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Enhanced photoelectric performance of GQDs anchored \( \text{WO}_3 \) with a ‘dot-on-nanoparticle’ structure

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Abstract

\( \text{WO}_3/\text{GQDs}-\text{H} \) composites were synthesized by a hydrothermal method using \( \text{WCl}_6 \) as the tungsten source. Various analyses were conducted to investigate the composition, structure, morphology and performance of the composites. \( \text{WO}_3/\text{GQDs}-\text{H} \) composites formed a special ‘dot-on-nanoparticle’ structure by anchoring GQDs on the surface of \( \text{WO}_3 \). The lattice spacings of 0.34 and 0.386 nm were attributed to the (002) facets of GQDs and \( \text{WO}_3 \), respectively. Compared to blank \( \text{WO}_3 \), an obvious shift to higher value in the binding energy of \( \text{W}^{6+} \) and \( \text{W}^{5+} \) and a decreased \( I_{13}/I_{11} \) value in the Raman spectra could be observed for \( \text{WO}_3/\text{GQDs}-\text{H} \) composites. The photocurrent value of hydrothermal synthesized \( \text{WO}_3/\text{GQDs}-\text{H} \) composites achieved \( 1.56 \times 10^{-5} \) A cm\(^{-2} \), which was obviously prior to that of blank \( \text{WO}_3 \) and mechanically mixed \( \text{WO}_3/\text{GQDs} \). The result indicated that the hydrothermal process promoted GQDs as a conductive route to transfer photoexcited electrons and improve the photoelectric performance of \( \text{WO}_3/\text{GQDs} \) in comparison to the mechanical mixture process.

1. Introduction

As an n-type semiconductor with a tunable bandgap (2.4–2.8eV), tungsten oxide (\( \text{WO}_3 \)) possessed rapid response to visible light, excellent gas sensitivity, and favorable electron transport ability. Therefore, it is widely used in the fields of photocatalysis, gas sensors, and photoelectronics [1–5]. For instance, Yang et al fabricated light-emitting devices based on n-typed \( \text{WO}_3 \) nanorod arrays [6]. Wang et al investigated the effects of crystallinity on the electron-transfer of sol-gel \( \text{WO}_3 \) films [7]. It is crucial for electron-transporting materials to retard the carrier recombination at transfer interfaces, but the photoelectric performance of pristine \( \text{WO}_3 \) was still limited by its low separation efficiency and high recombination rate of photogenerated electron–hole pairs. To solve these obstacles, various efforts have been made to improve the photoelectron transfer of \( \text{WO}_3 \) by introducing conductive materials. For example, Ibrahim et al employed a method of pulsed laser ablation in liquids to anchor \( \text{WO}_3 \) nanoparticles on reduced graphene oxide sheets [8]. Jun et al constructed reduced graphene oxide/tungsten trioxide heterojunction by coupling \( \text{WO}_3 \) preferential planes with graphene sheets [9]. The charge-transfer ability of \( \text{WO}_3 \)-graphene was promoted by the incorporation of \( \text{WO}_3 \) and graphene sheets, but the sheets at micrometer scale tend to aggregate in a stacking structure and precipitate in solvents, which significantly limits their photoelectric performances in nanometer-scale.

Nowadays, there are more and more in-depth studies on the development and structural-properties of carbon nanostructures [10–14]. As 2D graphene sheets were cut down to \( \text{0D} \) pieces, nano-sized graphene quantum dots (GQDs) have captured considerable attention due to the quantum confinement effect, small size effect, and superior electron-transfer ability [15–20]. Several reports on GQDs based composites are available in the literature. Li et al provided an approach in designing modified \( \text{MoS}_2 \)/graphene quantum dots heterostructures [21]. Fei et al prepared graphene quantum dots modified \( \text{Bi}_2\text{WO}_6 \) composites with a low recombination rate of photo-induced electrons [22]. Yuan et al employed a hydrothermal treatment to fabricate GQDs decorated graphitic carbon nitride nanorods [23]. GQDs can accelerate the photo-induced charge separation, shorten the charge-transfer path, and improve the conductivity and mobility of GQDs based
composites. However, literatures on the construction of ‘dot-on-nanoparticle’ structure with GQDs and WO$_3$ were rarely discussed, and reports integrating interfacial charge-transfer and photocurrent responses were scarcely investigated.

