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The Assembly of Vanadium (IV)-Substituted Keggin-type Polyoxometalate/Graphene Nanocomposite and its application in photovoltaic system

Dan Xu, Wei-Lin Chen*, Jian-Sheng Li, Xiao-Jing Sang, Ying Lu, Zhong-Min Su and En-Bo Wang*

1 Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX
DOI: 10.1039/c0xx00000x

The SiW$_{11}$V/graphene nanocomposite was firstly prepared and introduced into the TiO$_2$ film. It showed a significant photocurrent response, which can be attributed to the photoinduced electrons of SiW$_{11}$V. This work provides a promising strategy for exploring POMs sensitizer with a lower energy level than the CB of TiO$_2$.

Polyoxometalates (POMs) are a typical class of transition metal–oxygen clusters with a variety of structures, element compositions, and functionalities, which have received extensive attention owing to their excellent properties. POMs can undergo a stepwise multi-electron reversible redox process without any structure changes. In addition, the absorption spectra of POMs can be regulated by introducing multiple transition metal elements, which can even cover as much as the whole UV-Visible light spectrum. Recently, POMs have represented great potentials to apply in the Dye-sensitized solar cells (DSSCs) as the photosensitizers, and introduced into the TiO$_2$ and FTO, the 2D graphene behave as an electron acceptor in the solar photovoltaic system, owing to their low energy level and fast electron transport property, which may transport the photoinduced electrons of POMs rapidly and effectively. Graphene oxide (GO) is a precursor for POM/graphene nanocomposites synthesized by various reduction methods, such as UV photoreduction, electrochemical reduction, chemical reduction fabrication methods, and so on.

Graphene has an unusual feature that its band gap is exactly zero. The surface functional groups and lattice defects in graphene sheets can help to anchor and immobilize nanoparticles on it, and the stability of nanoparticles can be improved by dispersing on graphene. So graphene is the unique candidate as 2-D catalyst support due to these advantageous structural and physicochemical properties. Graphene has been introduced into the photoanode of DSSCs since the energy level of graphene is lower than the CB of TiO$_2$. Therefore, it is of great significance to explore alternative methods for effectively transferring the photoinduced electrons of POMs.

Herein, graphene may be the promising support for POMs, which has attracted considerable attentions owing to its high surface area, extraordinary electronic properties, electron transport capabilities and high mechanical and thermal properties. Furthermore, graphene has an unusual feature that its band gap is exactly zero. The surface functional groups and lattice defects in graphene sheets can help to anchor and immobilize nanoparticles on it, and the stability of nanoparticles can be improved by dispersing on graphene. So graphene is the unique candidate as 2-D catalyst support due to these advantageous structural and physicochemical properties. Graphene has been introduced into the photoanode of DSSCs since the energy level of graphene is lower than the CB of TiO$_2$ and FTO, the 2D graphene behave as an electron transfer channel in the photoanode, which brought a faster electron transformation and a lower recombination.

In this paper, SiW$_{11}$V/graphene nanocomposite is prepared by a simple two-step chemical reduction approach at room temperature, which is a facile and friendly environmental method. As shown in Fig. 1, in the first step, SiW$_{11}$V is reduced by mild reducing agents (LDAA and zinc powder), then the heteropoly blue (HPB) solution react with GO to assemble SiW$_{11}$V clusters on the graphene sheets. Otherwise, the excess LDAA in the first step can also reduce GO in this system, L-AA is the reductant for both SiW$_{11}$V and GO. Herein, the SiW$_{11}$V/graphene nanocomposites were introduced into the TiO$_2$ films, the photovoltaic performance of the composite films was investigated by photocurrent transient measurements, the photocurrent responses of which have a significant increase compared with the blank TiO$_2$ particle film. As far as we know, it is the first time that SiW$_{11}$V/graphene nanocomposite is prepared and introduced into the TiO$_2$ film.

Fig. 1 The process of the assembly of SiW$_{11}$V/graphene nanocomposite.
assembly of SiW$_{11}$V clusters on the RGO sheets were confirmed by the X-ray powder diffractions (XRD). Fig. S3 shows the XRD patterns of raw graphite (a), GO (b), RGO (c), SiW$_{11}$V (d) and SiW$_{11}$V/graphene-3 (e). The raw graphite shows a strong peak at 20 = 26.5°, corresponding to a d-spacing of 3.36 Å. As for GO, the peak of graphite is absent, while a new peak at 20 = 11.8° is arisen, which is consistent with an average interlayer spacing of 7.49 Å. Since GO has lots of oxygen-containing functional groups attached on its both sides, so the average interlayer spacing of GO is increased.[17] After the reduction process, there is a broad 002 peak at 23.5°, the interlayer spacing decreases from 7.49 Å of the pristine GO to 3.78 Å, indicating that RGO are successfully obtained. In the pattern of SiW$_{11}$V/graphene-3, the 002 reflection is broader than RGO, suggesting that the order of the SiW$_{11}$V/graphene-3 is very poor along the stacking direction, implying that the sample is mostly composed of single or a few layers of RGO.[17, 18] It also indicates that SiW$_{11}$V clusters are successfully incorporated into the adjacent graphene sheets. At the same time, the SiW$_{11}$V does not show the characteristic diffraction patterns in the pattern of SiW$_{11}$V/graphene-3, which implies that SiW$_{11}$V clusters exist with the dispersed state, but not the crystalline state.[13]

