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

Supporting Information

Nitrogen-doped layered oxide $Sr_5Ta_4O_{15-x}N_x$ for water reduction and oxidation under visible light irradiation

Shanshan Chen,[a,b] Jingxiu Yang,[a,b] Chunmei Ding,[a,b] Rengui Li,[a,b] Shaoqing Jin,[a,b] Donge Wang,[a] Hongxian Han,[a] Fuxiang Zhang*[a] and Can Li*[a]

[a] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian 116023, P. R. China

[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

*To whom corresponding author should be addressed.
TEL: +86-411-84379070, FAX: +86-411-84694447,

E-mail: fxzhang@dicp.ac.cn; canli@dicp.ac.cn; Web: http://www.canli.dicp.ac.cn

Materials and Reagents

For the preparation of $Sr_5Ta_4O_{15-x}N_x$, $Ba_5Ta_4O_{15-x}N_x$ and $Sr_2Ta_2O_{7-x}N_x$, $TaCl_5$ (99.99%, Alfa Aesar), $SrCO_3$ (99.0%, Sinopharm Chemical), $BaCO_3$ (99.0%, Sinopharm Chemical), ethylene glycol (99.0%, Sinopharm Chemical), anhydrous citric acid (99.5%, Sinopharm Chemical) and CH_3OH (99.5%, Bodi Chemical) were used. K_2IrCl_6 (98.3%, Alfa Aesar), $Co(NO_3)_2 \cdot 6H_2O$ (99.0%, Sinopharm Chemical) were employed as precursors of oxygen evolution cocatalysts and $[(NH_4)_2Pt]Cl_6$ (98.8%, Alfa Aesar), K_2IrCl_6 (98.3%, Alfa Aesar) and $Na_3RhCl_6 \cdot 12H_2O$ (99.8%, Alfa Aesar) were used as precursors of hydrogen evolution cocatalysts. $AgNO_3$ (99.9%, Alfa Aesar) and CH_3OH (99.5%, Bodi Chemical) were employed as sacrificial electron acceptor and donor, respectively. La_2O_3 (99.95%, Sinopharm Chemical) was applied as a buffer agent. All chemicals were used as-purchased without further purification.

Preparation of $Sr_5Ta_4O_{15}$[s1]

Typically, $TaCl_5$ was dissolved in methanol, and then anhydrous citric acid (CA) and ethylene glycol (EG) with the molar ratio of Ta/CA/EG = 1/15/60 were added. The reaction mixture was then mechanically stirred until it showed transparent, followed by addition of stoichiometric $SrCO_3$. Then it was further stirred and kept at 473 K for 5 h to promote polymerization to yield a polymeric gel. The obtained gel was pyrolyzed at 723 K for 4 h to form a powder precursor which was transferred into a muffle furnace for calcination at 1273 K in air for 60 h. The final product was well-crystalline white $Sr_5Ta_4O_{15}$ powder.

Deposition of CoO_x[s2]

Typically, a calculated amount of cobalt nitrate aqueous solution (2 mL) was added to the aqueous suspension of $Sr_5Ta_4O_{15-x}N_x$ (0.2 g), and heated at 353 K in a water-bath. The as-impregnated powder was transferred into a sealed quartz tube and heated at 973 K for 1 h under NH_3 flow with the flow rate of 250 $mL \cdot min^{-1}$. The deposited cobalt oxide cocatalyst was denoted as CoO_x here.

Preparation of IrO_2[s2,s3]

Typically, a given amount of K_2IrCl_6 was added to a 100 mL deionized water and adjusted the pH value to ca. 12 by KOH (aq.). The reaction mixture was heated in a flask at 353 K until complete dissolution of K_2IrCl_6. The obtained transparent solution was then cooled to room temperature in an ice-water bath, and the pH value of the cooled solution was adjusted to 8.5-9.5 with diluted HNO_3 solution. Further heating at 353 K for 1 h, a deep blue IrO_2 colloid solution was finally formed.