Based on the above analysis and our previous work [24–26], a continuing effort was proposed to construct GQDs anchored WO$_3$ nanoflakes, which was aimed to obtain a special structure to break the shackles of WO$_3$ widely used in sensors and supply the foundation in the field of photoelectronics. A simple hydrothermal process was employed to prepare WO$_3$/GQDs composites, and various analyses are conducted to determine the structure, morphology, and materials performance of the synthesized composite.

2. Experimental details

2.1. Materials

Tungsten hexachloride (WCl$_6$) was produced by Shanghai Macklin Biochemical Co., Ltd Natural flake graphite, sodium nitrate (NaNO$_3$), sulfuric acid (H$_2$SO$_4$), hydrogen peroxide (H$_2$O$_2$), absolute ethanol (CH$_3$CH$_2$OH), nitric acid (HNO$_3$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Potassium permanganate (KMnO$_4$) was obtained from Tianjin Hengfa Chemical Reagent Co., Ltd. Nafion solution were provided by DuPont China Group Co., Ltd.

2.2. Preparation of graphene quantum dots

GQDs were prepared by an uncomplicated and simplified process where the nitric acid was considered as a shearing agent [27]. In brief, 50 mg of graphite oxide prepared by the modified Hummers’ method was dispersed in 50 ml of concentrated nitric acid solution, and the mixture was ultrasonicated for 4 h. Subsequently, the brownish-yellow solution was poured into an autoclave and heat-treated at 180 °C for 24 h. After the resulting product was washed several times with ethanol and deionized water, it was transferred into a tube furnace and annealed at 400 °C for 2 h under the protection of nitrogen. The resulting black powders were GQDs.

2.3. Preparation of WO$_3$/GQDs composites

WO$_3$/GQDs composites were synthesized by a hydrothermal method (WO$_3$/GQDs-H). Briefly, 1.0 g of WCl$_6$ was dispersed in 60 ml of deionized water, and then a certain amount of GQDs powders were added to the mixed solution. The solution was mixed for 1 h and autoclaved at 180 °C for 24 h. After the resulting product was washed several times with ethanol and deionized water, it was transferred into a tube furnace and annealed at 400 °C for 2 h under N$_2$ atmosphere. For contrast, blank WO$_3$ was prepared by the same way in the absence of GQDs. The prepared WO$_3$ and GQDs were mechanically mixed, and the mixture was denoted as WO$_3$/GQDs-M.

2.4. Characterization

The structure and morphology were characterized via a D8/Advance x-ray diffractometer (XRD), a Zeiss Ultra Plus Fließ emission scanning electron microscope (FESEM) and a JEM-2100F transmission emission microscopy (TEM), respectively. The thickness of GQDs was characterized via a Multimode 8 atomic force microscopy (AFM). The Raman spectra of samples were measured on a RENISHAW Raman microscope. The detailed chemical components of samples were characterized by an ESCALAB 250XI XPS. UV–vis absorption spectra were recorded on a UV5500 spectrophotometer. Photocurrent-time, linear sweep voltammetry and interfacial impedance curves were recorded using a standard three-electrode electrochemical workstation (CHI650E) with a saturated calomel reference electrode, a Pt counter electrode, and a working electrode coated with WO$_3$ or WO$_3$/GQDs.

