

*Electronic Supplementary Information*

## Controlled Nitridation of Tantalum (Oxy)Nitride Nanoparticles towards Optimized Metal-Support Interactions with Gold Nanocatalysts

Xiaoyun Yang,<sup>†</sup> Sina He,<sup>†</sup> Yijin Shu,<sup>†</sup> Zhangping Shi,<sup>‡</sup> Yulin Guo,<sup>†</sup> Qingsheng Gao<sup>\*†</sup> and Yi Tang<sup>‡</sup>

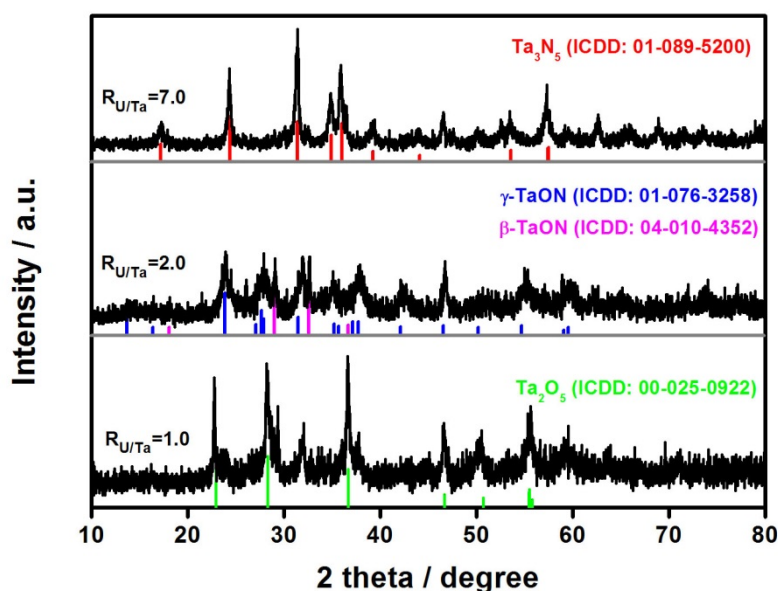
<sup>†</sup> Department of Chemistry, Jinan University

No. 601 Huangpu West Avenue, Guangzhou, 510632, P. R. China

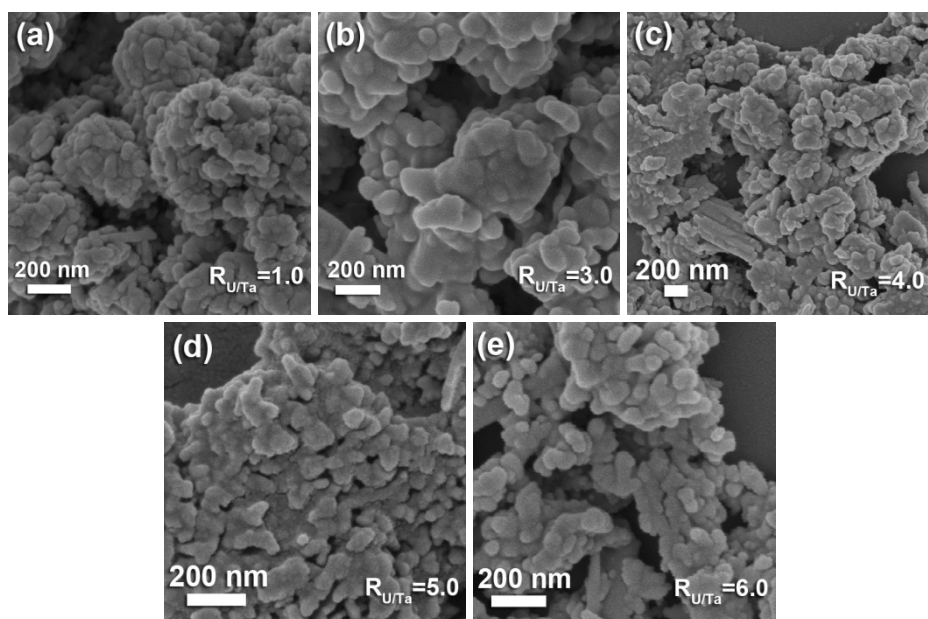
E-mail: tqsgao@jnu.edu.cn

<sup>‡</sup> Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Laboratory of Advanced Materials and Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University