Moreover, the high resolution transmission electron microscope (HRTEM) images and the energy dispersive X-ray spectroscopy (EDS) further indicate that the SiW$_{11}$V clusters exist in the dispersed state on graphene. The TEM images of RGO and SiW$_{11}$V/graphene-3 (Figs. S4 and 2a) exhibit crumpled and paper-like nanosheet morphology of the samples. In the high magnification HRTEM image of SiW$_{11}$V/graphene-3 (Fig. 2b), SiW$_{11}$V clusters can be observed clearly as small dark spots, no agglomerate or nanocrystal can be detected, and the size of clusters are around 1−3 nm. Besides that, the SiW$_{11}$V clusters on the graphene surface are in a uniformly dispersed state, which is consistent with the XRD results. The EDS analysis of SiW$_{11}$V/graphene-3 shows the C, Si, W and V elements can be observed obviously (Fig. S5).

X-ray photoelectron spectra (XPS) was also used to detect the reduction degree of GO. Fig. 3a shows the C 1s XPS spectra of GO, four types of carbon with different chemical states are observed: 284.6 eV (sp$^2$ C), 286.7 eV (C=O), 287.7 eV (C=O), and 288.8 eV (O=C=O), respectively. After the reduction, the content of oxygen-containing groups decreases dramatically, especially the peak of C=O (Fig. 3b and 3c). In addition, there is an additional component at 285.4 eV corresponding to sp$^3$ C in the spectra of SiW$_{11}$V/graphene-3, which reveals that the reduction can effectively remove most oxygen-containing groups.[15] Since SiW$_{11}$V/graphene-3 has less oxygen-containing functional groups than SiW$_{11}$V/graphene-1, the relatively high original concentration of SiW$_{11}$V may result in a more efficient and deeper reduction of GO. The W4f XPS spectra of SiW$_{11}$V/graphene-3 nanocomposite shown in Fig. 3d indicates that the W$^{6+}$F$_{5/2}$ and W$^{5+}$F$_{5/2}$ peaks are located at 35.0 eV and 37.1 eV, which are consistent with the W$^{6+}$ oxidation state, indicating the oxidized state form of the POM anions.[15]

Moreover, thermogravimetric analyses (TGA) are carried out to study the significant structural changes occurring during the chemical reduction process, the contents of SiW$_{11}$V clusters on the SiW$_{11}$V/graphene nanocomposite and the thermal stability of the samples. The thermal stability investigations of K$_4$[SiW$_{11}$V$_6$O$_{40}$]·7H$_2$O (Fig. S6) indicate that there is no significant mass loss observed even heated to 600 °C, suggesting the good thermal stability of the chosen POM.

Fig. S7a shows the TGA curves of GO, RGO and SiW$_{11}$V/graphene-3. The first stage of all the samples (20−100 °C) corresponds to the loss of the adsorbed and crystallization water molecules. The second weight loss of GO occurs at ca. 200 °C, which corresponds to the loss of labile oxygen-containing functional groups in GO.[20] The final weight loss of GO occurred between 500 and 600 °C is attributed to the combustion of carbon matter.[21] The TG curve of graphene presents the structural change induced by the reduction using L-AA, which also confirms that some oxygen functionalities in the GO are not reduced. However, no significant mass loss of SiW$_{11}$V/graphene-3 is detected, revealing that the most oxygen containing functional groups are removed after the reduction and the thermal stability is increased dramatically. The weight residual of SiW$_{11}$V/graphene-3 has a remarkable increase compared to graphene, which may be caused by the SiW$_{11}$V assembled on the graphene.

Under the same conditions, the increasing of the original mass of SiW$_{11}$V results in the increase of the thermal stability and more weight residual for the SiW$_{11}$V/graphene, as shown in Fig. 7b. These observations are consistent with the XPS results (see above), which indicate that the more efficient reduction of GO and more SiW$_{11}$V assemble on RGO can be realized by the relatively high original mass of SiW$_{11}$V. All the studies confirm that SiW$_{11}$V clusters have been successfully attached onto the RGO sheets.

POMs have a strong affinity with graphene, which may be attributed to the electron transfer interaction between graphene and POMs and the protonation-induced electrostatic interaction between POMs and the oxygen-containing groups (such as hydroxyl and carboxyl groups) on the surface of graphene. [14, 22, 23] In our case, the former should be the dominating one,
because the mass of the loaded SiW₁₁V clusters increasing dramatically and the content of retained oxygen-containing groups decreased remarkably as we increasing the original mass of SiW₁₁V. Moreover, the W⁴f₅/₂ and W⁴f₇/₂ peaks of SiW₁₁V/graphene-3 nanocomposite (Fig. 3d) shift to lower binding energies compared with those of SiW₁₁V (the W⁴f₅/₂ and W⁴f₇/₂ peaks of SiW₁₁V are located at 35.8 eV and 37.8 eV in Fig. S8), it also indicates that the electron transfer interaction is the dominating affinity between graphene and POMs in SiW₁₁V/graphene-3 nanocomposite.

