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Supporting information

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

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Experimental

Chemicals and materials: $K_6[SiW_{11}V^{IV}O_{40}]\cdot 7H_2O$ and graphene oxide (GO) were prepared according to the literature method and characterized by IR.[a,b] All the other reagents are of analytical grade and used as received without further purification. All the aqueous solutions were prepared with double distilled water.

Characterization Methods: IR spectra were recorded using KBr pellets on a Bruker AXS TENSOR-27 FTIR spectrometer in the range of 4000−400 cm^{-1}. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C·min^{-1}. X–ray powder diffraction data was collected on a Bruker AXS D8 Advance diffractometer using Cu $K\alpha$ radiation (λ = 1.5418 Å) in the 2θ range of 5–60° with a step size of 0.02°. Energy dispersive X-ray spectroscopy (EDS) was obtained from FEI Quanta 200F microscope operated at an accelerating voltage of 20kV. High resolution transmission electron microscope (HRTEM) images were carried out on a JEOL-2100F transmission electron microscope with an accelerating voltage of 200 kV. XPS was performed on F-dopped SnO_2 glass using an ESCALAB-MKΠ photoelectronic spectrometer with an Mg $K\alpha$ (1253.6eV) achromatic X-ray source. Cyclic voltammograms were recorded on a CHI601D Electrochemical Workstation (Shanghai Chenhua Instrument Corp., China), using a glassy carbon electrode as the working electrode, a Pt wire as the counter electrode, and a Ag/AgCl reference electrode. A NaAc/HAc buffer solution with a pH of 5.5 was used as the supporting electrolyte. The diffuse reflectivity spectra were collected on a UV-2600 SHIMADZU UV−vis spectrophotometer in reflectance mode, which was measured from 200 to 800 nm using barium sulfate ($BaSO_4$) as a standard with 100% reflectance.

Photoelectrochemical measurements: All photoelectrochemical experiments were performed on a Model CS350 electrochemistry workstation (CH Instruments, Wuhan CorrTest Instrument Corporation, PRC) at room temperature equipped with a 100W Xenon lamp as the light source. A three-electrode system was employed in a quartz cell comprising of the FTO electrode coated by the TiO_2 film as the working electrode, Ag/AgCl as the reference electrode and Pt wire as the counter electrode. All photocurrent transient experiments were carried out at a constant bias of 0 V. The photoelectrochemical measurements were carried out in a 0.1 M Na_2SO_4 electrolyte which was exposed to air.

Synthesis of reduced GO (RGO): RGO was synthesized following the modified method of literature.[c] In short: As-prepared GO (4 mg) was dispersed in water (15 mL) under stirring and went on sonication for 1 h at room temperature. Then 25 mg L-ascorbic acid was added to the aqueous dispersion, and the mixture was stirring for 48 h at room temperature. The resulting material was filtered off, washed with water and ethanol and dried under vacuum at 80 °C for 12 h. The resultant material was labeled RGO.

Synthesis of Polyoxometalate/Graphene hybrid material (POM/graphene): As-prepared GO (4 mg) was dispersed in water (15 mL) under stirring and went on sonication for 1 h at room temperature. 10 mg $SiW_{11}V$ was dissolved in 4 mL of water by stirring to form a dark purple solution. At room temperature, 25 mg L-ascorbic acid and 10 mg zinc powder were simultaneously added to the $SiW_{11}V$ solution under stirring, while the solution colour changed from purple to dark blue. The resulting mixture was centrifuged at 5000 rpm for 3 min, and the heteropoly blue solution was dropped into the GO aqueous dispersion under stirring. The obtained suspension was further stirred for 24 h at room temperature. Then the mixture was filtered off, washed with water and ethanol and dried under vacuum at 80 °C for 12 h. The resultant material was labeled $SiW_{11}V$/graphene-1.

The synthesis processes for $SiW_{11}V$/graphene-2, $SiW_{11}V$/graphene-3 were similar to $SiW_{11}V$/graphene-1, except that 20 mg and 40 mg $SiW_{11}V$ were used.

