*Supporting information*

# Pt-substituted Polyoxometalate Modification on Low-cost TiO2 Surface with High-efficient H2 Evolution Performance

Yun-Dong Cao,[a] Di Yin,[a] Ming-Liang Wang,[a] Tao Pang,[a,c] Yuguang Lv,[c] Bo Liu,[b] Guang-Gang Gao*[a] Lulu Ma,[a] Hong Liu,*[a,c]

[a] *School of Materials Science and Engineering, University of Jinan, 250022, Jinan, China*
[b] *Key Laboratory of Preparation and Application of Environmental Friendly Materials, The Ministry of Education, Jilin Normal University, Siping, 136000, China*
[c] *College of Pharmacy, Jiamusi University, 154007, Jiamusi, China*

*E-mail: mse_gaogg@ujn.edu.cn; mse_liuh@ujn.edu.cn*

# Contents

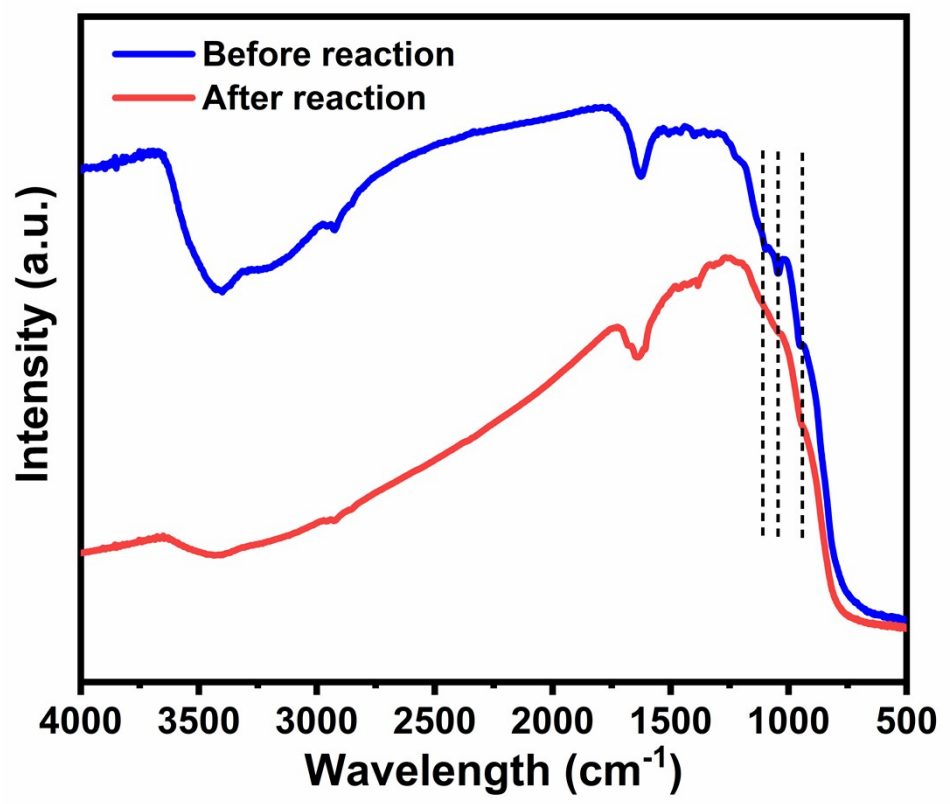


**Fig. S1** FTIR spectra of **$TiO_2$-$SiNH_2$-$PW_{11}Pt_2$** before and after photocatalytic hydrogen evolution reaction.

