Enhanced photocatalytic performance of partially reduced graphene oxide under simulated solar light through loading gold nanoparticles

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ABSTRACT

Partially reduced graphene oxide (PRGO) was prepared by reduction of graphene oxide with L-ascorbic acid, a mild reducing agent. As-prepared PRGO showed favorable photocatalytic performance for the degradation of methyl orange (MO) under simulated solar light irradiation. After loading Au nanoparticles (NPs) on the PRGO sheet, significant enhancement was found in the degradation of MO due to the electron traps, surface plasmon resonance excitation and UV excitation of Au NPs.

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1. Introduction

Graphene has stimulated more and more interest [1,2] since it was first obtained by Geim in 2004 [3]. One method consisting of oxidization of graphite, subsequent exfoliation into graphene oxide (GO), and then reduction of GO, is widely used to synthesize graphene [4]. Thus GO is the intermediate state between graphene and graphite, and could be regarded as graphene functionalized by carboxylic acid, hydroxyl, and epoxide groups [5]. Though an ideal graphene is a zero-bandgap semiconductor, its energy gap could be opened by oxidation of graphene, and the value of the energy gap depends on the oxidization degree of graphene [6]. Therefore, the oxidation level of GO can be used to tune the electronic properties [7]. Yan reported that the bandgap of GO could be modulated from 4.0 eV to 0.1 eV by controlling its oxygenated sites and oxidization level [8]. Yeh have prepared GO semiconductor with a moderate oxidation level (2.4–4.3 eV bandgap) for H_2 production [9]. The reduced graphene oxide (rGO) has a narrower bandgap due to losing oxygen functional groups. It was found that rGO can degrade dyes under visible-light, but with a very slow rate [10,11], which may be correlated with its high reduction level of GO, in other words, low oxidation level of GO. Therefore, improvement is required to greatly increase efficiency of rGO in photocatalytic applications.

Au nanoparticles (NPs) show strong absorption of visible light due to surface plasmon resonance (SPR) effect [12]. Recently,

supported Au NPs have been widely used as visible light responding photocatalyst because of its extraordinary SPR effect [13,14]. Furthermore, supported Au NPs can also absorb UV light via electron interband transitions from 5d to 6sp [13]. These characteristics imply the solar spectrum can be effectively utilized for driving reactions with Au NPs as potocatalyst. Therefore, it is expected that the photocatalytic performance of rGO can be improved after loading Au NPs.

In this study, GO was prepared according to our previous work [15] and then reduced by L-ascorbic acid, a mild reducing agent. Due to its moderate reduction performance, GO was only partially reduced by L-ascorbic acid, which was confirmed by selective area electron diffraction (SAED) patterns and XPS results. Furthermore, the partially reduced GO (PRGO) exhibited favorable photocatalytic activity for degradation of MO under simulated solar irradiation. After loading Au NPs on PRGO sheets, significant improvement was observed in the degradation of MO due to the electron traps, SPR excitation and UV excitation of Au NPs.

2. Experimental

Preparation of PRGO and Au–PRGO composites: graphene oxide (GO) was prepared by a Hummers method. Au–PRGO composites were synthesized, using GO suspension (1 mg/mL) and chlorauric acid solution (0.35 mM) as the starting materials. In a typical experimental procedure, L-ascorbic acid aqueous solution (0.1 M) was added dropwise into the mixture of GO suspension and a desirable amount chlorauric acid solution. The mixture was degassed under nitrogen for 20 min and then heated at 80 °C for

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24 h in an oil bath under stirring. The resulting Au x%–PRGO (x means the weight percentages of gold in composites) composites was filtered and washed with de-ionized water. The collected sample was dried overnight in vacuum at 60 °C. The PRGO was prepared in a similar manner but without the addition of chlorauric acid solution.

Characterization of samples: the X-ray powder diffraction (XRD) patterns were obtained on a Rigaku X-ray diffractometer to determine the crystallite identity of samples. The microstructure of PRGO and Au–PRGO samples was investigated with a JEM 2100 transmission electron microscope (TEM). UV–visible absorbance spectra were obtained for the dry-pressed disk samples with a UV–visible spectrophotometer (UV-2550, Shimadzu, Japan). $BaSO_4$ was used as a reflectance standard in a UV–visible diffuse reflectance experiment. The X-ray photoelectron spectroscopy (XPS) measurement was made on a KRATOS Analytical AXISHSi spectrometer with a monochromatized Al Kα x-ray source (1486.6 eV photons). The binding energy scale was calibrated by the Au 4f 7/2 peak at 83.9 eV as well as Cu 2p 3/2 peak at 76.5 and 932.5 eV.

Photocatalytic activity measurement: the photocatalytic activities of samples were evaluated by degradation of methyl orange (MO) under simulated solar light irradiation (500 W Xe lamp). In a typical experiment, 10 mg of photocatalyst was added into 50 mL of MO solution (24 mg/L). Prior to irradiation, the suspensions were magnetically stirred in the dark for 2 h to obtain the saturated absorption of MO onto the catalysts. At irradiation time intervals of every 0.5 h, the suspensions were collected. The concentration of the MO was monitored using a UV–vis spectrophotometer during the photodegradation process.

