticky suspension was purified by dialysis for 2 weeks to remove other impurities. The graphite oxide suspension with high concentration was dewatered using anhydrous ethanol and then was dispersed in ethanol by bath sonication of graphite oxide suspension at a power of 300 W for 30 min to obtain the GO ethanol dispersion solution.

2.2 Fabrication of Cu_2O film by MOD

The metal-organic deposition (MOD) method is widely used for the preparation of oxide film because of cost effective and high deposition rate [34]. Here, the MOD pre-

cursor solution was prepared in the ambient atmosphere. Copper (II) acetate monohydrate was dissolved in propionic acid. After heating with continuous stirring, a stable bottle green-colored precursor solution was obtained. The yttria stabilized zirconia (YSZ) single crystal substrate was cleaned by sonication in acetone for 20 min. And the precursor was spin-coated onto YSZ single crystal substrate, followed by heat-treatment at 1000°C for 30 min in a reducing forming gas atmosphere of $\text{Ar-4\%H}_2$. At the end of the heat-treatment cycles, finally, the sample was quenched to room temperature in the same atmosphere.

2.3 Preparation of Cu_2O film by self-oxidation reaction

Just like other metals and alloys, copper is widely used in many fields due to its series of advantages, such as high strength, high corrosion resistance, and easy processing [35–37]. On the other hand, thermal oxidation techniques are often used to improve some significant performance of metal, without special requirements for substrate geometries [38]. Thus, Cu was chosen as the substrate for self-oxidation of Cu_2O film. Cu substrate was obtained by rolling and then annealing in vacuum at 800°C for 3 h. In order to improve the surface quality of the metallic substrate, the electropolishing modification was carried out. The Cu substrate was cleaned by sonication in ethanol and acetone for 30 min, respectively. The sample was introduced into a furnace and heat-treated at 900°C for 30 min in a flowing gas atmosphere of Ar. After heat-treatment cycles, the sample was quenched to room temperature with the same atmosphere.

2.4 Photocatalytic reduction of GO on Cu_2O film

The as-prepared GO sheets were deposited on the as-grown Cu_2O films through drop-casting the GO ethanol dispersion solution onto the films fabricated on the different substrates. Then the coating GO/ Cu_2O samples were dried at room temperature for 24 h in darkness. For comparison, the same method was also used to deposit GO sheets on YSZ substrate. To investigate the photocatalytic reduction of the GO sheets deposited on the Cu_2O films grown on the different substrates using different deposition methods, the samples were irradiated by an ultraviolet lamp for different times at room temperature. Some of the samples were also exposed to the visible light of the environment to realize photocatalytic reduction of GO.

2.5 Characterization

The thickness of GO sheets and the microstructure of Cu_2O films prepared by different methods were performed using a digital instruments nanoscope SPI3800-SPA-400 atomic force microscopy (AFM) in tapping mode. Cu_2O films were characterized by using X-ray diffraction (XRD), which was performed to carry out θ - 2θ scan by using $\text{CuK}\alpha$ radiation at 40 kV and 50 mA, for phase purity, crystallinity and texture. X-ray photoelectron spectroscopy (XPS) was performed to identify the phase constitution of Cu_2O films and GO sheets using an X-ray photoelectron spectrometer equipped with a monochromatic X-ray source of $\text{AlK}\alpha$. $\text{Cu}2p$, $\text{O}1s$ and $\text{C}1s$ core level XPS spectra were measured.

3 Results and discussion

Figure 1 shows the AFM 2D image and the high profile diagram of GO sheets deposited on Si single crystal substrate by drop-casting. Irregularly shaped individual GO sheet, with about two hundred nanometers in size and one nanometer in height is observed. This height is corresponding to the typical thickness of exfoliated single-layer GO sheet, which is greater than that of pristine single-layer graphene sheet due to the insertion of the oxygen-containing groups.

Figure 1: AFM image and high profile diagram of exfoliated GO sheets

XRD diffraction patterns for Cu_2O films deposited by different deposition methods were collected at room temperature to find the phase purity and growth orientation of crystalline grains, as shown in Figure 2. It can be found that all the as-fabricated Cu_2O films have completely crystallized by different synthesis methods. And the Cu_2O films prepared by two methods are not essentially single preferred oriented because both the Cu_2O (111) and (200) diffraction peaks appear in the patterns. However, the intensity ratio of the (111) to (200) peaks for self-oxidation- Cu_2O film is significantly greater than that for MOD- Cu_2O film. There is a big difference in photocatalytic activity between different crystallographic planes in Cu_2O . In addition, Cu_2O (111) crystal plane has a better photocatalytic activity and stability than its (100) plane [39–41]. Therefore, the as-prepared self-oxidation- Cu_2O film may have better photocatalytic efficiency compared with the MOD- Cu_2O film.

