Electronic Supplementary Information

Interfacial self-assembly engineering for constructing 2D flexible superlattices polyoxometalate/rGO heterojunction for high-performance photovoltaic devices

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1. Materials and Reagents

 $K_8H[P_2W_{15}V_3O_{62}]$ ·9H₂O (P₂W₁₅V₃-I), $K_6[a-P_2W_{18}O_{62}]$ ·14H₂O (P₂W₁₈) and reduced graphene oxide (rGO) were synthesized according to the literature.¹⁻⁴ Hexadecyltrimethyl ammonium bromide (C₁₉H₄₂BrN, HDA·Br), tetrabutyl ammonium bromide (C₁₆H₃₆BrN, TBA·Br) and ethyl benzoate (C₉H₁₀O₂) were purchased from Alfa Aesar. Trichloromethane (CHCl₃), acetonitrile, and copper acetate (Cu(CH₃COO)₂·H₂O) were purchased from Aladdin. FTO (F-doped SnO₂ glass, transmittance of 90%, 15Ω cm⁻²), Degussa P25, the Pt counter electrode, quartz substrates, silicon wafers (Si (100) polished on one side) and N719 dye were purchased from Wuhan Jinge Solar Energy Technology Co., Ltd. TiO₂ paste was synthesized according to the literature.⁵ All of the reagents were used without further purification.

2. Experimental Section

Preparation of P₂W₁₅V₃heteropoly blue.

First, 500 mg of P₂W₁₅V₃-I was dissolved in 10 mL of 80°C water with a pH of 1.5. Then, added the aluminum sheet $(1.5 \times 1.5 \text{ cm})$ to the solution, the color of the solution changed gradually from orange yellow to dark green. Finally, the solution was stationary at room temperature, and dark green crystals were precipitated on Al tablets after 30min. In addition, added 50 mg of ascorbic acid to the another same solution (500 mg of P₂W₁₅V₃-I in 10 mL of 80°C water with a pH of 1.5),the color of the solution changed rapidly from orange yellow to dark brown, and the brownish solids were precipitated after 30 min at room temperature. The products are labelled (P₂W₁₅V₃-II) and (P₂W₁₅V₃-III), respectively. The P₂W₁₅V₃-IV was obtained by aluminum sheet and ascorbic acid co-reduced.

Preparation of P₂W₁₈ heteropoly blue.

First, 500 mg of P_2W_{18} was dissolved in 10 mL of 80°C water. Then, added the aluminum sheet (1.5×1.5 cm) to the solution, the color of the solution changed

gradually dark blue, and dark blue crystals were precipitated on Al tablets after 30min at room temperature. The product is labelled P_2W_{18} (HPB).

3. Materials Characterization

X-ray powder (XRD) diffraction were performed on a Bruker AXS D8 Advance diffractometer with Cu K α radiation (λ =1.5418 Å). Uv-vis spectra test were investigated in the range of 200-800 nm⁻¹. Fourier-transform infrared (FTIR) spectrum was recored using BRUKE Vertex 70 in the range of 400-4000cm⁻¹. The thermogravimetric (TG) analysis was recorded on a PerkinElmer TGA7 instrument from 30°C to 800°C in the air. The surface morphology, composition and structure of superlattice POMs were characterized by scanning electron microscopy (SEM JEOL JSM 4800F), transmission electron microscopy (TEM HitachiH-7650), atomic force microscopy (AFM) and energy dispersive X-ray spectroscopy was collected on a nickel grid (EDX FEI Quanta 200F microscope). X-ray photoelectron spectroscopy (XPS) measurement was performed using an ESCALAB-MK[] photoelectronic spectrometer with Mg K α (1253.6 eV) achromatic X-ray source. The elemental mass ratio of Cu/W was tested by inductively coupled plasma atomic emission spectrometer (ICP-AES). Elemental analyses of C, H and N in the surfactant-encapsulated POMs and superlattice POMs were performed with a Vario EL analyzer.

4. Solar cells measurements

The photocurrent measurements were recorded using a three electrode configuration comprising of counter electrode (Pt wire), reference electrode (Ag/AgCl), and working electrode in a quartz cell at a constant bias of 0 V under simulated solar illumination. The active area of the working electrode is *ca*. 1 cm². The electrolyte was 0.5 M Na₂SO₄ aqueous solution. The photocurrent-voltage (*J-V*) characteristics of solar cell was carried out under AM1.5 simulated solar illumination at 100 mW·cm⁻² with a metallic black mask. The electrochemical impedance was measured using the Gamry Reference 3000 electrochemical workstation. The incident-photon-to-current conversion efficiency (IPCE) was obtained using a direct current method under 0.3-0.9 mW cm⁻² monochromic light illumination without bias illumination.