3. Results and discussion

AFM image of GQDs was shown in figure 1(a). GQDs prepared by nitric acid shearing presented a thickness of 1.8 – 3 nm corresponding to 3 – 6 graphene layers. The statistical distribution of thickness was demonstrated in figure 1(b). In order to obtain further morphology of WO$_3$/GQDs-H composites, the SEM, EDS with elemental mapping images of WO$_3$/GQDs-H composites were shown in figures 2(a)–(e). As shown in figure 2(a), WO$_3$/GQDs-H composites exhibited the nanolamellae-like structure. GQDs weren’t observed in this image due to the possible reason that the size of GQDs was too small to be observed. Only W, O and C were observed in EDS image (figure 2(b)) for WO$_3$/GQDs-H composites, and no other hetero elements existed. It could be seen in element mapping images of W, O, and C (figures 2(c)–(e)) that GQDs were evenly distributed in WO$_3$. TEM images of WO$_3$/GQDs-H composites prepared via a one-step hydrothermal method were shown in
It could be seen from the figures that WO$_3$/GQDs-H composites were constructed by the nanolamellae-like structure as shown in SEM results. In the enlarged HRTEM images of WO$_3$/GQDs-H composites, three interplanar spacings of 0.386, 0.377 and 0.365 nm were indexed to the (002), (020) and (200) planes of WO$_3$, respectively. Moreover, the interplanar distance of 0.34 nm was ascribed to the (002) plane of GQDs which were anchored on the surface of WO$_3$ nanoplates to form ‘dot-on-nanoparticle’ structure. The SAED pattern of WO$_3$/GQDs-H composites was shown in figure 3(e). The (200) and (1120) facets were attributed to WO$_3$ and GQDs, respectively. The highly crystalline monoclinic phase of WO$_3$ can still be maintained with adding GQDs.

The XRD patterns of pure WO$_3$ and hydrothermally synthesized WO$_3$/GQDs-H composites were shown in figure 4(a). Three strong diffraction peaks of WO$_3$/GQDs-H appeared at 23.00°, 23.48° and 24.26°, matching (002), (020), and (200) crystal planes of WO$_3$, respectively [9]. Other diffraction peaks were also assigned to JCPDS 72-0677, and no impurities were observed in the patterns of WO$_3$/GQDs. According to the Bragg’s Law: $2d\sin \theta = n\lambda$, where $d$, $\theta$, $\lambda$ and $n$ represented interplanar spacing, glancing angle, wavelength of x-rays, and diffraction order, respectively. Three kinds of interplanar spacings corresponding to three strong diffraction peaks could be calculated as 0.38636 nm, 0.37860 nm, and 0.36657 nm, respectively. The theoretical calculation results were also roughly consistent with the interplanar spacing observed by figures 3(c) and (d). The diffraction peaks of WO$_3$ were similar to those of WO$_3$/GQDs-H, indicating that GQDs anchored on WO$_3$ nanolamellae-like structure could not change the crystalline phase of WO$_3$. Moreover, the XRD pattern of GQDs was provided in figure 4(b). A broad diffraction peak attributed to GQDs appeared at around 2$\theta$ of 25.6°, and the corresponding lattice spacing calculated according to Bragg’s Law is 0.34768 nm. The broad peak of GQDs was not observed from WO$_3$/GQDs-H, which was ascribed to the possible reason that the amount of GQDs was too low to be detected.

Furthermore, the structure of the samples was characterized by Raman spectroscopy. As shown in figure 5, the Raman spectrum of GQDs (curve a) exhibited the D and G peaks at 1351 and 1600 cm$^{-1}$, respectively. The intensity ratio of D and G peaks ($I_D/I_G$) achieved 0.95, which was used to demonstrate the structural disorder of graphite materials. Meanwhile, the Raman spectrum of hydrothermally synthesized WO$_3$/GQDs-H (curve b) presented the D and G peaks at 1351 and 1591 cm$^{-1}$, respectively, and the value of $I_D/I_G$ decreased to 0.90. The results demonstrated that the hydrothermal process lowered the structural disorder and promoted to form a
stable ‘dot-on-nanoparticle’ structure. The characteristic peaks of WO₃ (inset) at 721 and 810 cm⁻¹ were attributed to the stretching vibration of O-W-O, and those at 274 and 331 cm⁻¹ were indexed to the bending vibration of O-W-O [28].

