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: K₅[SiW₁₁V⁴⁺O₄₀]·7H₂O 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 N₂ 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 Kα 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 SnO₂ glass using an ESCALAB-MKI photoelectronic spectrometer with an Mg Kα (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 (BaSO₄) 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 TiO₂ 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 Na₂SO₄ 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 SiW₁₁V 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 SiW₁₁V 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 SiW₁₁V/graphene-1.
The synthesis processes for SiW\textsubscript{11}V/graphene-2, SiW\textsubscript{11}V/graphene-3 were similar to SiW\textsubscript{11}V/graphene-1, except that 20 mg and 40 mg SiW\textsubscript{11}V were used.

**Preparation of SiW\textsubscript{11}V/graphene-\textit{n}@TiO\textsubscript{2} films:** Firstly, the SiW\textsubscript{11}V/graphene-\textit{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\textsubscript{11}V/graphene-\textit{n}@TiO\textsubscript{2} paste was prepared according to the literature.\textsuperscript{[d]}

The FTO conductive glass was ultrasonic cleaned with surfactant, isopropanol and ethanol respectively. The screen-printing technique was used to coat the SiW\textsubscript{11}V/graphene-\textit{n}@TiO\textsubscript{2} paste on the FTO.\textsuperscript{[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 (10 min) and 400 °C (60 min).

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


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\(_2\)O.
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 K₆[SiW₁₁V⁴O₄₀]·7H₂O.

Fig. S7 (a) TG curves of GO, RGO and SiW₁₁V/graphene-3, (b) SiW₁₁V/graphene-1 and SiW₁₁V/graphene-3.

Fig. S8 The W4f XPS spectra of SiW₁₁V (a) and SiW₁₁V/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.