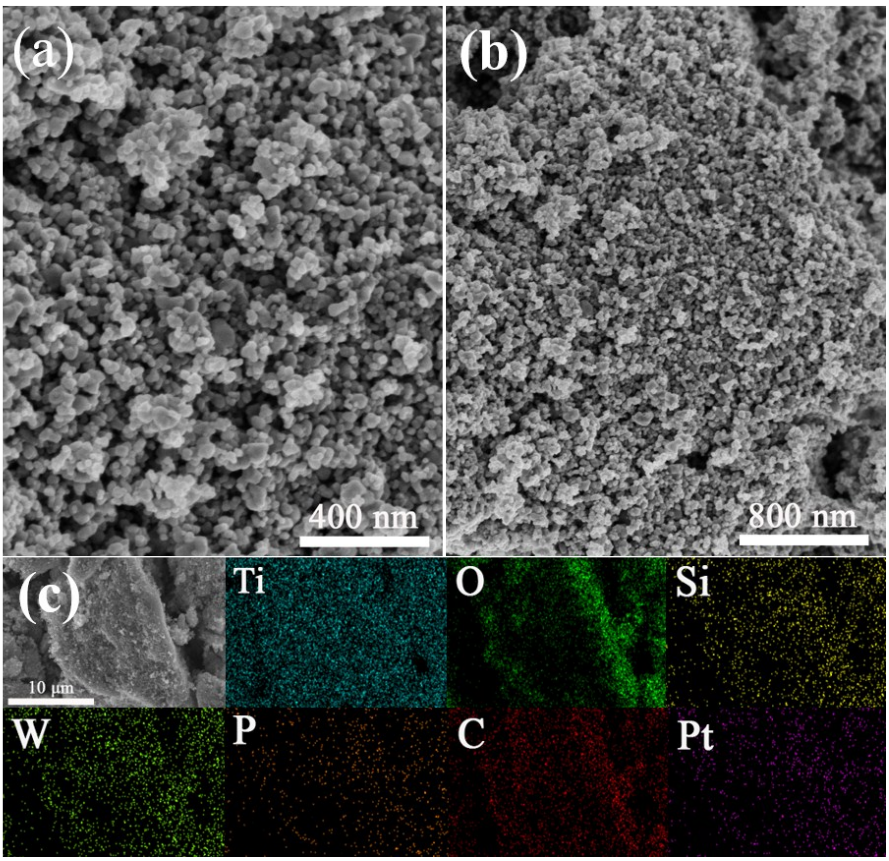


**Fig. S2** SEM image of $TiO_2$-$SiNH_2$-$PW_{11}Pt_2$ at different resolution of (a) 400 nm and (b) 800 nm. (c) The essential elemental mapping images.