S1

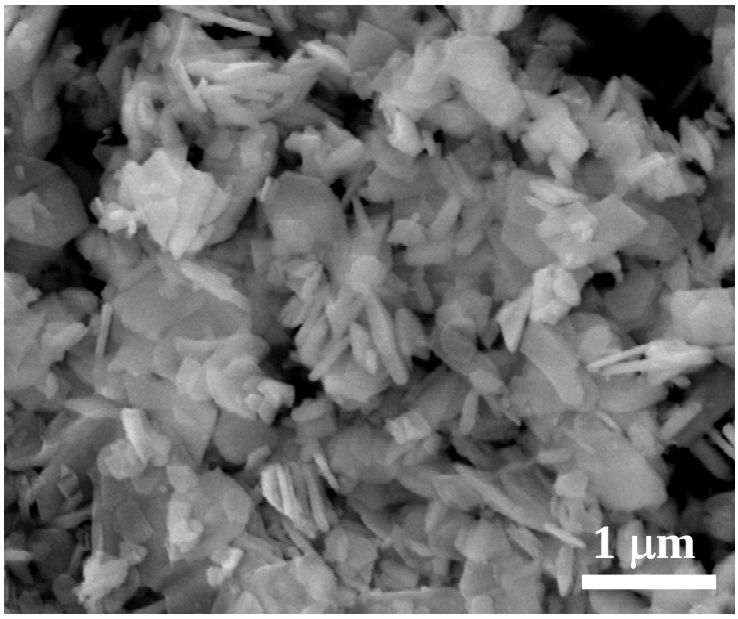

Figure S1. SEM image of the synthesized $Sr_5Ta_4O_{15}$.

S2

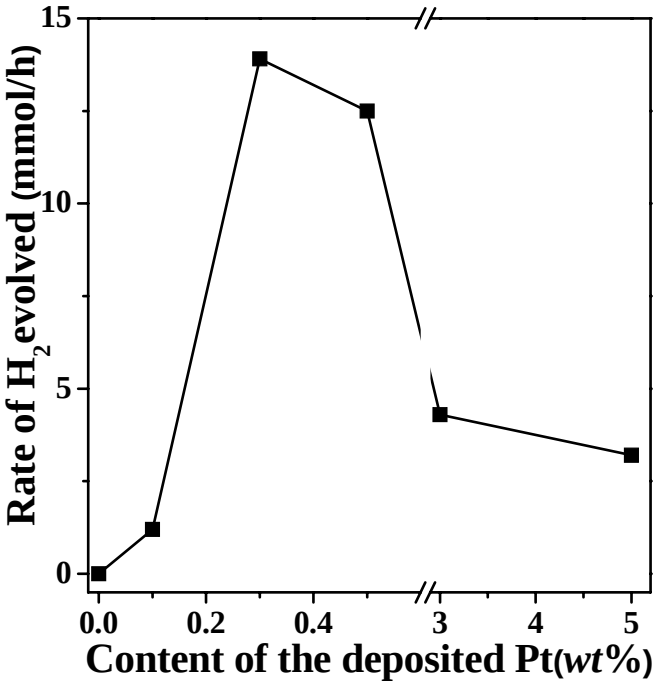

Figure S2. Rate of H_2 evolution on $Pt/Sr_5Ta_4O_{15-x}N_x$ samples as a function of platinum content. Reaction condition: 0.15 g catalyst; 150 mL 20 v% methanol solution; 0.15 g La_2O_3; 300 W Xe lamp ($\lambda \geq 420$ nm); 5 h irradiation.

S3

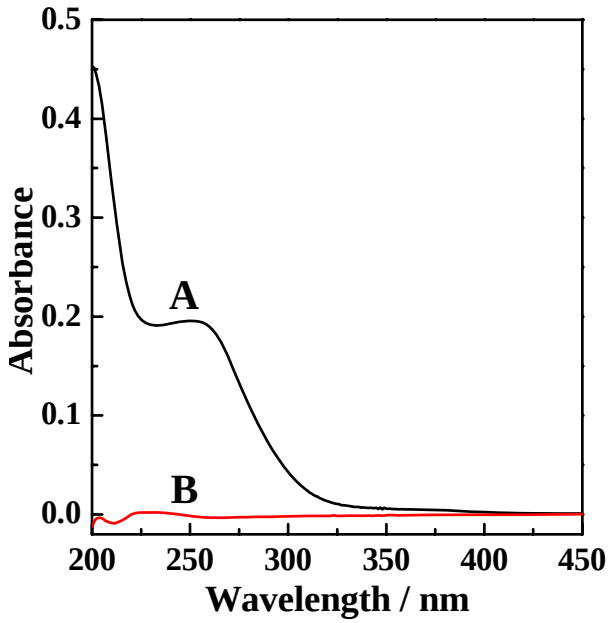

Figure S3. UV-Vis absorption spectra of the platinum solutions before and after 5 h photodeposition: (A) before photodeposition; (B) after photodeposition.