Preparation of $SiW_{11}V$/graphene-n@TiO_2 films: Firstly, the $SiW_{11}V$/graphene-n was re-dispersed in 10 mL of acetone and sonicated for 1 h. 0.05 g pristine Degussa P25 was slowly added to the suspension while stirring and sonicated for 5 min, getting blue precipitate. The blue precipitate was dried at room temperature, and the obtained powder was mixed with 0.55 g pure P25. Then $SiW_{11}V$/graphene-n@TiO_2 paste was prepared according to the literature. [d]

The FTO conductive glass was ultrasonic cleaned with surfactant, isopropanol and ethanol respectively. The screen-printing technique was used to coat the $SiW_{11}V$/graphene-n@TiO_2 paste on the FTO.[d] The electrodes were gradually heated in an electric stove in an air atmosphere, which the temperature gradient program has three levels at 325 °C (5 min), 375 °C (10min) and 400 °C (60min).

For comparison purposes a blank experiment (no RGO and $SiW_{11}V$/graphene) was carried out. For this, the pure P25 electrodes were prepared.

a N. Yang, J. Zhai, D. Wang, Y. Chen and L. Jiang, *ACS Nano*, **2010**, 4, 887–894.

b C. Galli, P. Gentili, A. S. N. Pontes, J. A. F. Gamelas and D. V. Evtuguin, *New J. Chem.*, **2007**, 31, 1461–1467.

c J. L. Zhang, H. J. Yang, G. X. Shen, P. Cheng, J. Y. Zhang and S. W. Guo, *Chem. Commun.*, 2010, **46**, 1112–1114.

d S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy, M. Grätzel, *Photovolt: Res. Appl.*, **2007**, 15, 603–612.

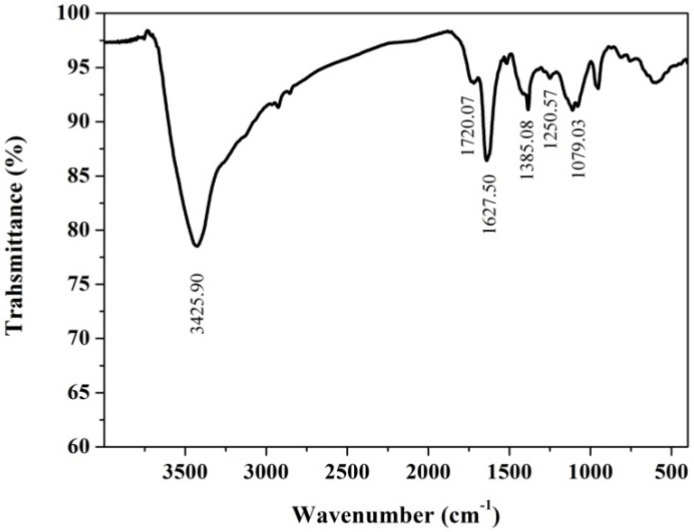


Fig. S1 FTIR spectrum of GO. The O–H stretching at 3425.90 cm^{-1}, the C=O stretching at 1720.07 cm^{-1}, the O–H deformation at 1385.08 cm^{-1}, the C–OH stretching at 1250.57 cm^{-1} and the C–O stretching at 1079.03 cm^{-1}, which are all oxygen-containing functional groups in GO. The peak at 1627.50 cm^{-1} is due to the skeletal vibrations of remnant sp^2 species.

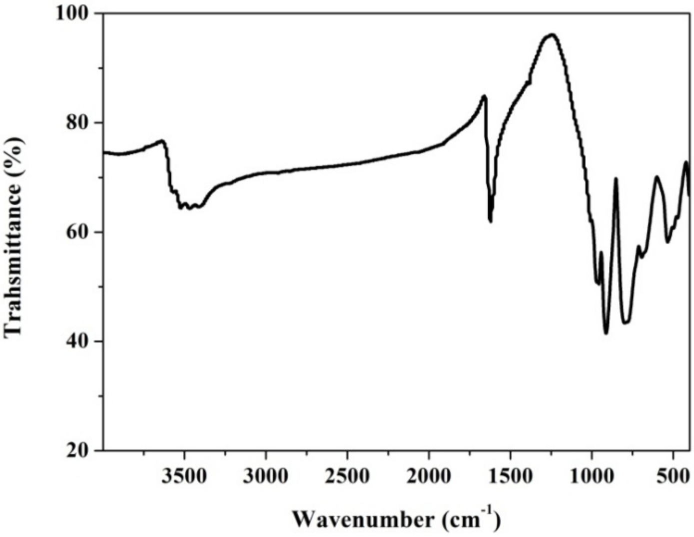


Fig. S2 FTIR spectrum of $K_6[SiW_{11}V^{IV}O_{40}]\cdot 7H_2O$.