Wang et al. have confirmed that 0.6 wt% GO in the photoanode of DSSCs would get the best efficiency. So 4 mg of GO has been used to prepare the SiW₁₁V/graphene nanocomposite, and the composite was introduced into the TiO₂ film (see ESI). The photocurrent response experiments for SiW₁₁V/graphene-3@TiO₂ film, RGO@TiO₂ film and pure TiO₂ film were measured at a constant bias of 0 V (Fig. 4a). This investigation was carried out in the presence of 0.1M Na₂SO₄ aqueous solution. The films were exposed under Xe lamp for 20 s and kept in the dark for another 20 s. As shown in Fig. 4a, the photocurrent response of the RGO@TiO₂ is slightly higher than the pure TiO₂ film. However, compared to the pure TiO₂ and RGO@TiO₂, a more 3-fold increase has been observed of the SiW₁₁V/graphene-3@TiO₂ film.

Fig. 4 I-t curves for the photocurrent response of the films.

In order to examine the operational principle, the energy levels of all the materials are summarized. The energy levels and band gap of SiW₁₁V can be obtained by the CV and diffuse reflectivity spectra. The LUMO of SiW₁₁V is -4.31 eV, which was estimated by the initial reduction potential of SiW₁₁V (-0.19 V vs NHE) in the CV curve (Fig. S9). And the band gap could be determined by the plot of Kubelka–Munk function F against energy E, the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge is the band gap. As can be seen in Fig. S10, the band gap (Eg) of SiW₁₁V was estimated to be 2.67 eV.

The energy level and electron-transfer processes are illustrated in Scheme 1. It can be seen clearly that the energy level of graphene is between the CB of TiO₂ and FTO, graphene in the RGO@TiO₂ film can transport the photoinduced electrons quickly and suppress the recombination and back electron transfer. However, the RGO@TiO₂ film does not have an apparent increase because TiO₂ can only be excited by UV light. As for SiW₁₁V/graphene-3@TiO₂ film, SiW₁₁V has an appropriate band gap, which can be excited by nearly the whole UV-Visible light spectrum, it can be an electrons donor. The LUMO of SiW₁₁V is higher than the energy level of graphene. So the excited electrons of SiW₁₁V can be captured and transported to the FTO rapidly and effectively through the graphene bridges under illumination. On the other hand, SiW₁₁V also act as an electron acceptor and play the role of electron mediator to accelerate the electron transmission and suppress the carrier recombination since the LUMO of SiW₁₁V is lower than the CB of TiO₂. In this system, SiW₁₁V not only acts as an electron acceptor, but also as a sensitizer (electron donor) which has a lower energy level than the CB of TiO₂. Fig. 4b shows the photocurrent responses of SiW₁₁V/graphene-n@TiO₂ film (n = 1, 2, 3), the photocurrent responses of the films are highly dependent on the mass of SiW₁₁V clusters on graphene, the photocurrent increases gradually with the increasing of the mass of SiW₁₁V clusters. This result is attributed to the more absorbance of the UV-Visible light and more electrons injecting to graphene of the SiW₁₁V clusters.

Scheme. 1 Energy level and electron-transfer processes diagram of SiW₁₁V/graphene@TiO₂ film.

In summary, it is the first report that the SiW₁₁V/graphene nanocomposites have been successfully prepared with a simple two-step chemical reduction approach. And the SiW₁₁V/graphene nanocomposite was introduced into the TiO₂ film, which showed a significant photocurrent response. This remarkable increase of the photocurrent response may be attributed to SiW₁₁V can be excited by nearly the full spectrum, and the quick and effective transformation of the photoinduced electrons of SiW₁₁V through the graphene sheets. In this system, SiW₁₁V act as both electron acceptor and electron donor. This work opens a new way for the fabrication of various POM/graphene nanocomposites, and this method is generally suitable for common POMs. Furthermore, it also provides a promising strategy for exploring POMs sensitizer with a lower energy level than the CB of TiO₂.

This work was financially supported by the National Natural Science Foundation of China (no. 21131001 and 21201031), Ph.D. station Specialized Research Foundation of Ministry of Education for Universities (no. 2012043120007), Science and
Notes and references
5 Department of Chemistry, Key Laboratory of Polyoxometalates Science of Ministry of Education, Northeast Normal University, Changchun, 130024, China. Fax: (+86) 431-85098787, E-mail: wangeb889@nenu.edu.cn, chenwl@nenu.edu.cn
† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/


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SiW_{11}V in the nanocomposite can absorb nearly full spectrum, the excited electrons of which can be transferred through the graphene.