Condition: A desired amount (0.3 wt%) of platinum precursor ($[(NH_4)_2Pt]Cl_6$) was mixed with the solution containing 20 v% methanol solution (150 mL), 0.15 g $Sr_5Ta_4O_{15-x}N_x$ and 0.15 g La_2O_3. Prior to reaction, about 6 mL suspension was withdrew and denoted as sample A. The solution was then evacuated to ensure complete air removal, and irradiated from the top side with a 300 W Xenon lamp using a filtration mirror which was equipped with an optical filter (Hoya, L-42; $\lambda \geq 420$ nm) to cut off the ultraviolet light. After 5 h irradiation, about 6 mL suspension was also withdrawn and remarked as sample B. No H_2 evolution was detected. Sample A and B were centrifuged at the rate of 12000 rpm for 5 min, and their supernatants were measured by UV-Vis absorption spectra. Compared to the Sample A, the disappearance of the absorption peak in the Sample B demonstrates that the platinum precursor has been almost photodeposited on the surface of $Sr_5Ta_4O_{15-x}N_x$.

S4

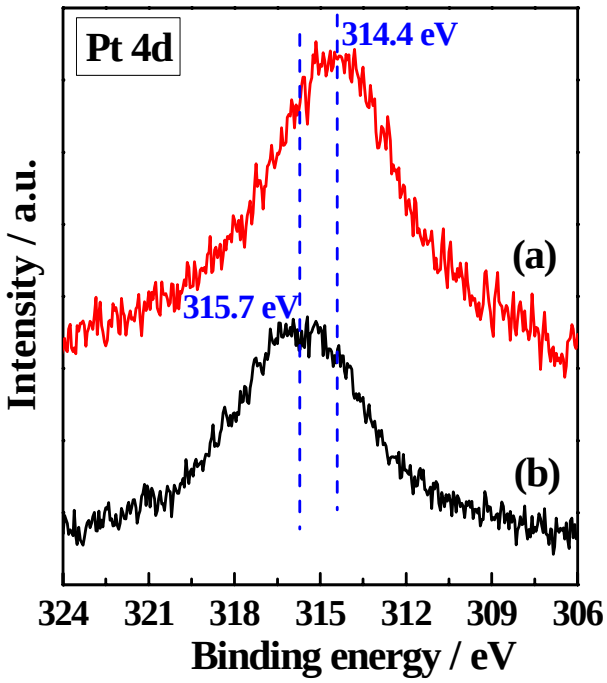

Figure S4. Pt 4d XPS spectra of samples: (a) Pt(Imp.-H_2)/$Sr_5Ta_4O_{15-x}N_x$; (b) Pt(P.D.)/$Sr_5Ta_4O_{15-x}N_x$.

Based on the binding energies located at 314.4 and 315.7 eV, the impregnated and photodeposited platinum on the surface of $Sr_5Ta_4O_{15-x}N_x$ can be deduced to mainly exist as Pt and PtO, respectively.[S4,S5]