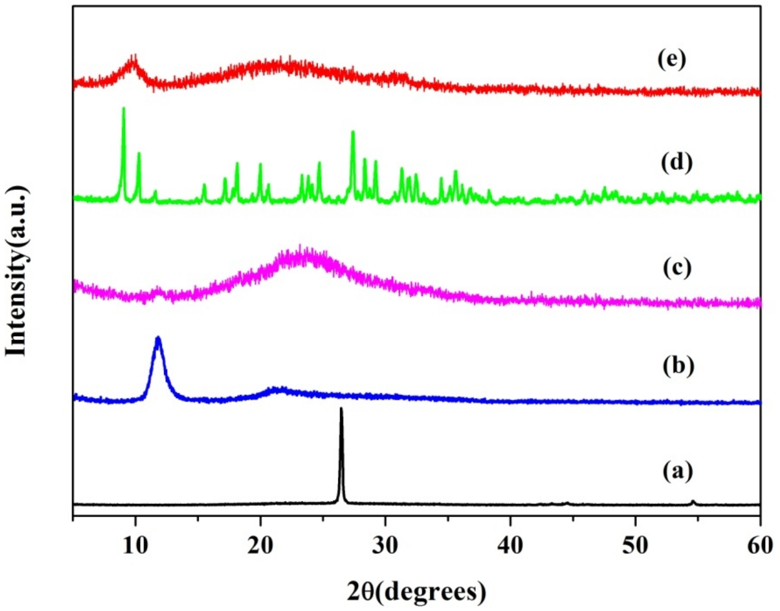


Fig. S3 XRD patterns of raw graphite (a), GO (b), RGO (c), $SiW_{11}V$ (d) and $SiW_{11}V$/graphene-3 (e).

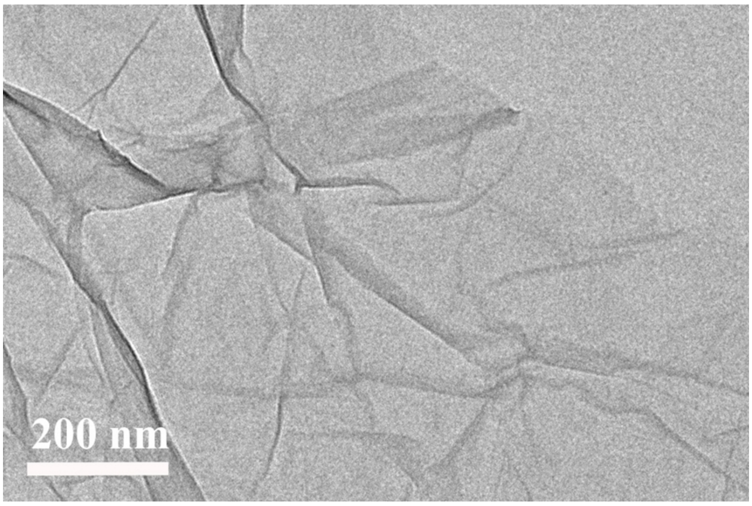


Fig. S4 HRTEM images of RGO.

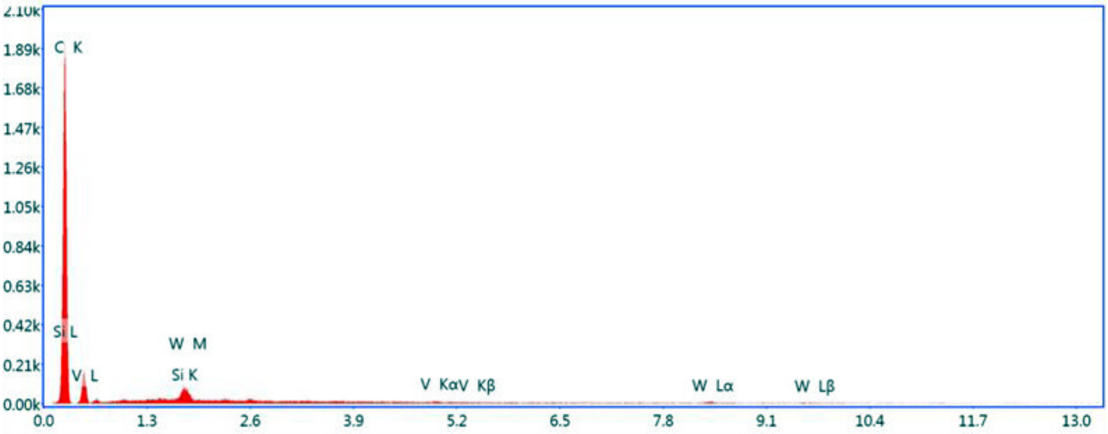


Fig. S5 EDS of $SiW_{11}V$/graphene-3.