Figure 2: θ - 2θ XRD patterns of the as-prepared Cu_2O films by different deposition methods, (a) MOD, (b) self-oxidation

AFM investigation was also carried out on Cu_2O films grown on YSZ and Cu substrates by different deposition methods, as shown in Figure 3. There is much difference between the surface topology of $\text{Cu}_2\text{O}/\text{YSZ}$ and that of $\text{Cu}_2\text{O}/\text{Cu}$ sample. The scanning area of films is $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$. AFM line scans of $\text{Cu}_2\text{O}/\text{YSZ}$ and $\text{Cu}_2\text{O}/\text{Cu}$ surfaces show an average elevation of 20 nm and 10 nm, respectively. Average size of the cuprous oxide grains on the surface of MOD- Cu_2O film is $\sim 60\text{ nm}$, while it is $\sim 100\text{ nm}$ for the self-oxidation- Cu_2O film. However, the grain size on the surface of $\text{Cu}_2\text{O}/\text{YSZ}$ sample shows bad size-uniformity compared with that of $\text{Cu}_2\text{O}/\text{Cu}$. Therefore, the root mean square roughness (R_{rms}) of the scanned area is 6.99 nm for $\text{Cu}_2\text{O}/\text{YSZ}$ and 2.27 nm for $\text{Cu}_2\text{O}/\text{Cu}$. It indicates that self-

Figure 3: Topography 2D images, high profile diagram and grain size distribution on the surface of Cu_2O films fabricated by different methods, (a) MOD, (b) self-oxidation

oxidation reaction is an effective method to prepare high-quality Cu_2O film.

Figure 4 shows Cu 2p core-level spectra of cuprous oxide films grown on YSZ and Cu substrates by different deposition methods. Cu2p peak has significantly split spin-orbit components of 2p_{3/2} and 2p_{1/2} with energy splitting of 19.9 eV. The appearance of asymmetric shape with a high binding energy tail indicates that little quantity of CuO is formed in films. It is believed that the oxidation of a very small amount of Cu_2O to CuO occurred during the calcination process as reported in other studies [23]. Nevertheless, the over-oxidation was very minimal because no obvious CuO diffraction peaks were observed in the XRD pattern discussed above. Moreover, Cu(I) is predominant in the film due to the presence of a very weak satellite at ~934 eV, which is associated with the existence of Cu(II) oxide. After the deconvolution of the each spectrum into two doublets, which corresponds to the chemical states of Cu(I) (at 932.5 and 952.4 eV, respectively) and Cu(II) (at 934.0 and

953.9 eV, respectively), as shown in Figure 4(a). Thus the Cu(I) percent of the film can be calculated accordingly. It is clear that a percent of Cu(I) is about 79.99% for the MOD- Cu_2O film, whereas Cu(I) percent is around 99.99% for self-oxidation Cu_2O film. It indicates that Cu_2O film with high purity is favorable to be synthesized by self-oxidation reaction compared using MOD methods due to the difference of the driving force from the interface between the substrate and the top oxide film.

XPS is also employed to analyze the as-deposited GO and the degree of photocatalytic reduction of exfoliated GO sheets on Cu_2O film fabricated by different methods. The high-resolution C1s spectra of the as-prepared GO/YSZ and GO/ Cu_2O /YSZ as well as GO/ Cu_2O /Cu exposed to UV light irradiation for different times are shown in Figure 5. For GO sheets deposited on YSZ substrate dried in dark, an asymmetric line shape indicates that there are different types of carbon existing on the surface of GO/YSZ, as seen in Figure 5(a). The assumption being that the C1s spec-

Figure 4: XPS high resolution spectra of Cu2p core level region for Cu₂O films fabricated by different methods, (a) MOD, (b) self-oxidation

trum is attributed to the non-oxygenated ring C including C-C and C=C bonds (at ~284.8 eV), carbonyl C in C-OH bond (at ~286.5 eV), ether C in C-O-C bond (at ~287 eV), ketone C in C=O (at ~287.9 eV), carboxyl C in O=C-OH (at ~289 eV) [18, 19]. After irradiated in environment for 24 h, the intensities of the oxygen functionality peaks on the surface of GO/Cu₂O/YSZ sample decrease obviously compared with those of as-deposited GO sheets, as show in Figure 5(b). However, the intensities of C1s peaks with oxygen-containing functional group decrease dramatically for the GO/Cu₂O/YSZ sample after 6 h UV-vis light irradiation. And further 18 h UV-vis light irradiation shows a very weak reduction for GO deposited on Cu₂O/YSZ substrate. Nevertheless, a small amount of oxygen-containing functional groups still exists in GO sheets deposited on the surface of Cu₂O/YSZ when 24 h UV-vis light irradiation is adopted. It is noteworthy that no obvious deconvoluted peak corresponding to oxygen-containing functional groups is observed on the surface of GO/Cu₂O/Cu sample after 24 h UV-vis light irradiation. It indicates that the self-oxidation Cu₂O film shows a more effective photocatalytic reduction for the GO sheets compared with the MOD-Cu₂O film.