S5

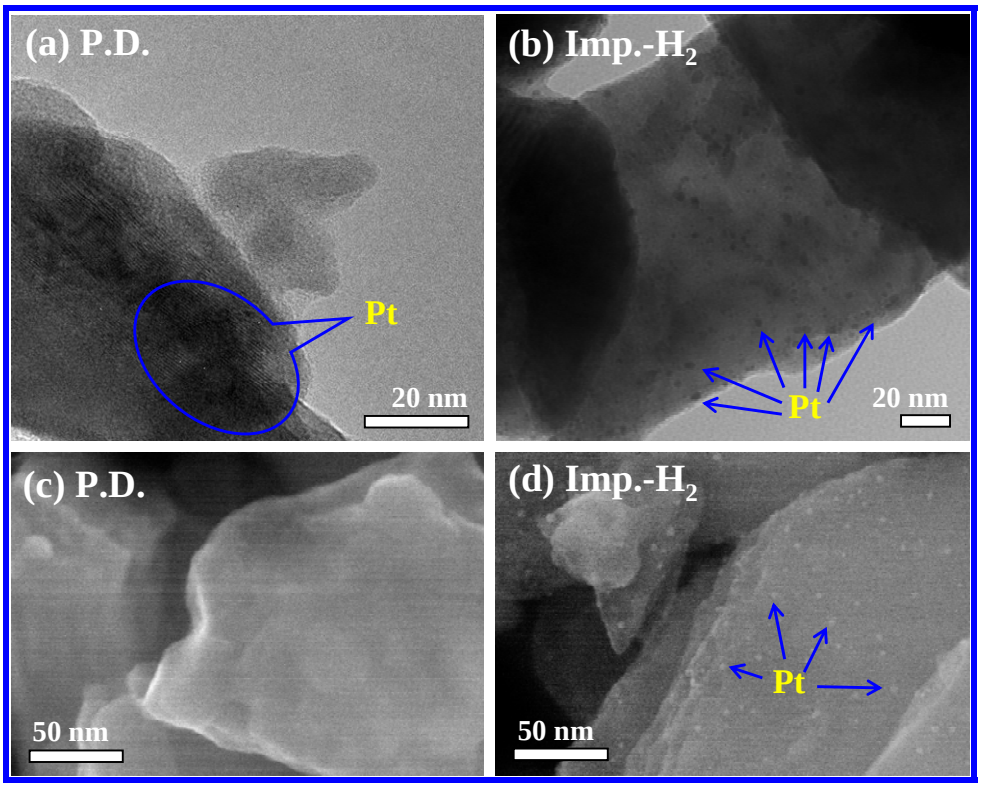

Figure S5. Typical TEM (a, b) and SEM (c, d) images of Pt(P.D.)/$Sr_5Ta_4O_{15-x}N_x$ and Pt(Imp.-H_2)/$Sr_5Ta_4O_{15-x}N_x$.

S6

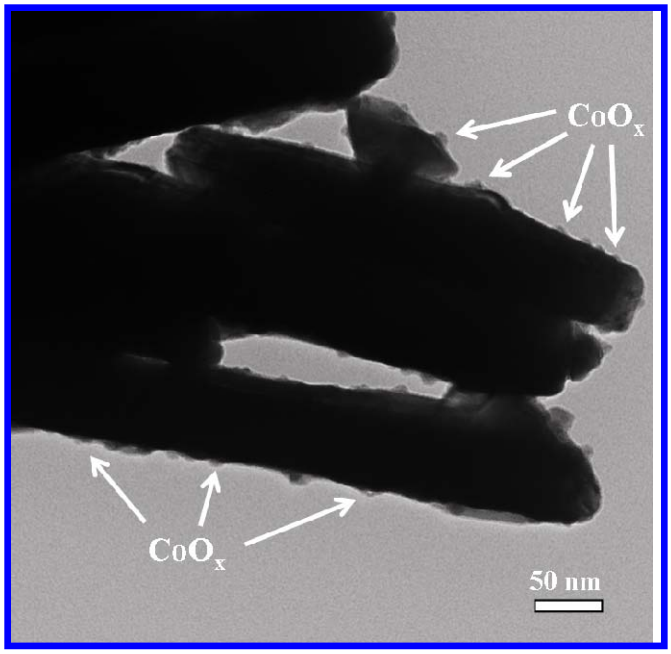

Figure S6. Representative TEM image of $CoO_x/Sr_5Ta_4O_{15-x}N_x$.