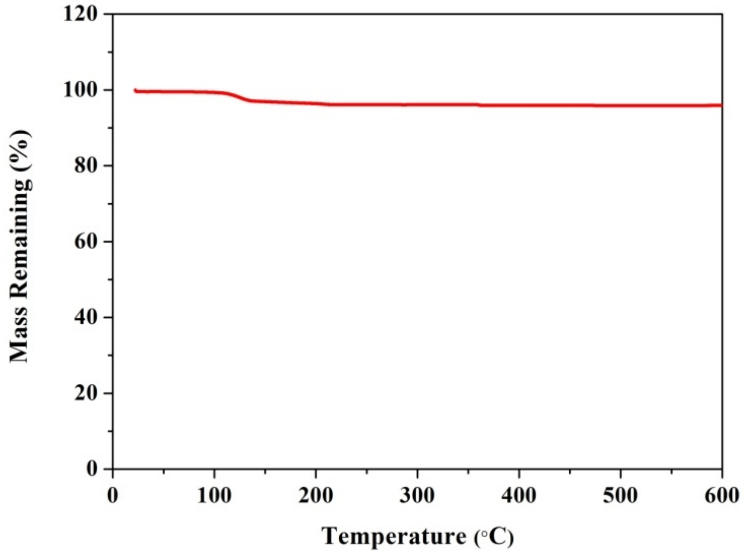


Fig. S6 TG curve of $K_6[SiW_{11}V^{IV}O_{40}]\cdot 7H_2O$.

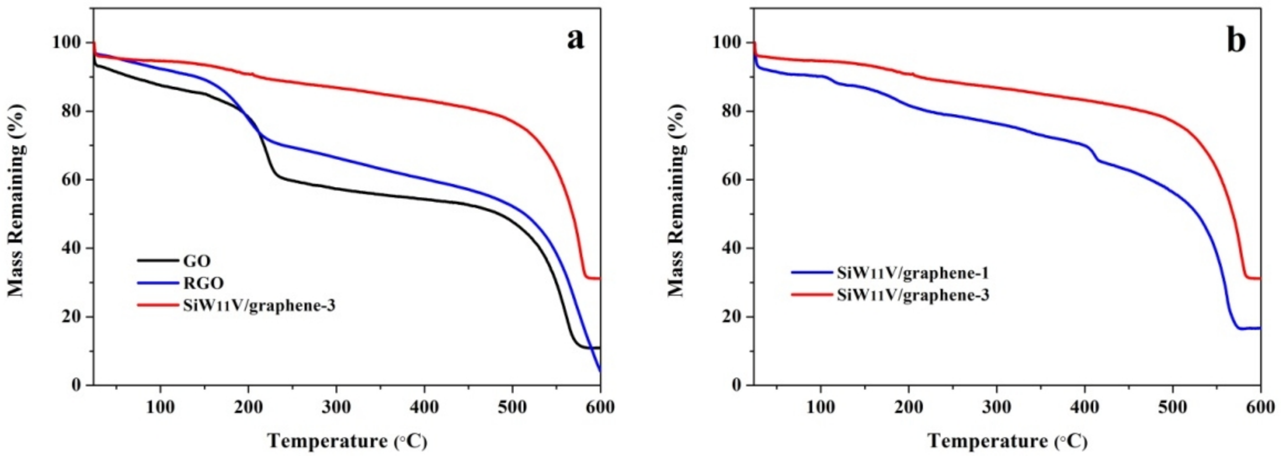
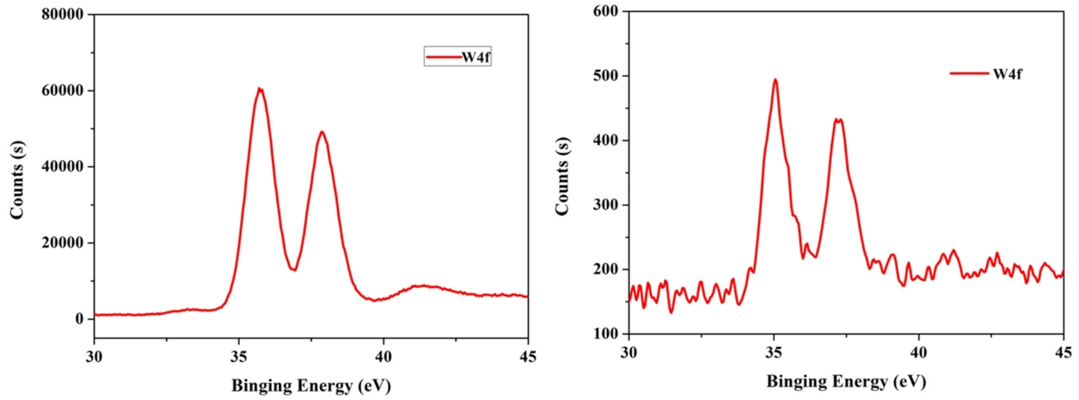