Fig. S1 IR spectra and TG curves of the $P_2W_{15}V_3$ and P_2W_{18} .



Fig. S2 Crystal photographs of $P_2W_{15}V_3$ and its different reducing states; (a) XRD patterns and (b) UV-vis absorption spectra of the samples.

Fig. S2b shows the UV-vis absorption spectra of the $P_2W_{15}V_3$ and its related HPBs. The spectrum of $P_2W_{15}V_3$ -I with the absorption peak range at 320~450 nm is ascribed to oxygen-to-metal (W and V) charge transfer (OMCT). The absorption spectra of $P_2W_{15}V_3$ -I exhibit no peaks in the visible wavelength region, as expected for fully oxidized POMs. The absorption peak in the ultraviolet region is shifted to longer wavelength when $P_2W_{15}V_3$ was reduced ($P_2W_{15}V_3$ -II, $P_2W_{15}V_3$ -III and $P_2W_{15}V_3$ -IV). With the increase of reduction degree, the absorption intensity in the ultraviolet region decreases, a broad band appears in the visible region which is attributed to intervalence-charge transfer (IVCT) indicating the formation of heteropoly blue, and the absorption peak gradually moves to the long wavelength region. The order of the absorption peak position is $P_2W_{15}V_3$ -II (420 nm) < $P_2W_{15}V_3$ -III (525 nm) < $P_2W_{15}V_3$ -IV (630 nm).



Fig. S3 UV-vis absorption spectra of P_2W_{18} and the corresponding P_2W_{18} (HPB).

UV-vis absorption spectra of $P_2W_{15}V_3$, P_2W_{18} and the corresponding HPBs with the same concentration show that the absorption range of $P_2W_{15}V_3$ gradually expands from the ultraviolet region of about 380 nm to the visible region of 520 nm and extends to the 675 nm. The position of the intervalence-charge transfer (IVCT) bands of P_2W_{18} (HPB) at 585 nm, which indicates the six electron reduction and coincide with the previous report.

Table S1 Summary of elemental analysis for $(HDA)_3(TBA)_3P_2W_{18}O_{62}$ and superlattice P_2W_{18} .

Sample		C/%	H/%	N/%	W/%	Cu/%
SEPs	Found	20.92	3.49	1.37	52.69	-
	Calcd	22.31	4.05	1.52	55.89	-

superlattice	Found	21.29	3.57	1.37	46.90	2.78
	Calcd	22.56	4.02	1.38	43.21	2.74

We chose Wells-Dawson POMs and the corresponding HPBs as the building blocks to prepare surfactant-encapsulated POMs (SEPs) using a two-phase approach. Table S1 shows the elemental analysis of the $(HDA)_3(TBA)_3P_2W_{18}O_{62}$ and superlattice P_2W_{18} , which support the successful synthesis of SEPs.



Fig. S4 The FT-IR spectra of rGO, superlattice $P_2W_{15}V_3$ and superlattice $P_2W_{15}V_3/rGO$.



Fig. S5 (a) The low-magnification TEM images of the superlattice with $(HDA)_3(TBA)_3P_2W_{18}O_{62}$ build block; (b) The high-resolution TEM of the superlattice

with $(HDA)_3(TBA)_3P_2W_{18}O_{62}(HPB)$ build block. (The inset is the structure of Wells-Dawson P_2W_{18}).



Fig. S6 The EDX mapping of the superlattice P_2W_{18} (N, light blue; P, yellow; Cu, purple; O, red; W, green).



Fig. S7 (a) AFM image of rGO; (b) the thickness data of rGO.



Fig. S8 Wide-scan XPS spectra (a) of $P_2W_{15}V_3$ - I /rGO heterojunction and high-resolution XPS spectra of the V 2p (b) and W 4f (c).

Fig. S8 shows the XPS spectra of oxidized superlattice POMs $P_2W_{15}V_{3}$ -/rGO heterojunction composite. (a) The full XPS spectrum of the superlattice $P_2W_{15}V_{3}$ -I /rGO heterojunction composite material. As can be seen from the width scan spectrum, the sample contains W, V, P, N, Cu and O elements. (b) The peak of V 2p, and the binding energy of V $2p_{3/2}$ and V $2p_{1/2}$ were 517.6±0.05eV and 524.2±0.05eV, respectively, which matched with complete oxidation (V⁵⁺). (c) The optical signal of W 4f in the superlattice $P_2W_{15}V_3$ - I /rGO heterojunction composite material. The binding energy of W $4f_{7/2}$ and W $4f_{5/2}$ are respectively 35.7 ± 0.05 eV and 37.8 ± 0.05 eV (peak area ratio 4:3). The positions and shapes of these two peaks are consistent with the highest oxidation state of W⁶⁺.⁶



Fig. S9 High-resolution XPS spectra of reduced superlattice HPBs $P_2W_{15}V_3$ - II/rGO (a, d), $P_2W_{15}V_3$ -III/rGO (b, e), and $P_2W_{15}V_3$ -IV/rGO (c,f).