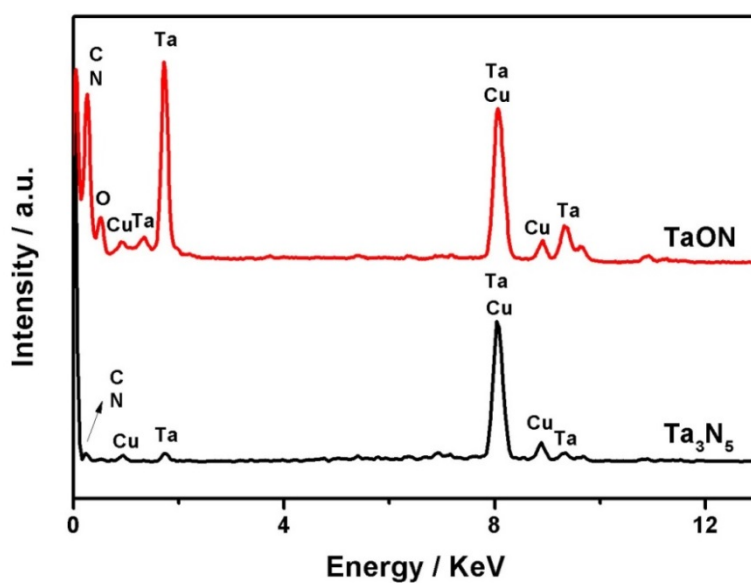
No. 220 Handan Road, Shanghai, 200433, P. R. China



**Fig. S1** XRD patterns of three typical products received at  $R_{U/Ta} = 1.0$ , 2.0 and 7.0 with the standard ones obtained from PDF database.



**Fig. S2** SEM images of products synthesized via a  $\text{Sr}^{2+}$ -mediated ionothermal method with the  $R_{\text{U/Ta}}$  ratio of (a) 1.0, (b) 3.0, (c) 4.0, (d) 5.0 and (e) 6.0.

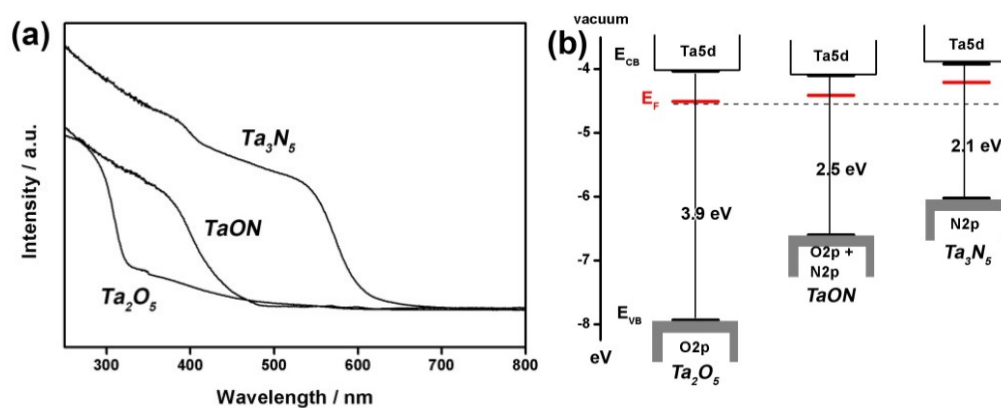


**Fig. S3** EDS taken on  $\text{TaON}$  and  $\text{Ta}_3\text{N}_5$  nanoparticles after a treatment with 1 M HCl for 48 hours, which are synthesized with the  $R_{\text{U/Ta}}$  of 2.0 and 7.0, respectively.

