Photoreduction of graphene oxide with polyoxometalate clusters and its enhanced saturable absorption

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ABSTRACT

We investigated the photocatalytic abilities of three Keggin-type polyoxometalate (POM) clusters, $H_3PW_{12}O_{40}$ (PW), $H_4SiW_{12}O_{40}$ (SiW), and $H_3PMo_{12}O_{40}$ (PMo) to reduce graphene oxide (GO) under UV-irradiation in water. UV–vis absorption and X-ray photoelectron spectroscopy were performed and show that PW and SiW can photoreduce GO effectively, in contrast to PMo. We conclude that the LUMO levels of POMs should be located energetically above the work function of GO to enable electron transfer from POM to GO. We also investigated the saturable absorption of GO and reduced GO by means of z-scan experiments at 532 nm. The POM-assisted photoreduction of GO can greatly enhance the saturable absorber properties of GO, which appears useful for modelocking in ultrafast laser systems.

1. Introduction

Graphene has attracted significant attention due to its extraordinary electronic and optical properties, as well as high robustness and environmental stability, which enable many applications [1–4]. Moreover, its broadband optical absorption is useful for saturable absorption [4–11] and makes it suitable for ultrafast laser applications [4,12–15]. Recent developments employ graphene oxide (GO) as precursor for graphene based materials, which needs a suitable process to obtain reduced graphene oxide (rGO) by chemical, thermal, or photoinduced processes [16–18].

Recently, we demonstrated polyoxometalate (POM) assisted photoreduction of GO and its nanocomposite formation [19]. POM clusters are used as both photocatalyst and stabilizer to produce water dispersible graphene sheets. We also found that the POM-assisted photoreduction of GO can occur in layer-by-layer assembled films which can be further processed into graphene based electronic devices such as transistors and microelectrodes [20]. Furthermore, rGO–POM nanocomposites with multicomponent, sensitive electroanalytic, and high efficient electrocatalytic properties have also been fabricated through the POM-assisted photoreduction approach [21–24]. These works demonstrated that POMs are suitable nanoscale photocatalysts for preparing rGO. Moreover, POMs possess good electron-acceptor ability and

zero-dimensional semiconductor features [25]. However, the mechanism of POM-assisted photoreduction is not fully resolved yet as it turns out that the photoreduction yield can depend on the type of POM used as photocatalyst. To resolve this open question, an improved understanding of relationships between energy levels and photoreduction capabilities of POMs is required.

Therefore, we compared the photocatalytic capabilities of three Keggin-type POMs, $H_3PW_{12}O_{40}$ (PW), $H_4SiW_{12}O_{40}$ (SiW), and $H_3PMo_{12}O_{40}$ (PMo) for reducing GO. Their structures are shown in Fig. 1. We used UV–vis, X-ray photoelectron spectroscopy (XPS) and the so-called z-scan technique to characterize the amount of photoreduction of GO and its resulting nonlinear optical properties. We will derive the insight that the LUMO level of POMs should be higher than the work function of GO to ensure an efficient photoreduction.

2. Experimental

The materials $H_3PW_{12}O_{40}$ (PW), $H_4SiW_{12}O_{40}$ (SiW), $H_3PMo_{12}O_{40}$ (PMo), and graphite flakes were all purchased from Aldrich. GO was prepared by a modified Hummers method [26]. An aqueous solution which contains 0.1 mg/mL GO, 2.5 mM POM, and 0.1 M isopropanol was placed in a 1 cm thick quartz cuvette. Subsequently, it was illuminated by UV light (high pressure mercury lamp, WG 320 filter, $\lambda > 320$ nm) for 10 min.

UV–vis absorption spectra were measured on a Perkin–Elmer Lambda 900 UV–vis spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Escalab 250 XPS instrument.

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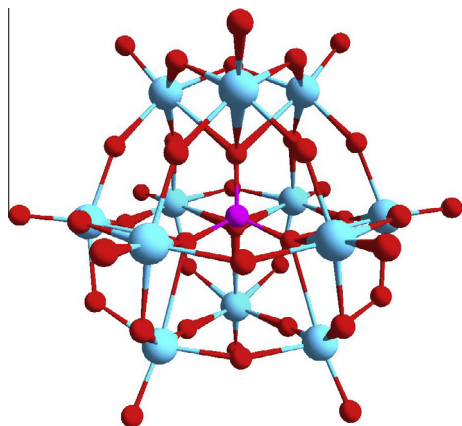
Fig. 1. Ball and stick structure of the Keggin-type PW cluster: the pink, blue and red balls correspond to P, W, and O atoms, respectively; the structures of SiW and PMo are similar to PW, only the P and W atoms are replaced by Si and Mo, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Nonlinear optical properties of GO were investigated with an open-aperture z-scan experiment [27] by means of a mode-locked Nd:YAG laser (EKSPLA model PL 2143B) at 532 nm with 10 Hz repetition rate and pulse duration τ_{FWHM} = 25 ± 2 ps. The laser beam was focused by a lens (20 cm focal length) which provided a beam waist radius of 32 μm at z = 0. The astigmatism of our laser system was compensated with lenses which were shifted slightly to off-axis positions. Pulse energies at z = 0 were measured with a pyroelectric detector (Laser Probe Model RjP-735). The aqueous solutions had GO and POM concentrations as described above, were filled in 1 mm cuvettes and moved through the focal region of the lens by a stepping motor controlled translation stage. The transmitted light was measured with a photodiode and a BOXCAR amplifier (SRS Model 250).