**Fig. S3** TEM image of pristine $TiO_2$.

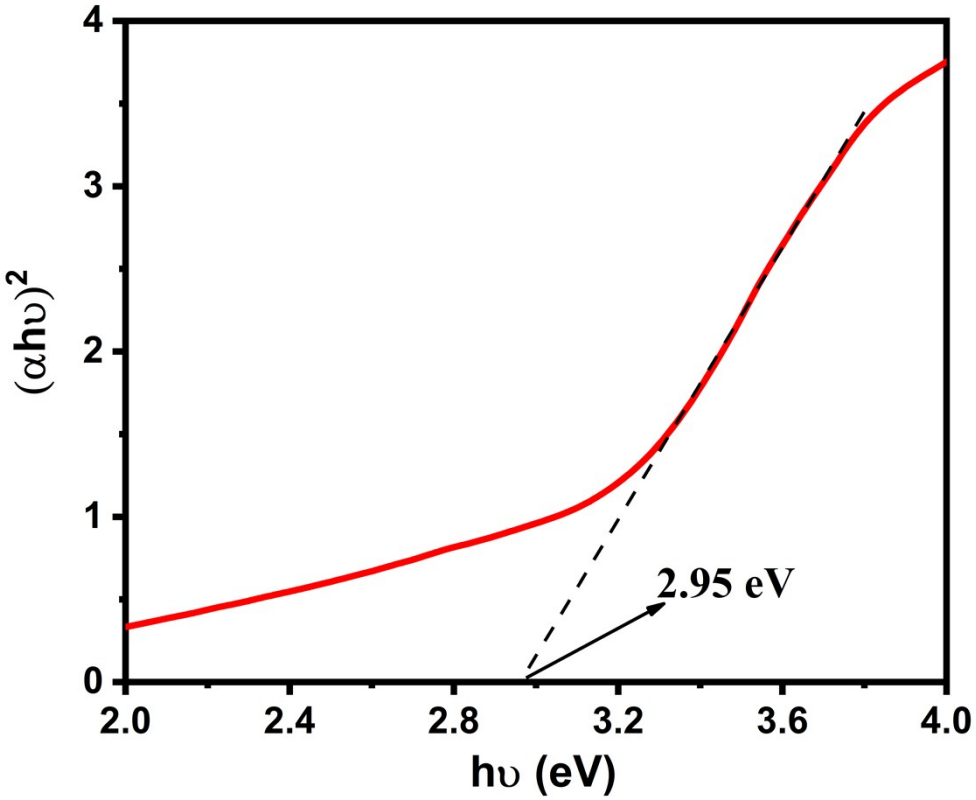


**Fig. S4** The plots of $(\alpha h\upsilon)^2$ vs. photon energy of **$TiO_2$-Pt**.

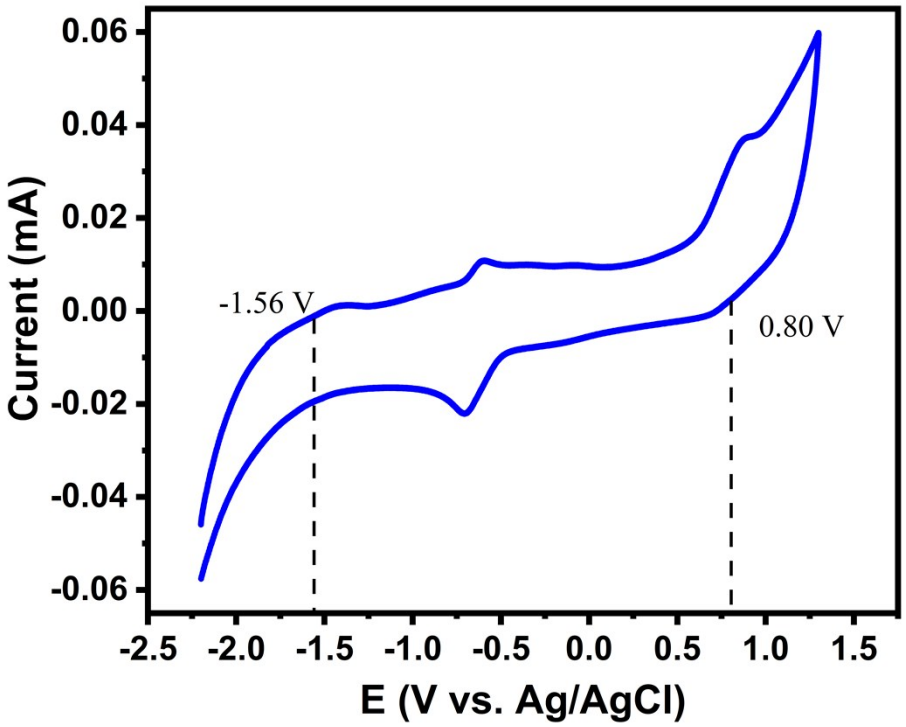


**Fig. S5** CVs of $\mathbf{PW_{11}Pt_2}$ in dimethyl sulfoxide containing 0.1 M $Bu_4NPF_6$ at a scan rate of 50 mV/s.

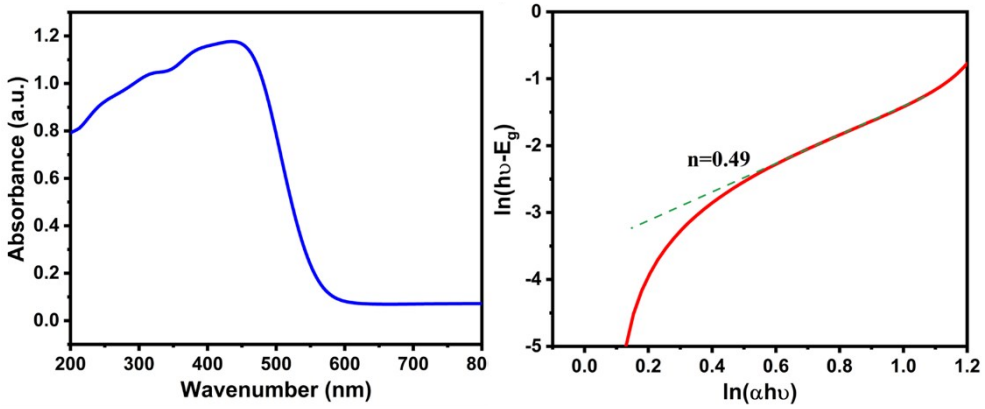


**Fig. S6** (a) UV-vis diffuse reflection spectra of $\mathbf{PW_{11}Pt_2}$. (b) The plots of ln($h\upsilon$-$E_g$) *vs.* ln($\alpha h\upsilon$) of $\mathbf{PW_{11}Pt_2}$.