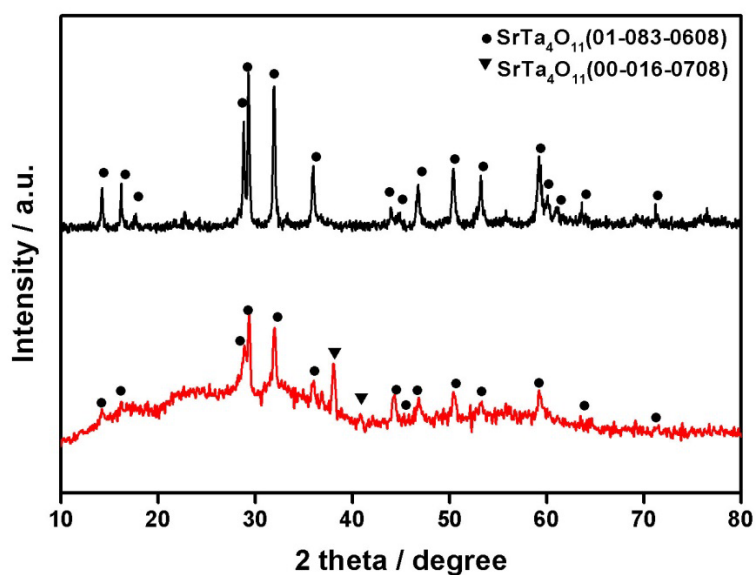
**Table S1** Textures of Ta-based supports and the corresponding supported Au nanocatalysts used in our work.

	$S_{\text{BET}}(\text{m}^2 \text{g}^{-1})^{\text{a}}$	N (wt%) <sup>b</sup>	Au (wt%) <sup>c</sup>	CO uptake ( $\text{mL} \cdot \text{g}^{-1}_{\text{Au}}$ ) <sup>d</sup>
Ta <sub>2</sub> O <sub>5</sub>	22.5	/	/	/
TaON	21.3	5.0	/	/
Ta <sub>3</sub> N <sub>5</sub>	25.6	9.5	/	/
0.9%Au/Ta <sub>2</sub> O <sub>5</sub>	17.9	/	0.88	47.0
0.8%Au/TaON	15.6	/	0.81	47.8
0.9%Au/Ta <sub>3</sub> N <sub>5</sub>	16.9	/	0.89	46.8

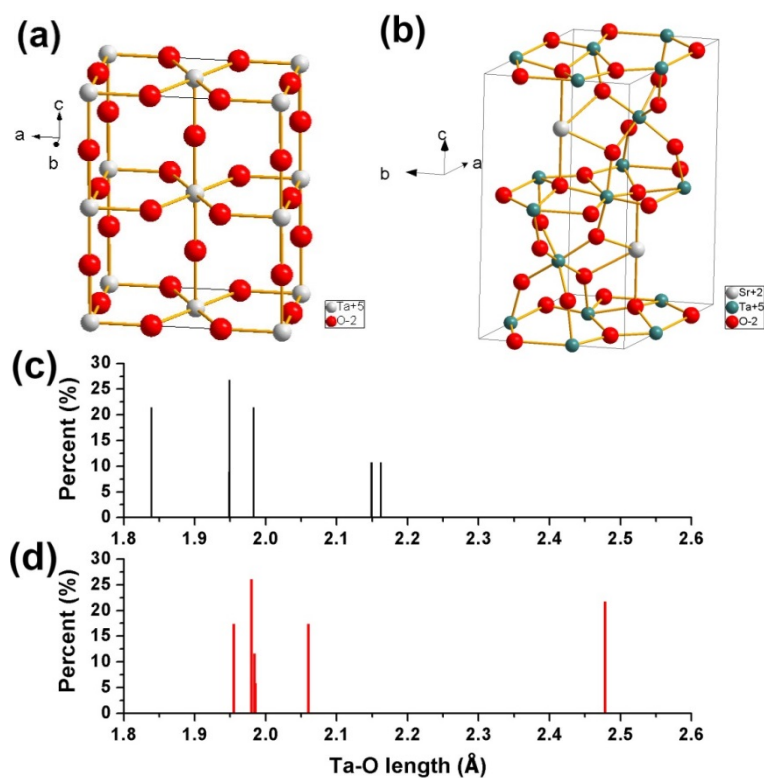
a: determined by N<sub>2</sub> isothermal sorption, b: detected by CHN elemental analysis, c: investigated by ICP-AES, d: measured by a chemisorption equipment.