3. Results and discussion

3.1. Absorption spectroscopy

The absorption spectra of POMs (PW, SiW and PMo) in pure water and their aqueous solutions mixed with GO are shown in Fig. 2. The steep rises of the absorbance between 350 nm and 450 nm result from the absorption edges of the POMs which we observe at ∼365 nm for PW and SiW, whereas the absorption edge of PMo is at ∼450 nm. The mixtures were also measured each before and after 10 min UV irradiation, see Fig. 2. After UV irradiation, the broad absorption bands in the visible and near-infrared regions increase by a factor ∼10 in case of GO–PW and GO–SiW samples, respectively. But only a marginal increase is observed for the GO–PMo sample although PMo absorbs more of the UV-irradiation

light. It should be noted that the pure GO solution cannot be photo-reduced at our irradiation condition, as confirmed already in our earlier work [19]. We conclude that the increasing absorption of GO at λ > 400 nm is directly related to the formation of rGO. Obviously, the abilities of the three POMs are different in reducing GO: They are large for PW and SiW, but very small for PMo.

3.2. X-ray photoelectron spectroscopy (XPS)

Dried samples of GO and the 3 mixtures with POMs were analyzed by XPS to study the change of binding states of carbon atoms induced by photoreduction, as shown in Fig. 3A. The observed C 1s signals can be classified into three types: the nonoxygenated ring carbon (C—C), the carbon in C—O bonds (hydroxyl and epoxy), and the carbonyl carbon (C=O) [28]. The XPS spectra were fitted to evaluate the relative areas of the peaks, and the results are shown in Table 1. Inspection of Fig. 3 and Table 1 shows that the relative areas of the oxygen-containing groups decreased after GO was photoreduced by means of POMs. Furthermore, the reduction degrees for the cases of using PW and SiW are similarly large, but PMo was significantly less active as photocatalyst. The XPS results are in line with the UV–vis results and demonstrate that the photoreduction capabilities of PW and SiW are significantly larger than PMo. Furthermore, Raman spectra were also used to study the photoreduction degree of GO under different conditions, as shown in Fig. 3B. For all the samples, two typical vibration bands of graphene are observed at *ca.* 1600 and 1355 cm^{-1}, which correspond to the G and D bands, respectively [29]. It has been reported that the increase in I_D/I_G reflects an increased number of small sp^2 domains on GO nanosheets, as is usually observed for rGO [30]. In our work, the I_D/I_G values of GO photoreduced by PW and SiW are 1.12 and 1.10 respectively, obviously larger than the GO reduced by PMo which is 0.92. This means that the reduction degree of PMo-photoreduced GO is the smallest and thus PMo possesses the lowest photoreduction capability among the three POMs. The Raman results are consistent with XPS and UV–vis results.

3.3. Photoreduction model

According to the literatures, Keggin type POM clusters such as PW, SiW and PMo possess a photocatalytic activity similar to semiconductor nanoparticles, such as TiO$_2$ nanoparticles [25]. Under UV-irradiation, the oxygen-to-metal charge-transfer band in the POM clusters is excited, which leads to electron–hole separation. The holes and electrons are oxidative and reductive, respectively. When a sacrifice reagent is available to react with the holes, the residual electrons can be trapped and delocalized in the cage-type framework of POMs, forming the reduced POMs which is generally named "polybule". The polybules are widely used as reductants. For example, they can reduce metal ions to metal nanoparticles [31,32]. In our work, isopropanol is chosen as the sacrifice reagent. In principle, it can be oxidized by the holes in POMs, and the
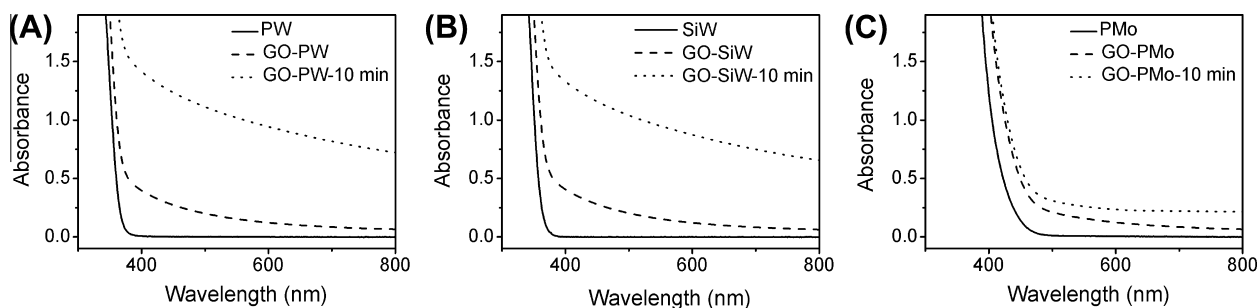
Fig. 2. UV–vis spectra of (A) PW, GO–PW and GO–PW-10 min; (B) SiW, GO–SiW and GO–SiW-10 min; (C) PMo, GO–PMo and GO–PMo-10 min, respectively.