Supplementary Information

Zr modified SrNbO₂N as active photocatalyst for water oxidation under visible light illumination

Guoan Lin^{a,b}, Ran Wang^{a,b}, Tongcheng Cao*a, Liangxi Yuan*c and Xiaoxiang Xu*a,b

^aShanghai Key Lab of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, 1239 Siping Road, Shanghai, 200092, China. E-mail: <u>xxxu@tongji.edu.cn</u>; <u>ctc@tongji.edu.cn</u>; Tel: +86-21-65986919. ^bClinical and Central Lab, Putuo People's Hospital, Tongji University, 1291 Jiangning Road, Shanghai, 200060, China.

^cVascular department, Changhai hospital, Navy Military Medical University, Shanghai, 200433, China. Email: <u>yuanlx116@163.com</u>

List of Content

Figure S1. TGA curves of $SrNb_{1-x}Zr_xO_{2+y}N_{1-y}$ ($0 \le x \le 1$) from room temperature to 1473 K in air. These metal oxynitrides will be oxidized above 400 °C and a mass increase is seen due to the replacements of N with O. Nitrogen content can be qualitatively evaluated by the mass increase and is consistent with the trend of theoretical values that Zr leads to decrement of N content. Page S3 Figure S2. X-ray photoelectron spectroscopy spectra of as prepared samples $SrNb_{1-x}Zr_xO_{2+y}N_{1-y}$ ($0 \le x \le 1$),: (a) Nb 3d, (b) O 1s, (c) N 1s, (d) Zr 3d. Page S4 Figure S3. Element mapping of of $SrNb_{0.2}Zr_{0.8}O_{2+y}N_{1-y}$ (x = 0.8) under scanning electron microscopy conditions. Page S5

Figure S4. (a) Transmission electron microscopy (TEM) and (b) high resolution TEM images of $SrNb_{0.2}Zr_{0.8}O_{2+y}N_{1-y}$ (x = 0.8), lattice fringes marked corresponds to (110) planes. Page S5

Figure S5. (a) Recycling tests for O₂ evolution on $SrNb_{0.2}Zr_{0.8}O_{2+y}N_{1-y}$ (x = 0.8) under visible light illumination ($\lambda \ge 400$ nm), 0.05 M Na₂S₂O₈ aqueous solutions and 1 wt% CoO_x were used as a sacrificial agent and cocatalyst, respectively; (b) XRD of $SrNb_{0.2}Zr_{0.8}O_{2+y}N_{1-y}$ (x = 0.8) after before and after photocatalytic experiment.

Page S6

Table S1. AQE of oxynitride photocatalysts for O2 evolution from aqueous solutions

Page S6

Page S6-S7

References



Figure S1. TGA curves of $SrNb_{1-x}Zr_xO_{2+y}N_{1-y}$ ($0 \le x \le 1$) from room temperature to 1473 K in air. These metal oxynitrides will be oxidized above 400 °C and a mass increase is seen due to the replacements of N with O. Nitrogen content can be qualitatively evaluated by the mass increase and is consistent with the trend of theoretical values that Zr leads to decrement of N content.



Figure S2. X-ray photoelectron spectroscopy spectra of as prepared samples $SrNb_{1-x}Zr_xO_{2+y}N_{1-y}$ ($0 \le x \le 1$),: (a) Nb 3d, (b) O 1s, (c) N 1s, (d) Zr 3d.



Figure S3. Element mapping of SrNb_{0.2}Zr_{0.8}O_{2+y}N_{1-y} (x = 0.8) under scanning electron microscopy conditions.



Figure S4. (a) Transmission electron microscopy (TEM) and (b) high resolution TEM images of $SrNb_{0.2}Zr_{0.8}O_{2+y}N_{1-y}$ (x = 0.8), lattice fringes marked corresponds to (110) planes.



Figure S5. (a) Recycling tests for O₂ evolution on $SrNb_{0.2}Zr_{0.8}O_{2+y}N_{1-y}$ (x = 0.8) under visible light illumination ($\lambda \ge 400$ nm), 0.05 M Na₂S₂O₈ aqueous solutions and 1 wt% CoO_x were used as a sacrificial agent and cocatalyst, respectively; (b) XRD of $SrNb_{0.2}Zr_{0.8}O_{2+y}N_{1-y}$ (x = 0.8) after before and after photocatalytic experiment.

	J 1	J	1	
Photocatalyst	P.M	Co-catalyst	AQE (%) at 420 nm	Ref.
$SrNb_{0.2}Zr_{0.8}O_{2+y}N_{1-y}$	PC	1 wt% CoO _x	1.44	This
				work
CaNbO ₂ N	PC	-	1.1	1
LaTiO ₂ N	PC	2 wt% IrO ₂	1.5	2
La _{0.3} Ca _{0.7} TiO _{2.7} N _{0.3}	Co-precipitation	1 wt% CoO _x	3.13	3
SrMg _{0.2} Nb _{0.8} O _{2+y} N _{1-y}	PC	1 wt% CoO _x	5.13	4
LaTa _{0.9} Zr _{0.1} O _{1+y} N _{2-y}	PC	2 wt% CoO _x	0.93	5
BaTaO ₂ N	Flux	2 wt% CoO _x	0.24	6

Table S1. AQE of oxynitride photocatalysts for O₂ evolution from aqueous solutions

P.M means preparation method. PC denotes polymerized complex method

References

- B. Siritanaratkul, K. Maeda, T. Hisatomi and K. Domen, Synthesis and Photocatalytic Activity of Perovskite Niobium Oxynitrides with Wide Visible-Light Absorption Bands, *ChemSusChem*, 2011, 4, 74-78.
- A. Kasahara, K. Nukumizu, G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi and K. Domen, Photoreactions on LaTiO2N under visible light irradiation, *J Phys Chem A*, 2002, 106, 6750-6753.

- 3. F. F. Wu, G. Liu and X. X. Xu, Efficient photocatalytic oxygen production over Ca-modified LaTiO2N, J. Catal., 2017, 346, 10-20.
- 4. X. Q. Sun, G. Liu and X. X. Xu, Defect management and efficient photocatalytic water oxidation reaction over Mg modified SrNbO2N, *Journal of Materials Chemistry A*, 2018, **6**, 10947-10957.
- Y. W. Wang, S. Jin, G. X. Pan, Z. X. Li, L. Chen, G. Liu and X. X. Xu, Zr doped mesoporous LaTaON2 for efficient photocatalytic water splitting, *Journal of Materials Chemistry A*, 2019, 7, 5702-5711.
- M. Hojamberdiev, E. Zahedi, E. Nurlaela, K. Kawashima, K. Yubuta, M. Nakayama, H. Wagata, T. Minegishi, K. Domen and K. Teshima, The cross-substitution effect of tantalum on the visible-light-driven water oxidation activity of BaNbO2N crystals grown directly by an NH3-assisted flux method, *J. Mater. Chem. A*, 2016, 4, 12807-12817.