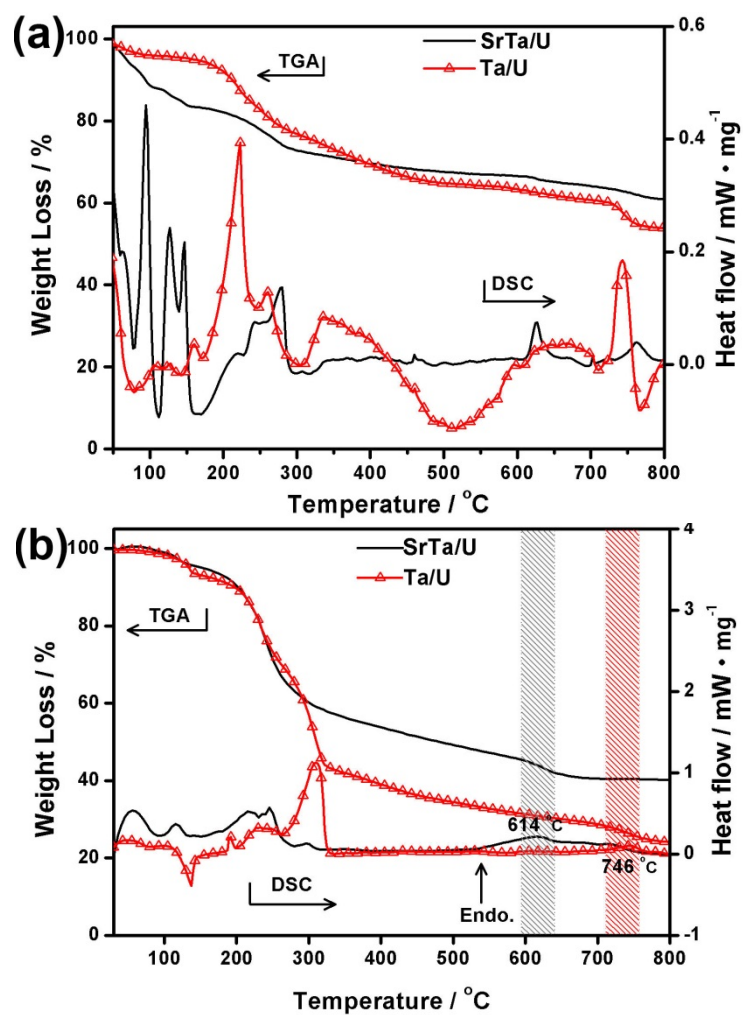
**Fig. S4** (a) UV-Vis DRS and (b) schematic band structures of Ta<sub>2</sub>O<sub>5</sub>, TaON and Ta<sub>3</sub>N<sub>5</sub>, respectively. The increased Fermi level ( $E_{\text{F}}$ ) in TaON and Ta<sub>3</sub>N<sub>5</sub> due to nitridation is highlighted in (b), as compared with that of Ta<sub>2</sub>O<sub>5</sub>.