Fig. S7 (a) TG curves of GO, RGO and $SiW_{11}V$/graphene-3, (b) $SiW_{11}V$/graphene-1 and $SiW_{11}V$/graphene-3.



(a) **(b)**

Fig. S8 The W4f XPS spectra of $SiW_{11}V$ (a) and $SiW_{11}V$/graphene-3 nanocomposite (b).

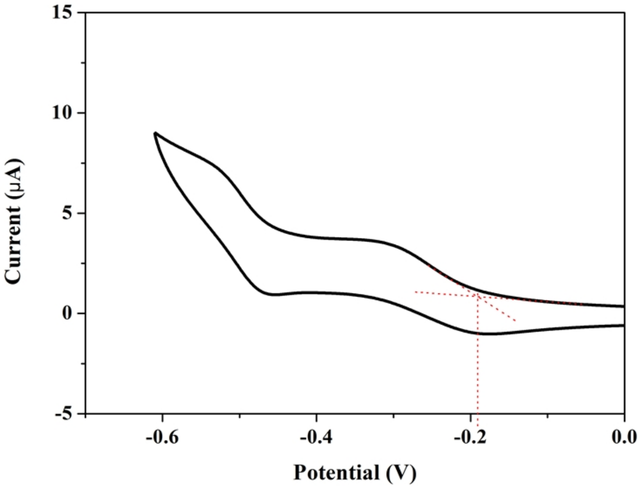


Fig. S9 Cyclic voltammograms of $SiW_{11}V$ in NaAc/HAc buffer with pH 5.5 for the stability of POMs in solution (*vs* NHE).

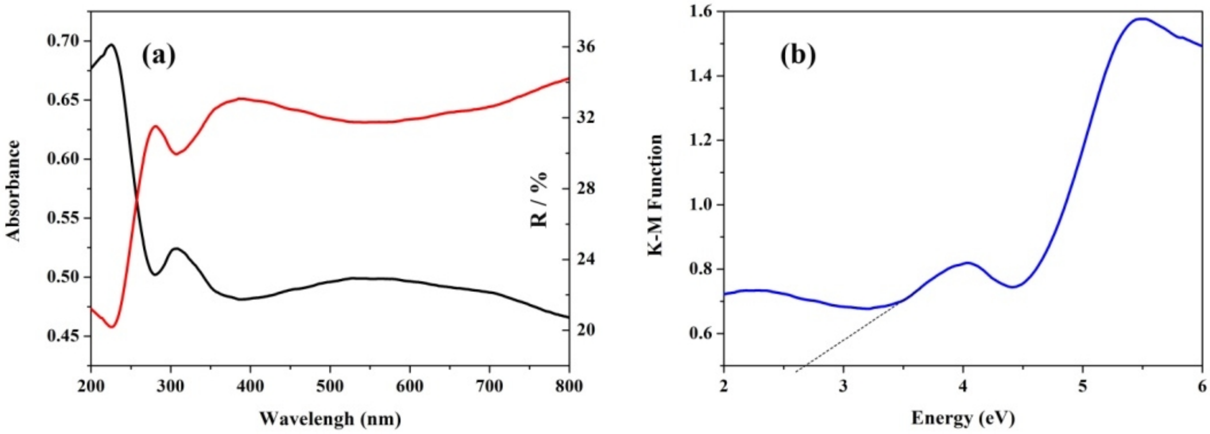


Fig. S10 UV-Vis absorption spectrum (a dark line), the diffuse reflection spectrums (a red line) and plot of K-M function against energy *E* (b blue line) of $SiW_{11}V$.