Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2018

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

This journal is © The Royal Society of Chemistry 2018

Supplementary Information

One-pot synthesis of Cu-modified HNb<sub>3</sub>O<sub>8</sub> nanobelts with enhanced photocatalytic hydrogen production

Yifang Zhao<sup>a</sup>, Jian Li<sup>a</sup>, Cong Lin<sup>b</sup>, Yaming Qiu<sup>a</sup>, Yanquan Yang<sup>a</sup>, Xiaoge Wang<sup>a</sup>, Fengjuan Pan<sup>a</sup>, Ligang Wang<sup>a</sup>, Jianhua Lin<sup>a</sup>\*, Junliang Sun<sup>a</sup>\*

a. Beijing National Laboratory for Molecular Science (BNLMS),

State Key Laboratory of Rare Earth Materials Chemistry and Applications,

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China E-mail: junliang.sun@pku.edu.cn, jhlin@pku.edu.cn

b. College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China



Figure S1. Home-made photocatalytic activity test system.



Figure S2. a) XRD patterns of  $K_7HNb_6O_{19}$  and products obtained without  $NH_3 \cdot H_2O$ ; b) SEM image of products obtained with NaOH instead of  $NH_3 \cdot H_2O$ .



Figure S3. a) XRD pattern and b) SEM image of products obtained without CH<sub>3</sub>COOH.



Figure S4. SAED of the  $Nb_3O_8^-$  nanobelts. The SAED pattern could be indexed to the diffraction spots along the [010] zone axis of  $HNb_3O_8$ .



Figure S5. AFM image and cross-sectional profiles of 1Cu-HNb<sub>3</sub>O<sub>8</sub> nanobelts. The thickness of the nanobelts is about 2.75nm, which is close to the thickness of double [Nb<sub>3</sub>O<sub>8</sub>]<sup>-</sup> layers.



Figure S6. a) SEM, b) TEM, c) HRTEM images of 0.5Cu-HNb<sub>3</sub>O<sub>8</sub> samples; d) SEM, e) TEM, f) HRTEM images of 1Cu-HNb<sub>3</sub>O<sub>8</sub> samples; g) SEM, h) TEM, i) HRTEM images of 10Cu-HNb<sub>3</sub>O<sub>8</sub> samples for three days.



Figure S7. XRD patterns of 0.5Cu, 1Cu, 10Cu-HNb<sub>3</sub>O<sub>8</sub> samples.



Figure S8. TEM image and mapping results of 10Cu-HNb<sub>3</sub>O<sub>8</sub> samples. The mapping results of element Nb and Cu corresponded well to the image profile, while the results of elements N and O were not as influenced by nickel grid.



Figure S9. XPS spectra of HNb<sub>3</sub>O<sub>8</sub> nanobelts. High resolution XPS spectrum of the a) Nb 3d core level; b) N 1s core level; c) O 1s core level.



Figure S10. XPS spectra of calcined HNb<sub>3</sub>O<sub>8</sub> nanobelts. High resolution XPS spectrum of the a) Nb 3d core level; b) N 1s core level; c) O 1s core level.



Figure S11. High resolution XPS spectrum of the Cu 3d core level in a) 0.5wt% Cu- HNb<sub>3</sub>O<sub>8</sub>; b) 1wt% Cu- HNb<sub>3</sub>O<sub>8</sub>; c) calcined 1wt% Cu- HNb<sub>3</sub>O<sub>8</sub>.



Figure S12. a) Nitrogen adsorption-desorption isotherms and b) pore size distribution from nitrogen adsorption of  $HNb_3O_8$  nanobelts. The BET specific surface area were calculated to be 134.1 m<sup>2</sup>/g.



Figure S13. a) Nitrogen adsorption-desorption isotherms and b) pore size distribution from nitrogen adsorption of Cu-HNb<sub>3</sub>O<sub>8</sub> nanobelts. The BET specific surface area were calculated to be  $107.9m^2/g$ .



Figure S14. TG curves of a)  $HNb_3O_8$ ; b) Cu- $HNb_3O_8$  nanobelts in air. The weight loss from room temperature to 300°C was about 12wt% and a slight loss of 1.6wt% at the range of 300°C to 700°C.



Figure S15. a) Mott-Schottky plots of HNb<sub>3</sub>O<sub>8</sub> and Cu-HNb<sub>3</sub>O<sub>8</sub> nanobelts in Na<sub>2</sub>SO<sub>4</sub> (aq).



Figure S16. Band gap analysis and proposed band gap structures of  $HNb_3O_8$  and  $Cu-HNb_3O_8$  nanobelts in  $Na_2SO_4$  (aq) at pH=2.0. The color of the samples depends on the wavelength of light that is reflected. And as the weak absorption in blue light range, the 10Cu-HNb<sub>3</sub>O<sub>8</sub> sample is bluish violet.