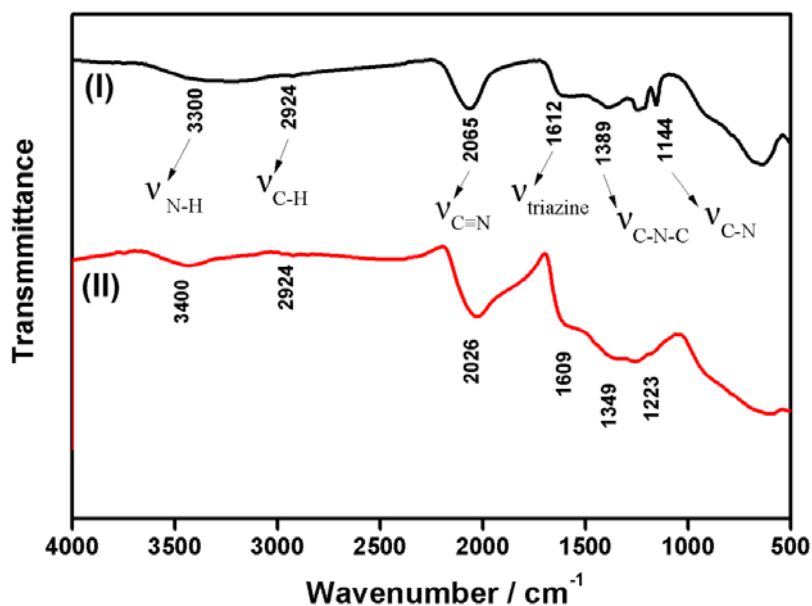
**Fig. S5** XRD patterns of products obtained (red) at 550 °C with a N<sub>2</sub> flow rate of 500 mL min<sup>-1</sup>, and (black) at 700 °C with a N<sub>2</sub> flow rate of 100 mL min<sup>-1</sup>, employing SrTa/U with R<sub>U/Ta</sub> = 2.0 as the precursor.



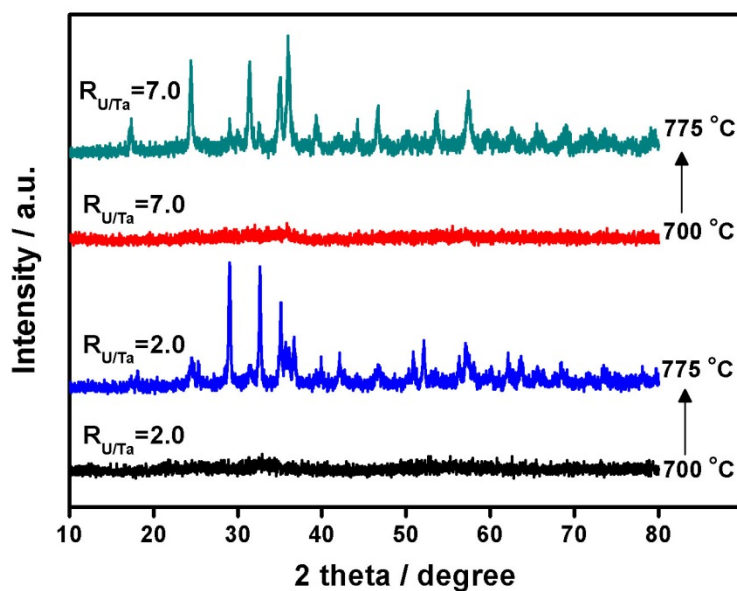
**Fig. S6** Unit cells of (a) Ta<sub>2</sub>O<sub>5</sub> and (b) SrTa<sub>4</sub>O<sub>11</sub>, and the corresponding length distribution of Ta-O bonds in (c) Ta<sub>2</sub>O<sub>5</sub> and (d) SrTa<sub>4</sub>O<sub>11</sub>.