Fig. S9 shows the XPS spectra of three heteropoly blues with different reduction degrees of $P_2W_{15}V_{3}$ - I . (a), (b) and (c) correspond to the optical signals of W 4f in $P_2W_{15}V_3$ - II /rGO heterojunction composite material, $P_2W_{15}V_3$ -III/rGO heterojunction composite material and $P_2W_{15}V_3$ -IV/rGO heterojunction composite material, respectively. the above three kinds of composites at lower binding energy are two obvious peak, W 4f_{7/2} = 34.8 eV and W 4f_{5/2} = 36.9 eV, respectively, and this also in superlattice HPB types (W⁵⁺) ions. The area of the two lower binding energy peaks are increased with reductive degree increase gradually, explain superlattice HPBs (W⁵⁺) ions content in the composite material increased. The emission peak signal at the lower binding energy (V 2p_{3/2} = 516.3±0.05 eV and V 2p_{1/2} = 523±0.05 eV) is consistent with the reduced state (V⁴⁺) vanadium ion, and the peak area of V 2p was not obvious change with the increase of reduction degree (d, e and f).⁷





The XPS spectrum of copper is tested to prove the copper ion is involved in the construction of superlattice POMs structure. The result shows the peaks located at 934.8 eV and 954.5 eV are attributed to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu(II) hydroxide, respectively. The small fitting peaks at 931.8 eV is ascribed to Cu(I)

oxide The extra shake-up satellite peaks at 941.6 eV (944.3 eV) and 962.4 eV further illustrated the existence of Cu(II) (Fig. S10).⁸



Fig. S11 SPV spectrum (a) and PL spectrum (b) of oxidation state superlattice $P_2W_{15}V_3$ - I and superlattice $P_2W_{15}V_3$ - I /rGO heterojunction.



Fig. S12 The SEM and EDX mapping of the superlattice P_2W_{18} (HPB)/rGO heterojunction modified TiO₂ anode film.

Table S2 Photovoltaic parameters of different DSSCs. The values of the data in the table are obtained from the average of five parallel DSSCs.

Cells	J_{sc} / mA cm ⁻	V_{oc} / V	FF	η / %
TiO ₂	15.20	0.68	0.61	6.48 ± 0.07
P ₂ W ₁₈ (HPB)/rGO@TiO ₂ -a	16.12	0.74	0.59	7.22±0.04
P ₂ W ₁₈ (HPB)/rGO@TiO ₂ -b	16.70	0.72	0.61	7.52±0.05

P ₂ W ₁₈ (HPB)/rGO@TiO ₂ -c	17.36	0.72	0.60	7.47±0.04
$P_2W_{18}(HPB)/rGO@TiO_2-d$	18.57	0.73	0.62	8.09±0.06
P ₂ W ₁₈ (HPB)/rGO@TiO ₂ -e	17.66	0.71	0.60	7.62±0.05

Table S3 The simulated R_{ct} and C_{μ} values of the N719 sensitized photoanode DSSCs at a bias voltage of -0.725 V.

Cells	TiO ₂	P ₂ W ₁₈ (HPB)/rGO@TiO ₂ -d
R_{ct}	38	133
$C_{\mu}/\mathrm{mF}\cdot\mathrm{cm}^{-2}$	3.42	3.67



Fig. S13 Variation curves of various performance parameters of the DSSCs with $P_2W_{18}(HPB)/rGO@TiO_2$ as photoanode.

References

- R. G. Finke, B. Rapko, R. J. Saxton and P. J. Domaille, *J. Am. Chem. Soc.*, 1986, **108**, 2947-2960.
- 2. C. R. Graham and R. G. Finke, Inorg. Chem., 2008, 47, 3679-3686.
- J. H. Lee, N. Park, B. G. Kim, D. S. Jung, K. Im, J. Hur and J. W. Choi, ACS Nano, 2013, 7, 9366-9374.
- 4. W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339.
- S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy, M. Grätzel, *Prog. Photovoltaics*, 2007, 15, 603.
- J. P Li, W. L. Chen, L. Chen, X. T. Zheng, G. S. Zhu and E. B. Wang. Adv. Optical Mater., 2018, 6, 1800225.

- M. T. Greiner, M. G. Helander, W. M. Tang, Z.-B. Wang, J. Qiu and Z.-H. Lu, *Nat. Mater.*, 2012, 11, 76-81.
- 8. J. P. Li, X. H. Li, T. Wang, P. He, F. R. Li, W. L. Chen and E. B. Wang, ACS Appl. Energy Mater., 2019, **2**, 5824-5834.