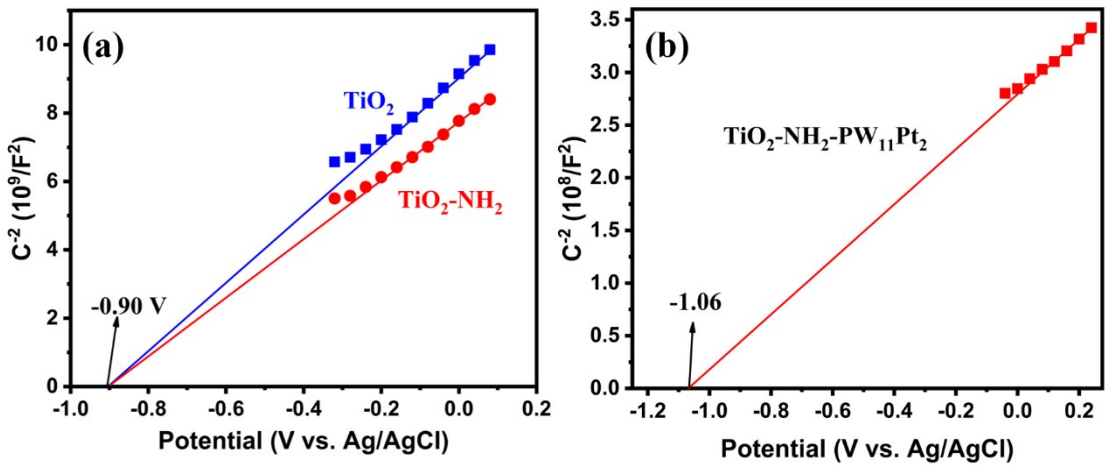


**Fig. S7** Mott–Schottky plots of (a) $TiO_2$, $TiO_2$-$NH_2$ and (b) $TiO_2$-$NH_2$-$PW_{11}Pt_2$.

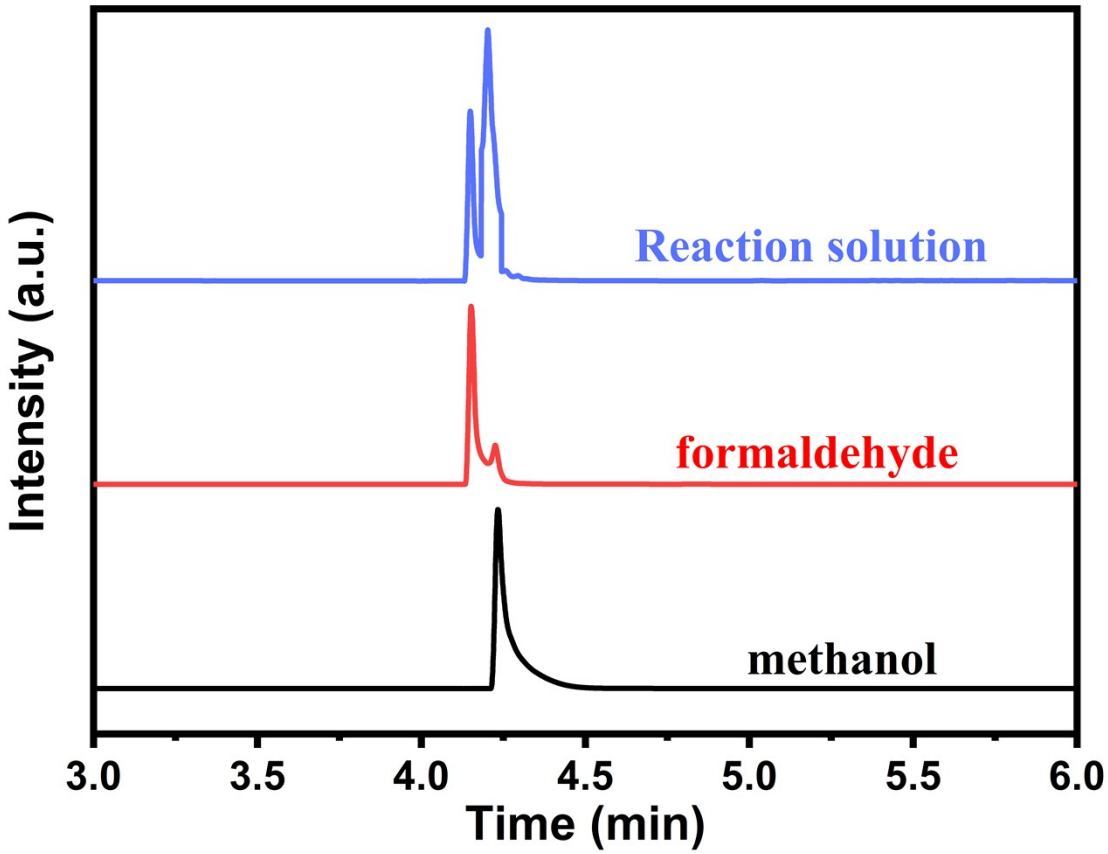


**Fig. S8** Gas chromatogram of reaction solution (after particating in 48 h of photocatalytic reaction), aqueous solution of formaldehyde (containing 8% methanol to prevent formaldehyde polymerization) and methanol.