Samples	Rec	ycle	Hyd	lrogen evo	olution ra	te (mmo	l h <sup>-1</sup> g <sup>-1</sup> )		Average
	ru	ns							rate
$HNb_3O_8$	1	0.33	0.34	0.34	0.34	0.35	0.34	0.34	0.34
		0.33	0.35	0.35	0.34	0.34	0.34		
	2	0.34	0.34	0.34	0.33	0.34	0.34	0.34	0.34
		0.33	0.34	0.34	0.34	0.35	0.34	0.33	
	3	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.33
		0.33	0.33	0.33	0.33	0.34	0.33	0.33	
0.5Cu	1	2.6	2.6	2.5	2.6	2.5	2.6	2.6	2.6
		2.5	2.5	2.5	2.6	2.6	2.5	2.5	
	2	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
		2.5	2.5	2.5	2.6	2.5	2.5	2.5	
1Cu	1	2.6	2.7	2.6	2.6	2.6	2.7	2.6	2.7
		2.7	2.6	2.7	2.6	2.6			
	2	2.7	2.8	2.7	2.7	2.7	2.7	2.7	2.7
		2.7	2.7	2.7	2.7	2.7			
	3	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
		2.7	2.7	2.7	2.7	2.7			
	4	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
		2.7	2.7	2.7	2.7	2.7	2.7		
	5	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
		2.7	2.7	2.7	2.7	2.7			
10Cu	1	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
		1.2	1.2	1.2	1.2	1.2	1.2	1.2	
	2	1.1	1.1	1.1	1.1	1.1	1.2	1.2	1.2
		1.2	1.2	1.2	1.1	1.1	1.1		
	3	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
		1.1	1.1	1.2	1.1	1.1	1.1	1.1	

Table S1. The real-time hydrogen evolution rate data of four samples

Note: 1. The corresponding loading amount of Cu ions are 0.5wt%, 1wt%, 10wt% and note as 0.5Cu, 1Cu, 10Cu, respectively.

2. Take the average as the hydrogen production activity after lighting the system at least three hours.

	Samples	Xenon lamp	Hydrogen evolution rate (mmol h <sup>-1</sup> g <sup>-1</sup> )			
_		300W	Pure water	10% methanol		
1	HNb <sub>3</sub> O <sub>8</sub>		0.07	0.34		
2	HNb <sub>3</sub> O <sub>8</sub>	Visible light	/	0.3		
3	1Cu-HNb <sub>3</sub> O <sub>8</sub>		0.34	2.7		
4	1Cu-HNb <sub>3</sub> O <sub>8</sub>	Visible light	/	2.5		
5	10Cu-HNb <sub>3</sub> O <sub>8</sub>		0.21	1.2		
6	1wt%Pt-HNb <sub>3</sub> O <sub>8</sub>		0.32	2.1		
7	1wt%Pt-Anatase TiO <sub>2</sub>		/	0.7		

Table S2. The hydrogen evolution rates of different samples

Note: 1. The experiments of 2 and 4 were performed by adding the UV filter (>400nm) after lighting the samples for an hour. Others were performed under Xenon lamp (300W, CEL-HXF300/CEL-HXUV300, Zhongjiaojinyuan Co. Ltd).

2. The hydrogen evolution data in the pure water were collected during the first two hours. The rate of  $HNb_3O_8$  samples began to decrease after two hours and became zero after four hours in pure water. The rates of 1Cu, 10Cu and 1wt%Pt began to decrease after about three hours in pure water. These materials could be used again as photocatalysts once exposed to the air.

3. No  $O_2$  were detected in the pure water tests, which may be caused by the dissolution of the trace amouts of oxygen, the strongly absorbed oxygen species like  $O_2^-$  or  $O_2^{2-}$  by Nb<sub>3</sub>O<sub>8</sub><sup>-</sup>, or the limited movements of the photoinduced holes without oxygen evolution cocatalysts<sup>S1, S2</sup>. We deduced that, under UV light irradiation, the photo-generated electrons in the VB of the materials can be excited to the CB and reduced hydrogen, inducing the formation and accumulation of holes in the VB. The excess holes acted as the recombination centers and made the activity decreased gradually to zero.

4. The anatase  $TiO_2$  (99.8% metals bases, 100nm) were purchased from Aladdin Industrial Corporation. The 1wt%Pt cocatalyst was loaded on the surface of nanobelts by the photodeposition method.

## **References:**

S1. F. E. Osterloh, *Chem. Mater.*, 2008, **20**, 35-54.
S2. A. Mills, G. Porter, *J. Chem. Soc., Faraday Trans.* 1, 1982, **78**, 3659-3669.