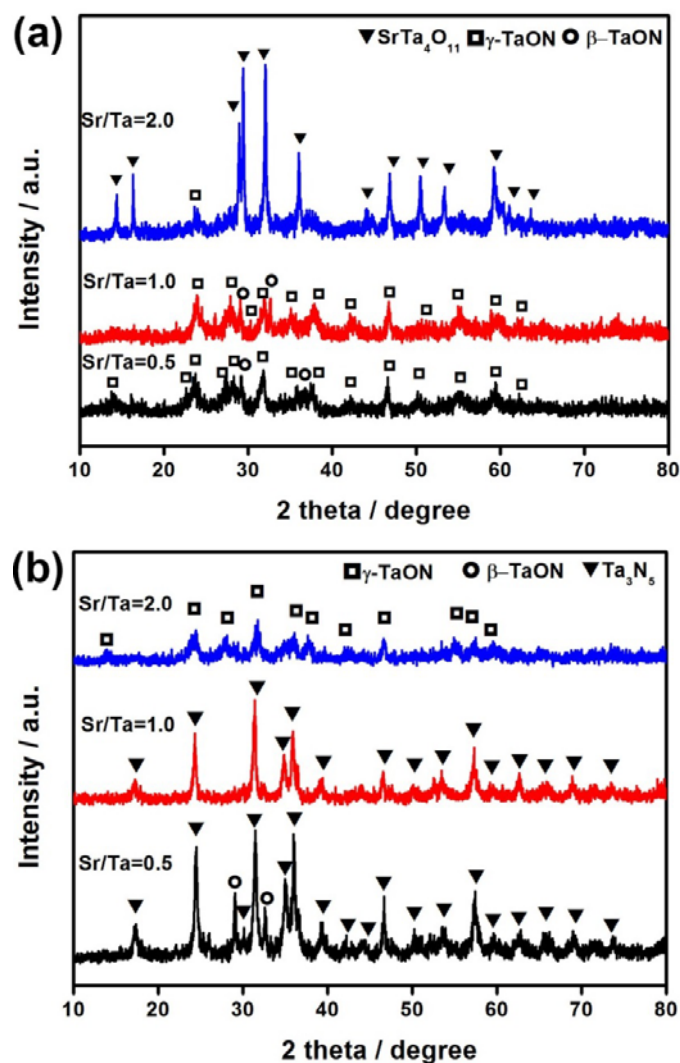
**Fig. S7** TGA/DSC curves of SrTa/U and Ta/U with the same  $R_{U/Ta}$  of (a) 2.0 and (b) 7.0.



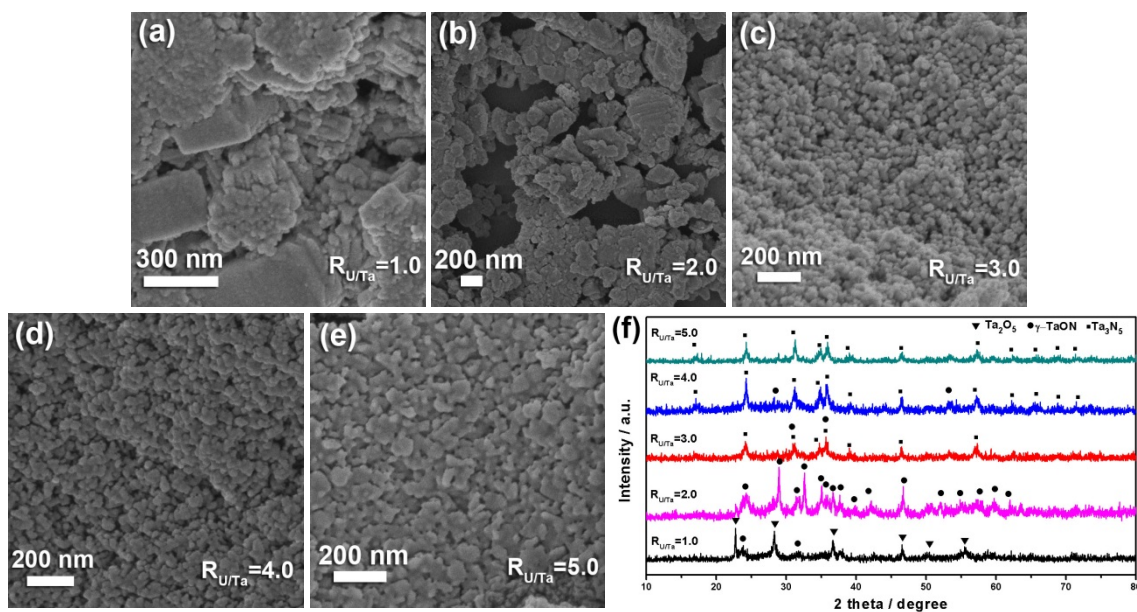
**Fig. S8** FT-IR spectra of products received from the calcination of (I) SrTa/U and (II) Ta/U with the same  $R_{U/Ta}$  of 2.0 at 500°C. The obvious adsorption bands for  $\nu_{N-H}$ ,  $\nu_{C-H}$ ,  $\nu_{C\equiv N}$ ,  $\nu_{\text{triazine}}$ ,  $\nu_{C-N-C}$  and  $\nu_{C-N}$  well confirm the presence of  $CN_x$  in the products derived from both SrTa/U and Ta/U.<sup>[1]</sup>