To explore the elemental composition and binding states of WO₃ and WO₃/GQDs-H, XPS was employed and displayed in figure 6. The XPS survey spectra of WO₃ (figure 6(a)) and hydrothermal synthesized WO₃/GQDs-H (figure 6(d)) demonstrated the existence of W&O and W&O&C atoms, respectively. The
element C was associated with GQDs in the composites, which was consistent with the results of Raman analysis.

The high-resolution spectrum of W 4f for WO$_3$ (Figure 6(b)) was deconvoluted into four peaks at the binding energy of 33.59, 34.94, 35.87, and 37.08 eV. Therein, two strong peaks of 34.94 and 37.08 eV corresponded to the binding energy of W 4f$_{7/2}$ and W 4f$_{5/2}$ of W$_6$ state, while two weak peaks located at 33.59 and 35.87 eV were

Figure 3. TEM images of WO$_3$/GQDs-H (a)–(b), HRTEM images of WO$_3$/GQDs-H (c)–(d) and the SAED pattern of WO$_3$/GQDs-H composites.
Figure 4. The XRD patterns of the prepared WO₃, WO₃/GQDs-H (a) and GQDs (b).

Figure 5. Raman spectra of GQDs (a) and WO₃/GQDs-H (b), inset: WO₃.
Figure 6. Survey (a) and high-resolution XPS spectra of W 4f (b) and O 1s (c) for blank WO$_3$; survey (d) and high-resolution XPS spectra of W 4f (e), O 1s (f) and C 1s (g) for WO$_3$/GQDs-H.
assigned to W\textsuperscript{5+} state \cite{29}. After GQDs were anchored on WO\textsubscript{3}, that of W 4f for WO\textsubscript{3}/GQDs-H (figure 6(e)) was split into two pairs of peaks including 35.24 & 37.39 eV and 34.08 & 36.11 eV, which were indexed to W\textsuperscript{6+} and W\textsuperscript{5+} states, respectively. Part of the reduced WO\textsubscript{3} might originate from the formation of surface defects, which was reported in other literatures \cite{30,31}. By comparing the high-resolution W 4f spectra of WO\textsubscript{3} and WO\textsubscript{3}/GQDs, the binding energy of W\textsuperscript{6+} and W\textsuperscript{5+} for WO\textsubscript{3}/GQDs-H shifted to higher values, probably owing to the interaction between WO\textsubscript{3} and WO\textsubscript{3}/GQDs during the hydrothermal synthesis of the composites. Two peaks at 529.8 and 530.3 eV appeared in the high-resolution O 1s spectrum of pure WO\textsubscript{3} (figure 6(c)), corresponding to the binding energy of lattice oxygen and the oxygen in WO\textsubscript{3}, respectively \cite{28}. While three peaks at 530.0, 530.5, and 531.2 eV in the high-resolution O 1s spectrum of WO\textsubscript{3}/GQDs-H, matching with the lattice oxygen, the lattice oxygen or O=C attributed to GQDs and chemisorbed oxygen species, respectively. Figure 6(g) exhibited three peaks at 284.2, 285.8, and 288.14 eV, which corresponded to the binding energy of C–C, C–O or C–OH, and C=O \cite{32}.

