Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2020

Supporting Information

For

Regulation of the rutile/anatase TiO₂ heterophase interface by Ni₁₂P₅ to improve photocatalytic hydrogen evolution

Chengwei Qiu, Jinjin Lin, Jinni Shen*, Dan liu, Zizhong Zhang, Huaxiang Lin, Xuxu Wang*

State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou,

PR China

E-mail: t15067@fzu.edu.cn, xwang@fzu.edu.cn

Table S1. The anatase content in $A/Ni_{12}P_5/R$, $Ni_{12}P_5/A/R$, and A/R.

Sample	A _{25.28°}	A _{27.45°}	A _{25.28°} /A _{27.45°}	W _A /W _R
A/Ni ₁₂ P ₅ /R	14100	62465	0.221	20.30%
Ni ₁₂ P ₅ /A/R	16302	81921	0.198	17.89%
A/R	13397	60355	0.225	19.86%

Note: $A_{25,28^\circ}$ represents the area of the 2 θ at 25.28° for anatase phase TiO₂ (101); $A_{27,45^\circ}$ symbolizes the area of the 2 θ at 27.45° for rutile phase TiO₂ (110); W_A stands for the weight ratio of anatase phase; W_R means the weight ratio of rutile phase.

Table S2. The measured $Ni_{12}P_5$ content in the sample of $A/Ni_{12}P_5/R$, $Ni_{12}P_5/A/R$, and $Ni_{12}P_5/R$.

Sample	Content (wt%)		
Ni ₁₂ P ₅ /R	0.29		
Ni ₁₂ P ₅ /A/R	0.24		
A/Ni ₁₂ P ₅ /R	0.25		

Table S3. Comparison between the added and the analyzed content of $Ni_{12}P_5$ in A/ $Ni_{12}P_5/R$ samples.

Sample	Content (wt						
	%)	%)	%)	%)	%)	%)	%)
$Ni_{12}P_5$ -adding	1	3	5	7	10	15	20
$Ni_{12}P_5$ -measuring	0.10	0.12	0.22	0.25	0.49	4.15	6.72

Note: The $Ni_{12}P_5$ -adding was theoretical value by the added $Ni_{12}P_5$ in the preparation process. The $Ni_{12}P_5$ -measuring was obtained from the ICP-mass analysis.



Fig. S1 (a) XRD spectra of mechanical mixture at 1:15, 1:10, 1:5, 1:1, 5:1, and 10:1 ratios of anatase phase to rutile phase with their corresponding magnified plots in the range of 2θ =24-28⁰. (b) The plot of (A_{25.28°}/A_{27.45°}) versus weight ratios of anatase phase to rutile phase (W_A/W_R). The plot of area ratios of the 20 at 25.28° represents anatase phase TiO₂ (101) and that at 27.45° stands for rutile phase TiO₂ (110).



Fig. S2 The average H₂ production rate on different samples.



Fig. S3 SEM images of $Ni_{12}P_5$ (a), R (b) and $Ni_{12}P_5/R$ (c) samples. The red circle points out the position of $Ni_{12}P_5$.



Fig. S4 STEM images (a) and EDX mapping of Ti (b), O (c), Ni (d)and P (e) elements in $Ni_{12}P_5/R$.



Fig. S5 TEM images of A/Ni $_{12}P_5/R$ with 7%(a) and 20%(b) $Ni_{12}P_5$ loading.



Fig. S6 TEM image of $Ni_{12}P_5/A$ and the red circle marks the position of anatase grains



Fig. S7 In situ FTIR spectra of CO adsorbed on $Ni_{12}P_5$ (a), $Ni_{12}P_5/R$ (b), $Ni_{12}P_5/A/R$ (c), $A/Ni_{12}P_5/R$ (d) and A/R (e) at room temperature with different time and CO dosage. The samples were evacuated before the characterization and then CO was injected at room temperature. The N_2 adsorption-desorption isotherms in (f) of A/R, $Ni_{12}P_5/A/R$ and $A/Ni_{12}P_5/R$.



Fig. S8 300 W Xe lamp was used to investigate the effect of light intensity on the photocatalytic activity of A/R, Ni₁₂P₅/A/R and A/Ni₁₂P₅/R samples. Through controlling the working current at 16 A, 17 A, 18 A and 19 A, different light intensity of the Xe lamp was realized, with the total irradiance at 1845.96, 1946.37, 2074.89 and 2145.89 mW.cm⁻², respectively.



Fig. S9 XRD patterns of $Ni_{12}P_5/R$, $Ni_{12}P_5/A/R$ and $A/Ni_{12}P_5/R$ with 70% $Ni_{12}P_5$ loading.



Fig. S10 CPDs of A, R and Ni₁₂P₅. The CPDs of A, R and Ni₁₂P₅ were carried out on the Kelvin probe system. The work function of the tip was corrected by a gold disk initially. The work function of the sample was calculated on the followed formula: $WF_{sample} = WF_{tip} + \Delta CPD/1000$.

Reference:

- 6. C. Ai, P. Xie, X. Zhang, X. Zheng, J. Li, A. Kafizas and S. Lin, ACS Sustainable Chemistry & Engineering, 2019, 7, 5274-5282.
- 12. J. Lin, T. Sun, M. Li, J. Yang, J. Shen, Z. Zhang, Y. Wang, X. Zhang and X. Wang, J. Catal., 2019, 372, 8-18.
- 42. R. Daghrir, P. Drogui and D. Robert, Ind. Eng. Chem. Res., 2013, 52, 3581-3599.
- 43. J. Lin, J. Hu, C. Qiu, H. Huang, L. Chen, Y. Xie, Z. Zhang, H. Lin and X. Wang, Catalysis Science & Technology, 2019, 9, 336-346.
- 45. D. O. Scanlon, C. W. Dunnill, J. Buckeridge, S. A. Shevlin, A. J. Logsdail, S. M. Woodley, C. R. A. Catlow, M. J. Powell, R. G. Palgrave, I. P. Parkin, G. W. Watson, T. W. Keal, P. Sherwood, A. Walsh and A. A. Sokol, *Nature Materials*, 2013, **12**, 798-801.
- 47. K. Edamoto, Y. Nakadai, H. Inomata, K. Ozawa and S. Otani, Solid State Commun., 2008, 148, 135-138.
- 48. Q. Li and X. Hu, Physical Review B, 2006, 74, 035414.