3. Results and discussion

The formation of Au NPs on PRGO was characterized by XRD as shown in Fig. 1(a). The PRGO sheets exhibit a (002) diffraction peak at 26° and a (100) peak at 44.5°. The (002) diffraction peak of PRGO is visible in the XRD patterns of composites though its intensity is low. It is clearly visible if the XRD pattern of composites such as 2.5% Au–PRGO is plotted separately in one figure, as shown by the inset in Fig. 1a. The prominent peaks at 2θ values of 38.2, 44.4, 64.7, and 77.6° correspond to the (111), (200), (220), and (311) crystallographic planes of Au NPs, respectively, indicating the formation of Au NPs on the PRGO surface [16]. Furthermore, the intensity of the Au NPs characteristic peaks increases gradually and their shapes become more and more sharp with the enhancement of the gold content, which means the larger diameter of Au NPs. It has been reported that SPR absorption appears in near-UV, vis, and near- or mid-infrared (IR) regions depending on the size and shape of the Au NPs [14]. As shown in Fig. 1(b), compared with PRGO, the Au–PRGO composites show the broad absorption band in the wavelength range around 400–700 nm, ascribing to the SPR absorption of the Au NPs on PRGO, which originates from the intraband excitation of 6sp electrons. Considerable absorption in the UV region is also observed for the composites. It results from the interband excitation of electrons from 5d to 6sp for Au NPs [13].

The direct evidence of the formation of Au NPs on PRGO is given by TEM in Fig. 2. The presence of wrinkles and folds on the sheet is the characteristic of few-layered rGO sheet as shown in Fig. 2a. Different from the clear six-spot SAED patterns of graphene [17], however, SAED patterns of our reduced GO show diffraction rings that can be indexed to a hexagonal structure close to those of partially reduced graphene oxide (PRGO). After reduction of GO sheets and Au (III) salt simultaneously by L-ascorbic acid, a few scattered NPs are generated on the nanosheets, as shown in
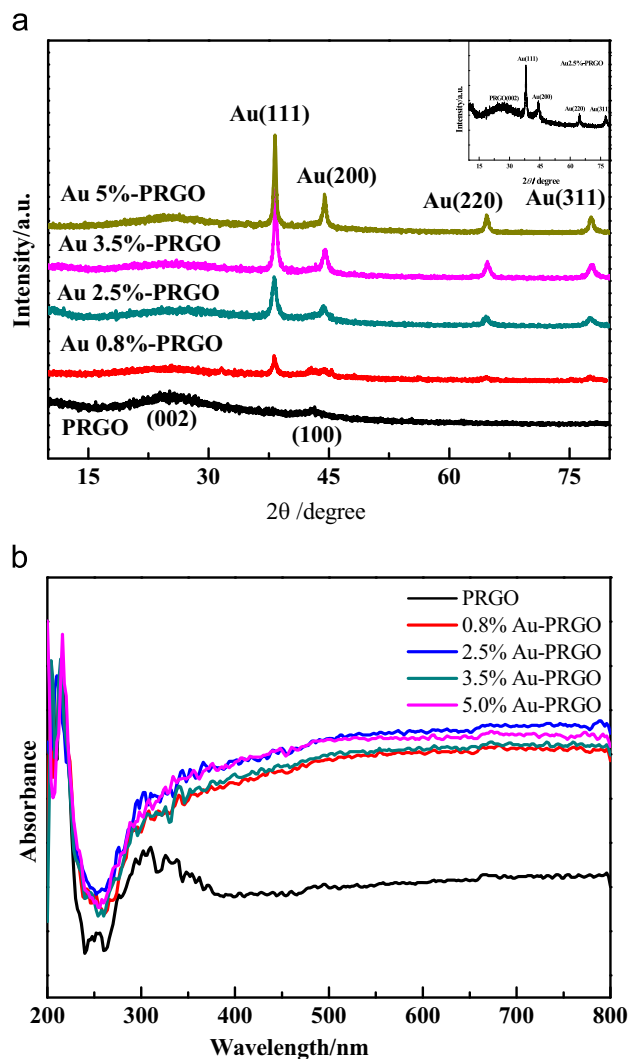
Fig. 1. (a) XRD patterns and (b) UV–vis diffuse reflectance spectra of samples.

Fig. 2b. The inset in Fig. 2b shows the high-resolution TEM (HRTEM) image of one single nanoparticle (NP), indicating it is spherical in shape. Furthermore, the HRTEM image reveals clear lattic fringes with an interplane distance of 0.23 nm, 0.20 nm, 0.15 nm and 0.12 nm corresponding to the (111), (200), (220) and (311) lattice planes, respectively [18], indicating the nanoparticle is Au NP. Such observations provide another evidence to support the formation of Au NPs on PRGO after reduction by L-ascorbic acid.

To investigate the reduction degree of GO and the state of the Au species after reduction treatment, the high-resolution XPS spectra of C1s and Au 4f were collected (Fig. S1). The peak at 284.6, 286.63, and 288.05 eV of the C1s core level spectrum of Au–PRGO composites can be assigned to C–C, C–O and O–C=O, respectively [19]. The reduction degree of the GO can be quantified by the relative content of oxygen-bound carbon, which is calculated based on the following equation [20]:

$$\%O - \text{bound } C = \frac{A_{O-C=O} + A_{C-O}}{A_{C-C} + A_{O-C=O} + A_{C-O}}$$

where $A_{O-C=O}$, A_{C-O}, and A_{C-C} are the peak areas for O–C=O, C–O, and C–C, respectively. According to the calculation, the as-obtained PRGO has 30% C–O and 6% O–C=O functional groups. However, GO has 51% C–O and 7% O–C=O. It is obvious that only part of the oxygen-containing functional groups were removed from the GO during the reduction process. The Au 4f XPS spectrum show two