A Facile Synthesis of Graphene-WO$_3$ Nanowire Clusters with High Photocatalytic Activity for O$_2$ Evolution

M.-J. Zhou, N. Zhang, and Z. H. Hou

School of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang 414000, China

Correspondence should be addressed to Z. H. Hou; zhqh96@163.com

Received 1 April 2014; Revised 24 June 2014; Accepted 8 July 2014; Published 24 July 2014

Academic Editor: Gianluca LiPuma

Copyright © 2014 M.-J. Zhou et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In the present work, graphene-WO$_3$ nanowire clusters were synthesized via a facile hydrothermal method. The obtained graphene-WO$_3$ nanowire clusters were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and ultraviolet-visible diffuse reflectance spectroscopy (DRS) techniques. The photocatalytic oxygen (O$_2$) evolution properties of the as-synthesized samples were investigated by measuring the amount of evolved O$_2$ from water splitting. The graphene-WO$_3$ nanowire clusters exhibited enhanced performance compared to pure WO$_3$ nanowire clusters for O$_2$ evolution. The amount of evolved O$_2$ from water splitting after 8 h for the graphene-WO$_3$ nanowire clusters is ca. 0.345 mmol/L, which is more than 1.9 times as much as that of the pure WO$_3$ nanowire clusters (ca. 0.175 mmol/L). The high photocatalytic activity of the graphene-WO$_3$ nanowire clusters was attributed to a high charge transfer rate in the presence of graphene.

1. Introduction

Since Fujishima and Honda reported the evolution of oxygen and hydrogen from a TiO$_2$ electrode under the irradiation of light in 1972 [1], photocatalysis is a very promising process to photodissociate water utilizing solar energy. Solar photolysis of water is one of the cleanest ways of producing hydrogen and oxygen, which has great potential in solving energy problems. Recently, tungsten oxide (WO$_3$) as an important photocatalytic material with a wide band gap ranging from 2.4 to 2.8 eV has attracted considerable interest because it has the potential ability to promote photocatalytic reactions under visible light irradiation [2–4]. The photocatalytic applications of several types of WO$_3$ nanomaterials have been reported, particularly for oxygen (O$_2$) evolution in the presence of an electron acceptor [5, 6]. However, WO$_3$ nanomaterials are usually not efficient photocatalysts because of the high electron-hole recombination rate [7]. This is one of the biggest obstacles hindering the development of WO$_3$ as a practical photocatalyst [8]. Recently, many attempts have been made to improve the efficiency of electron-hole pair separation in WO$_3$, such as morphology control, doping, and composites [9].

Recently, much effort has been focused on the synthesis of graphene- (GE-) based composites due to their potential application in the photocatalytic field [10–28]. The combination of GE with a well photocatalytic semiconductor is expected to result in a high performance in photocatalytic activity because GE has perfect two-dimensional carbon structure with high thermal conductivity and a large specific surface area [10]. GE is easy to produce from graphene oxide (GO). The presence of oxygen-containing functional group in GO and reduced GO makes it an excellent supporter to anchor photocatalytic semiconductors for the synthesis of GE-based composites. In general, these composites are prepared from the reduction of GO-based materials through a chemical method or heat treatment. However, these methods not only use toxic hydrazine hydrate, but also suffer from some harsh conditions.

To the best of our knowledge, no investigation concerning the nanocomposite which consisted of WO$_3$ nanowire clusters and GE nanosheets for water splitting has been reported. Guo et al. reported that WO$_3$@GE composite showed improved photocatalytic activity to drive the water-splitting reaction to produce oxygen [25]. Ng et al. incorporated reduced graphene oxide with WO$_3$ nanoparticles,
achieving 1.6 times improvement in the photocurrent generation [26]. In the present work, GE-WO₃ nanowire clusters were synthesized via a facile hydrothermal method. First, the structures and morphologies of the as-synthesized samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and ultraviolet-visible diffuse reflectance spectroscopy (DRS) techniques. Then, the photocatalytic O₂ evolution properties of the samples were investigated by measuring the amount of evolved O₂ from water splitting.

2. Experimental

2.1. Synthesis of GE-WO₃ Nanowire Clusters. All of the chemical reagents were analytical grade and were used without further purification. GO was synthesized from natural graphite powder based on modified Hummers method [11]. GE-WO₃ nanowire clusters were synthesized via a facile hydrothermal method. Typically, Na₂WO₄ · 2H₂O and polyethylene glycol (PEG-4000) were directly dissolved in deionized water, and the pH value of the solution was adjusted to 1.5 adding HCl/NaOH solution. Different weight ratios between GO powders and WO₃ nanowire clusters (at 1.0 wt%, 1.5 wt%, 2.0 wt%, 3.0 wt%, and 4.0 wt%) were dispersed rapidly in ethanol with ultrasonic. Then, the two solutions were mixed and transferred into the Teflon-lined stainless steel autoclave with a capacity of 100 mL. Hydrothermal treatments were carried out at 180°C for 30 h. After that, the autoclave was allowed to cool down naturally. Subsequently, the products were collected and washed with deionized water and ethanol several times and dried at 70°C for 12 h in air. Finally, the products were annealed at 400°C for 4 h under nitrogen atmosphere. Pure WO₃ nanowire clusters were also obtained through a similar procedure only in the absence of GO.