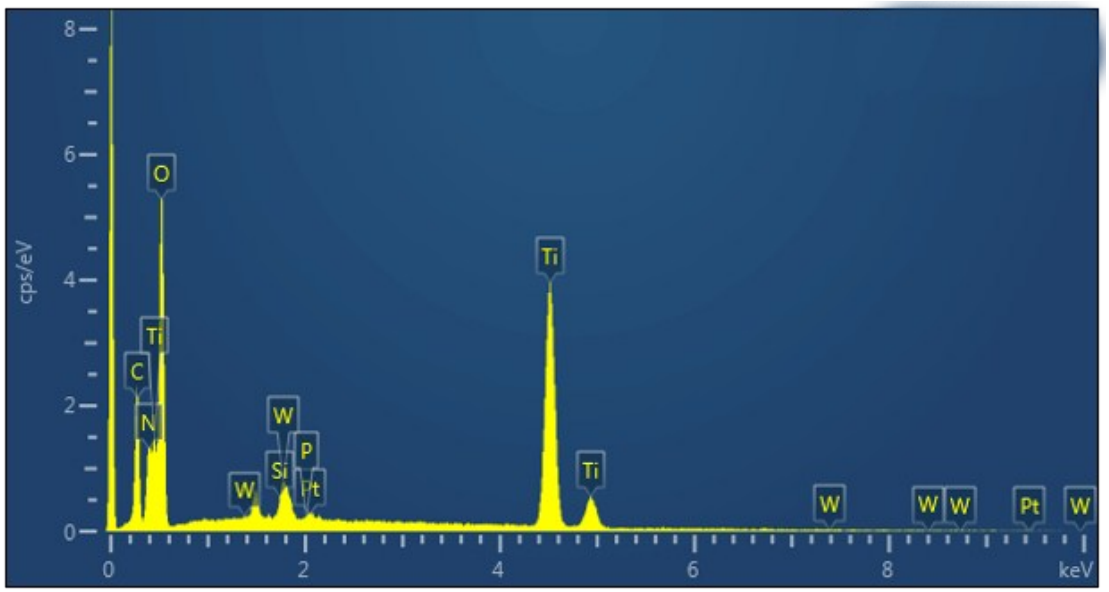


**Fig. S9** EDS spectrum of $\mathbf{TiO_2}$-$\mathbf{SiNH_2}$-$\mathbf{PW_{11}Pt_2}$.

**Table S1** The proportion of elements measured from EDS.

| Element | apparent concentration | K ratio | Wt% | Wt% Sigma | At% |
|---|---|---|---|---|---|
| C K | 0.58 | 0.00580 | 5.37 | 0.16 | 12.75 |
| N K | 0.00 | 0.00000 | 0.00 | 0.00 | 0.00 |
| O K | 1.42 | 0.01241 | 27.42 | 0.39 | 48.92 |
| Si K | 0.03 | 0.00030 | 0.18 | 0.11 | 0.19 |
| P K | 0.01 | 0.00013 | 0.08 | 0.07 | 0.07 |
| Ti K | 10.13 | 0.10133 | 62.80 | 0.46 | 37.42 |
| W M | 0.43 | 0.00433 | 3.51 | 0.27 | 0.55 |
| Pt M | 0.08 | 0.00080 | 0.64 | 0.22 | 0.09 |

**Table S2** Comparison of POM-$TiO_2$ photocatalytic systems.

| Catalyst | Photosensitizer | Co-catalyst | Electron donor | Hydrogen evolution rate | Reference |
|---|---|---|---|---|---|
| $K_{10}Na_{12}[\{Co_3(B\text{-}\beta\text{-}SiW_9O_{33}(OH))(B\text{-}\beta\text{-}$ | Colloidal $TiO_2$ | $K_2PtCl_4$ | Polyvinyl alcohol | 9.3 $\mu mol \cdot g^{-1} \cdot h^{-1}$ | [1] |
| $\alpha\text{-}K_8[SiW_{11}O_{39}] \cdot 8H_2O$/ $TiO_2$ | Eosin Y | 1.0 wt% Pt | TEOA | 1.3 $mmol \cdot g^{-1} \cdot h^{-1}$ | [2] |
| $\alpha_2\text{-}K_{10}P_2W_{17}O_{61} \cdot 15H_2O$ | – | $Pt/TiO_2$ | Glycerol | 29.0 $\mu mol \cdot g^{-1} \cdot h^{-1}$ | [3] |