S7

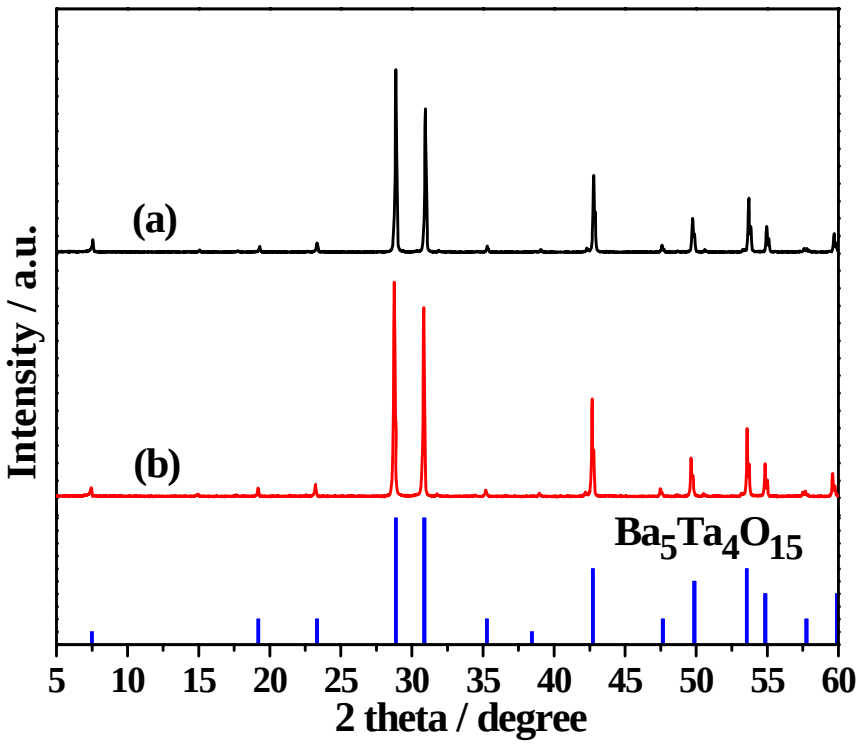

Figure S7. XRD patterns of the $Ba_5Ta_4O_{15}$ samples before (a) and after thermal ammonia treatment (b).

The XRD patterns of the synthesized $Ba_5Ta_4O_{15}$ oxide are in good agreement with the standard diffraction patterns of $Ba_5Ta_4O_{15}$ (PDF#18-0193). After nitrogen doping treatment, the diffraction peaks were maintained.

S8

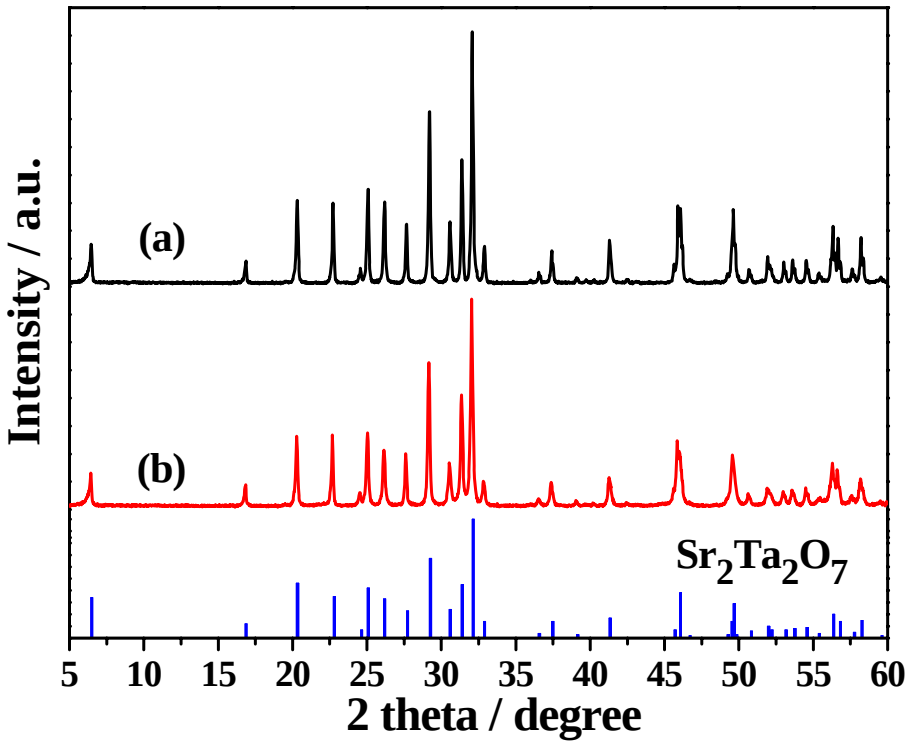

Figure S8. XRD patterns of the $Sr_2Ta_2O_7$ samples before (a) and after thermal ammonia treatment (b).

The XRD patterns of the synthesized $Sr_2Ta_2O_7$ oxide are in good agreement with the standard diffraction patterns of $Sr_2Ta_2O_7$ (PDF#30-1304). After nitrogen doping treatment, the diffraction peaks were maintained.