2.2. Characterization. The XRD patterns obtained on a D/max-III X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å) at a scan speed of 0.05° s⁻¹ were used to determine phase structure. The morphologies of the samples were evaluated by transmission electron microscopy (TEM, JEOL JEM-2010 at 200 kV). Fourier transform infrared (FT-IR) spectroscopy was recorded on a Bruker VECTOR22 FT-IR spectrometer using KBr pellets. Chemical bonding between the functional groups and carbon atoms was confirmed by X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA System). Raman spectra were recorded on a microscopic confocal Raman spectrometer (Renishaw 1000 NR). The UV-visible spectra were obtained via UV-visible spectrophotometer (Shimadzu UV-2500, Japan).

2.3. Photocatalytic Oxygen Evolution Experiments. Photocatalytic oxidation reactions were carried out in a self-made Lab Solar gas photocatalysis system with external light irradiation. The reaction temperature was kept at ca. 25°C using the temperature-controlled cooling water. The light source was a 150 W xenon lamp with λ = 400~700 nm and was used as the simulated sunlight source (CEL-HXUV150, China). Before the photochemical reaction, 500 mL of deionized water was degassed by boiling it for 0.5 h and cooling to room temperature and then adding it to the reactor. Then, 2 g of the obtained photocatalysts and 100 mL of 0.1 mol/L Fe₃(PO₄)₃ were added to the reactor under magnetic vigorous stirring to ensure the mixture suspend, using H₂SO₄ solution to adjust the pH of the mixture at 2. The amount of O₂ evolved was determined using gas chromatography (TCD: thermal conductivity detector, nitrogen carrier gas).

3. Results and Discussion

Figure 1 shows the XRD patterns of the as-synthesized samples. As for the GO, the sharp (001) diffraction peak at 10.46° illustrates that most of the natural graphite has been oxidized into GO. All the diffraction peaks of the pure WO₃ nanowire clusters can be indexed to hexagonal WO₃ (JCPDS card no. 33-1387). There are no peaks detected for other phases, indicating that single phase of WO₃ with high purity has been synthesized. The main diffraction peaks of the GE-WO₃ nanowire clusters with 2.0 wt% GE are similar to that of pure WO₃ nanowire clusters; no diffraction peak of GO can be seen, indicating the great of GO has been reduced to GE on this occasion. However, no characteristic peaks of GE are presented in the WO₃@GE nanocomposites because of the small content of GE used [28].

Raman spectra of the GO and GE-WO₃ nanowire clusters are shown in Figure 2. The Raman spectrum of GO displays two prominent peaks at around 1595 cm⁻¹ and 1346 cm⁻¹, which correspond to the well-documented G and D bands. The G band corresponds to the E₂g mode observed for sp² carbon domains, whereas the D band is associated with sp³ hybridized carbon or structural defects. The Raman spectrum of GE in GE-WO₃ nanowire clusters also contains both G and D bands (at around 1601 cm⁻¹ and 1359 cm⁻¹, resp.). However, an increased D/G intensity ratio is also observed in comparison with that of the GO spectrum. This change suggests a decrease in the average size of the sp² domains.

![Figure 1: XRD patterns of (a) GO, (b) WO₃ nanowire clusters, and (c) GE-WO₃ nanowire clusters.](image-url)
upon reduction of the exfoliated GO and can be explained by the creation of numerous new graphitic domains that are smaller in size than the ones presented in exfoliated GO.

Figure 3 shows the TEM images of WO\textsubscript{3} nanowire clusters and GE-WO\textsubscript{3} nanowire clusters with 2.0 wt% GE. It is apparent that the WO\textsubscript{3} samples display nanowire cluster-like morphology. Careful examination of the TEM image reveals that many thinner nanowires assembled together along the axis direction form nanowire clusters. The morphology of the GE-WO\textsubscript{3} nanowire clusters is consisting of WO\textsubscript{3} nanowire clusters and thin stacked flakes. It is obvious that WO\textsubscript{3} nanowire clusters are uniformly dispersed within the GE nanosheets. This nanostructure enables a multichannel environment to facilitate the efficient charge interaction.

X-ray photoelectron spectroscopy (XPS) is an effective technique to analyze surface chemical states. The C1s XPS spectra of GO and the GE-WO\textsubscript{3} nanowire clusters with 2.0 wt% GE are shown in Figure 4, respectively. For the GO, the peak with a binding energy of 284.6 eV can be attributed to the C–C and C–H bonds, while the other three peaks centered at the binding energies of 286.3, 287.7, and 289.2 eV can be assigned to the C–O, C=O, and O=C–OH functional groups, respectively. For the GE-WO\textsubscript{3} nanowire clusters, the relative intensity of the sp\textsuperscript{2} carbon (C–C, 284.6 eV) shows a significant increase, suggesting a sufficient reduction of GO to GE.