Figure 5: XPS spectra of C1s core level for GO sheets deposited on (a) YSZ substrate dried in dark, (b) MOD-Cu₂O film after 24 h visible light irradiation, (c) MOD-Cu₂O film after 6 h UV-vis light irradiation, (d) MOD-Cu₂O film after 24 h UV-vis light irradiation, (e) self-oxidation Cu₂O film after 24 h UV-vis light irradiation

Table 1: The peak area (A) ratio of oxygen-containing bonds to the non-oxygenated ring CC bonds for GO sheets deposited on YSZ substrate, MOD-Cu₂O and self-oxidation Cu₂O films after light irradiation, as compared to those of the vitamin C-reduced GO

Sample	GO	After 24 h in environment	GO/Cu ₂ O/YSZ After 6 h UV-vis irradiation	After 24 h UV-vis irradiation	GO/Cu ₂ O/Cu After 24 h UV-vis irradiation	RGO (vitamin C)
A_{COH}/A_{CC}	0.22	0.17	0.17	0.12	0.02	0.01
A_{COC}/A_{CC}	0.72	0.67	0.50	0.29	0.09	0.12
A_{CO}/A_{CC}	0.26	0.11	0.11	0.04	0.01	4e-6
A_{OCHO}/A_{CC}	0.05	0.04	0.04	0.03	3e-6	1e-6

To comparative study the reduction effect with light irradiation on oxygen-containing functional groups in GO sheets at different conditions, the peak area ratios of C-OH, C-O-C, C=O, O=C-OH bonds to the non-oxygenated ring CC bonds was calculated and given in Table 1. GO sheets deposited on MOD-Cu₂O film are slightly reduced after visible light irradiation for 24 h in the environment. And its reduction degree of GO is comparable to that of GO deposited on MOD-Cu₂O film after 6 h UV-vis light irradiation. However, GO deposited on MOD-Cu₂O film is not thoroughly reduced although further reduction happens with prolonging the UV-vis irradiation time. It illustrates that the UV part in UV-vis light irradiation does not play a leading role in the photocatalytic reduction of GO sheets deposited on Cu₂O film. The self-oxidation Cu₂O film, by contrast, shows an effective photocatalytic reduction to GO sheets, which can be even compared with the reduction effect of vitamin C to GO. Moreover, better reduction efficiency of self-oxidation Cu₂O is even observed on C-O-C bond in GO compared with that of vitamin C.

It is well known that photocatalytic activity mainly involves light absorption, generation and transport of electron-hole pair. The concentration, surface characteristics and contact angle with the GO and cuprous oxide photocatalyst are very important parameters for photocatalytic efficiency [5–7]. The higher content of Cu₂O in self-oxidation film promotes its excitation on the absorption of light, resulting in its better photocatalytic efficiency. In addition, small surface roughness of self-oxidation Cu₂O film enhances its contact area with GO sheets, which favors electron transport and further improves photocatalytic reduction of GO under UV-vis light irradiation. In particular, Cu₂O (111) crystal plane shows better stability and photocatalytic activity than (100) plane. Thus, self-oxidation Cu₂O film with larger ratio of (111)/(200) diffraction peaks show better photocatalytic performance than MOD-Cu₂O film.

4 Conclusion

In summary, we have demonstrated an environmentally-friendly and high-efficiency method for reduction of graphene oxide with cuprous oxide thin film. GO sheets coated on Cu₂O thin films, which are prepared by different methods, have been reduced by UV-visible light irradiation. Self-oxidation Cu₂O shows a better photocatalytic reduction efficiency on GO sheets than MOD-Cu₂O, which is related to their different morphologies and Cu(I) percentage in as-prepared Cu₂O films. Most importantly, the intensity ratio of (111) to (200) diffraction peaks of the self-oxidation-Cu₂O film is much larger than that of the MOD film. A better photocatalytic activity of the (111) crystal plane leads to higher photocatalytic efficiency of the former. Moreover, the photocatalytic reduction rate of self-oxidation Cu₂O on GO is even comparable to that of vitamin C. Such self-oxidation Cu₂O film can be used as a suitable photocatalytic agent for the reduction of GO sheets.

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