S9

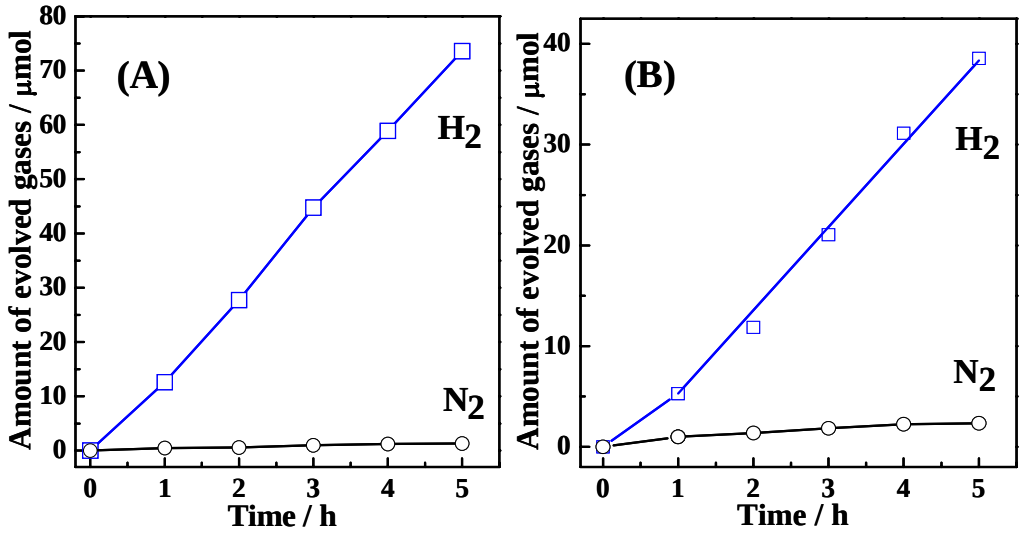

Figure S9. Typical time courses of H_2 evolution for the 0.3 wt% Pt/$Ba_5Ta_4O_{15-x}N_x$ (A) and 0.3 wt% Pt/$Sr_2Ta_2O_{7-x}N_x$ (B) under visible light irradiation. Reaction condition: 0.15 g catalyst; 150 mL 20 v% methanol solution; 0.15 g La_2O_3; 300 W Xe lamp ($\lambda \geq 420$ nm).

S10

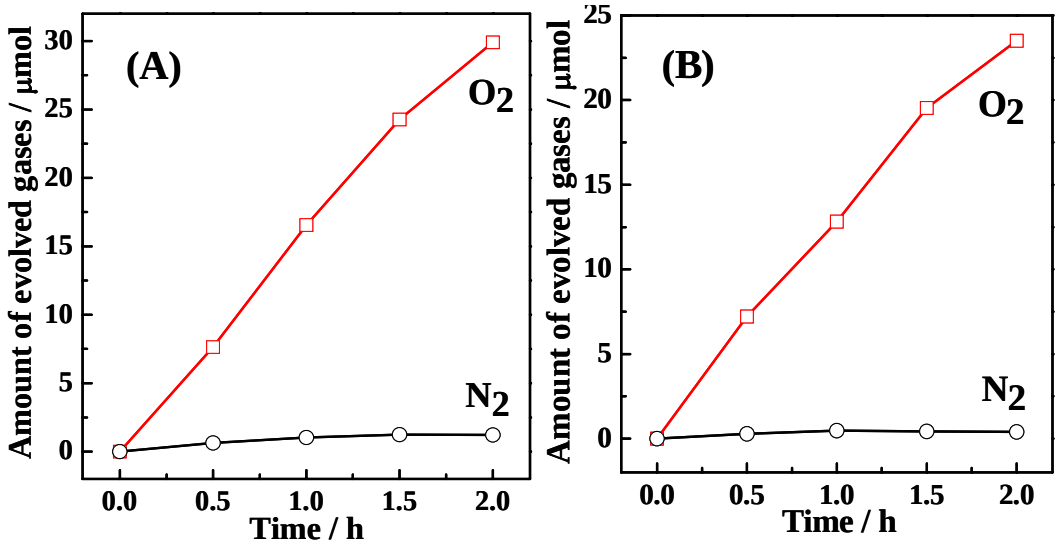

Figure S10. Typical time courses of O_2 evolution for the 1.0 wt% $CoO_x/Ba_5Ta_4O_{15-x}N_x$ (A) and 1.0 wt% $CoO_x/Sr_2Ta_2O_{7-x}N_x$ (B) under visible light irradiation. Reaction condition: 0.15 g catalyst; 150 mL 0.01 M $AgNO_3$ aqueous solution; 0.15 g La_2O_3; 300 W Xe lamp ($\lambda \geq 420$ nm).

Supplementary References

[S1] K. Yoshioka, V. Petrykin, M. Kakihana, H. Kato and A. Kudo, J. Catal. 2005, 232, 102..

[S2] F. X. Zhang, A. Yamakata, K. Maeda, Y. Moriya, T. Takata, J. Kubota, K. Teshima, S. Oishi and K. Domen, J. Am. Chem. Soc. 2012, 134, 8348.

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[S5] F. X. Zhang, J. X. Chen, X. Zhang, W. L. Gao, R. C. Jin, N. J. Guan and Y. Z. Li, *Langmuir* **2004**, *20*, 9329-9334