Figure 5 shows the FT-IR spectra of the GO and GE-WO\textsubscript{3} nanowire clusters with 2.0 wt% GE. For the GO, the broad absorption band at 3430.11 cm\textsuperscript{-1} is related to the stretching peak of the C–OH group, and the characteristic absorption bands of GO are observed at 984.21 cm\textsuperscript{-1} (epoxy stretching), 1099.91 cm\textsuperscript{-1} (alkoxy C–O stretching), 1224.89 cm\textsuperscript{-1} (phenolic C–OH stretching), 1401.85 cm\textsuperscript{-1} (carboxyl O–H stretching), and 1723.76 cm\textsuperscript{-1} (C=O stretching vibrations of carboxyl or carbonyl groups). The peak at 1624.76 cm\textsuperscript{-1} is related to H–O–H bending band of the adsorbed H\textsubscript{2}O molecules or the in-plane vibrations of sp\textsuperscript{2} hybridized C–C bonding. For the GE-WO\textsubscript{3} nanowire clusters, as compared to the peaks of the functional groups of GO, the broad absorption peak at 866.71 cm\textsuperscript{-1} is ascribed to the vibration of W–O–W bond. It is also found that the peaks at 1723.76 cm\textsuperscript{-1}, 1224.89 cm\textsuperscript{-1}, and 1089.91 cm\textsuperscript{-1} in the composites have disappeared, suggesting a sufficient reduction of GO to GE.

The UV-vis diffuse reflectance spectra of the WO\textsubscript{3} nanowire clusters and GE-WO\textsubscript{3} nanowire clusters with 2.0 wt% GE are shown in Figure 6. According to the spectrum, the WO\textsubscript{3} nanowire clusters show a sharp edge at about...
The C1s XPS spectra of (a) GO and (b) GE-WO₃ nanowire clusters.

The FT-IR spectra of GO and GE-WO₃ nanowire clusters.

The UV-vis diffuse reflectance spectra of WO₃ nanowire clusters and GE-WO₃ nanowire clusters.

The photocatalytic activities of the as-prepared GE-WO₃ nanowire clusters with different weight ratios of GE in terms of evolved O₂ from water splitting are measured, and the results are shown in Figure 7. For bare WO₃ nanowire clusters, the amount of evolved O₂ from water splitting after 8 h is ca. 0.175 mmol/L. The photocatalytic activity of the GE-WO₃ nanowire clusters can be enhanced with increasing the weight ratio of GO up to 2.0 wt%. This result indicates that the GE-WO₃ nanowire clusters with 2.0 wt% GE exhibit the maximum evolved O₂ from water splitting (ca. 0.345 mmol/L). This is attributed to GE which serves as an acceptor of the electrons generated in the WO₃ and effectively decreases the recombination probability of the photogenerated electron-hole pairs. Further increasing the weight ratio of GO will lead to a decrease, especially in GE-WO₃ nanowire clusters with 4.0 wt% GE. It is reasonable because the introduction of a large percentage of black GE leads to shielding of the active sites on the catalyst surface [19].

The efficient charge separation and transfer are crucial for the enhanced photocatalytic activity of the GE-WO₃ nanowire clusters. GE has a charge-carrier mobility of 200000 cm² V⁻¹ s⁻¹ at room temperature, so it is very possible that the incorporation of GE may enhance the charge separation efficiency and suppress the charge recombination as suggested in Figure 8. Under visible light irradiation, electrons (e⁻) and holes (h⁺) are generated in the WO₃ nanowire
clusters (see (1)). WO₃ is photocatalyst with weak reducing power, which prohibits the electron transfer to reduce H₂O to H₂. Therefore, only holes reaction with water to produce O₂ can occur spontaneously by using the photocatalyst (see (2)). However, photogenerated electrons can transfer to carbon atoms on the graphene sheets and then react with Fe³⁺ ions as the scavenger to reduce the recombination of electron-hole pairs (see (3)). Thus, GE serves as the photogenerated electrons acceptor and effectively suppresses the charge recombination in the GE-WO₃ nanowire clusters, leaving more positive charged holes on the WO₃ surface and promoting the production of oxygen:

\[
\text{WO}_3 \xrightarrow{hv} e^- + h^+ \quad (1)
\]

\[
2\text{H}_2\text{O} + 4h^+ \rightarrow 4\text{H}^+ + \text{O}_2 \quad (2)
\]

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad (3)
\]

4. Conclusions

In summary, GE-WO₃ nanowire clusters were synthesized by a facile hydrothermal method. The GE-WO₃ nanowire clusters with 2.0 wt% GE exhibited enhanced performance compared to pure WO₃ nanowire clusters for O₂ evolution from water splitting. The sensitization of WO₃ nanowire clusters by GE enhanced the visible light absorption property of GE-WO₃ nanowire clusters. The chemical bonding between WO₃ and GE reduced the recombination of the photogenerated electron-hole pairs, leading to improved photocatalytic activity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work was supported by the Natural Science Foundation of China (Grants nos. 51272075, 51372080) and the China Postdoctoral Science Foundation (2012M521220). This work was also financially supported by the Department of Education of Hunan Province, China (Grant no. 11B054).

References