To characterize the photo-response performances of WO\textsubscript{3} and WO\textsubscript{3}/GQDs-H, the UV–vis spectra, photocurrent-time curves and linear sweep voltammetry were performed and displayed in figures 7–9, respectively. GQDs (figure 7(a)) exhibited a shoulder peak in the range of 260–290 nm corresponding to the $\pi \rightarrow \pi^*$ transition of C=C \cite{33}. The characteristic absorption peak of WO\textsubscript{3} (figure 7(b)) appeared at 346 nm, while that of WO\textsubscript{3}/GQDs-H (figure 7(c)) presented a red-shift from 346 nm to 381 nm. Photocurrent responses curves of WO\textsubscript{3}, WO\textsubscript{3}/GQDs-H, and WO\textsubscript{3}/GQDs-M were collected in a standard three-electrode system with a continuous 60s ‘on/off’ procedure as illustrated in figure 8. The photocurrent value of WO\textsubscript{3}/GQDs-H was
boosted at $1.56 \times 10^{-5}$ A cm$^{-2}$, which is about 1.6 times as high as that of pure WO$_3$ ($0.98 \times 10^{-5}$ A cm$^{-2}$), while the value of WO$_3$/GQDs-M merely reached $1.05 \times 10^{-5}$ A cm$^{-2}$, which presented almost no significant improvement compared to that of pure WO$_3$. The results indicated that the hydrothermal synthesis played a vital role in improving the photoelectric properties of WO$_3$/GQDs in comparison to the mechanical mixture. Figure 9 showed the LSV curves of WO$_3$ and WO$_3$/GQDs-H composites under optical radiation. When the positive potential continues to increase, WO$_3$/GQDs-H composites had a more obvious advantage in generating a larger photocurrent density under the optical radiation. This result was also consistent with that of photocurrent responses. The possible reason for this result was that the introduction of GQDs promoted the
separation of electron-hole pairs in WO₃, in the meantime, GQDs could also generate photo-generated electrons. On the basis of photocurrent-time analyses, a possible mechanism was presented in figure 10 [34–38]. When the light source was irradiated on the surface of FTO glass coated with WO₃/GQDs, photo-generated electrons were transported from valence band (VB) to the conduction band (CB) and subsequently conducted to the FTO substrate. As shown in figure 10(a), GQDs served as a conductive route for photoexcited electrons, promoting the charge transfer rate of WO₃ and weakening the combination of electron-hole pairs in the hydrothermally synthesized composites. While nano-sized GQDs tended to aggregate instead of anchoring on the surface of WO₃ in the mechanical mixture system, as illustrated in figure 10(b), only a small part of electrons transported from WO₃ to GQDs since aggregated GQDs were not beneficial to anchor on the surface of WO₃, leading to a blocked route transported to the FTO substrate.

Electrochemical impedance spectra measurements of WO₃ (a), WO₃/GQDs-H (b), and WO₃/GQDs-M (c) were shown in figure 11 used a Nyquist diagram. The charge-transfer resistance of blank WO₃ was significantly larger than that of WO₃/GQDs composites synthesized by the hydrothermal method and mechanical mixture. The result showed that GQDs promoted a valid path to transport charges in the electrode-electrolyte interface [39]. The interfacial conductivity of WO₃/GQDs-H was prior to that of WO₃/GQDs-M since the smaller charge-transfer impedance and the faster charge-transfer rate occurred on the composites by hydrothermal decorating with GQDs.

4. Conclusion

In summary, a simple hydrothermal method was employed to combine WO₃ with GQDs and form a special ‘dot-on-nanoparticle’ structure. Compared to blank WO₃, the Raman spectrum of WO₃/GQDs-H presented a decreased I_D/I_G value corresponding to the higher order degree constructed by the hydrothermal process. Meanwhile, the binding energy of W⁶⁺ and W⁵⁺ for WO₃/GQDs shifted to higher values, probably owing to the interaction between WO₃ and WO₃/GQDs-H during the hydrothermal synthesis of the composites. The photocurrent value and charge-transfer resistance of hydrothermal synthesized WO₃/GQDs-H were prior to those of WO₃/GQDs-M and blank WO₃. The result showed that GQDs promoted a valid path to transport charges in hydrothermally synthesized WO₃/GQDs as compared to mechanically mixed composites. According to the existing results in this work, it is hoped that the WO₃/GQDs composites can be helpful in the field of photoelectronics, photocatalysis, etc.

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