| $Cs_3[PW_{11}O_{39}\{cis\text{-}Pt(NH_3)_2\}_2] \cdot 8H_2O$ | $TiO_2$ | – | EDTA·2Na | 31.7 $\mu mol \cdot g^{-1} \cdot h^{-1}$ | [4] |
| $K_{14}[O\{Re^V\text{-}(OH)(\alpha_2\text{-}P_2W_{17}O_{61})\}_2] \cdot 21H_2O$ | $TiO_2$ | – | EDTA·2Na | 3.96 $\mu mol \cdot g^{-1} \cdot h^{-1}$ | [5] |
| $K_{14}[O\{Re^V\text{-}(OH)(\alpha_2\text{-}P_2W_{17}O_{61})\}_2] \cdot 21H_2O$ | $TiO_2$ | Pt | EDTA·2Na | 80.3 $\mu mol \cdot g^{-1} \cdot h^{-1}$ | [6] |
| $TiO_2\text{-}SiNH_2\text{-}PW_{11}Pt_2$ | P25 | – | Methanol | 4.5 $mmol \cdot g^{-1} \cdot h^{-1}$ | This work |

## Reference


[1] R. J. Liu, X. K. Shang, C. X. Li, X. L. Xing, X. L. Yu, G. J. Zhang, S. J. Zhang, H. B. Cao, L. H. Bi, *Int. J. Hydrogen Energ.*, 2013, 38, 9954.

[2] X. Liu, Y. X. Li, S. Q. Peng, G. X. Lu, S. B. Li, *Int. J. Hydrogen Energ.*, 2013, 38, 11709.

[3] N. Fu, Z. L. Jin, Y. Q. Wu, G. X. Lu, D. Y. Li, *J. Phys. Chem. C*, 2011, 115, 8586.

[4] C. N. Kato, Y. Morii, S. Hattori, R. Nakayama, Y. Makino, H. Uno, *Dalton. Trans.*, 2012, 41, 10021.

[5] C. N. Kato, K. Hara, A. Hatano, K. Goto, T. Kuribayashi, K. Hayashi, A. Shinohara, Y. Kataoka, W. Mori, K. Nomiya, *Eur. J. Inorg. Chem.*, 2008, 2008, 3134.

[6] C. N. Kato, K. Hara, M. Kato, H. Amano, K. Sato, Y. Kataoka, W. Mori, *Materials*, 2010, 3, 897.