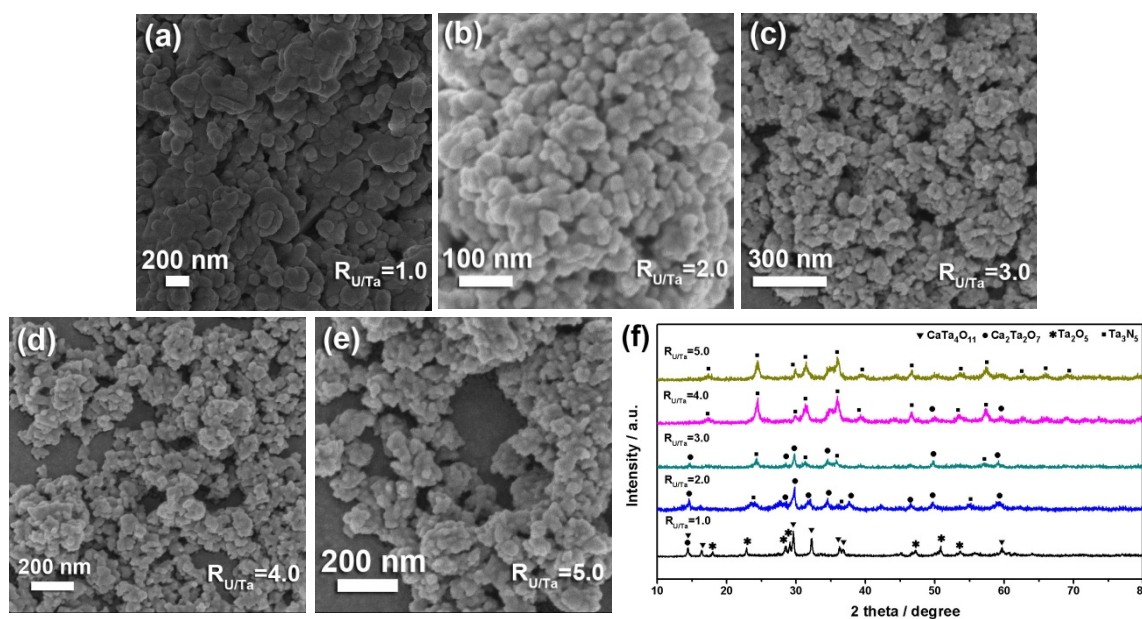
**Fig. S9** XRD patterns of the samples obtained from calcining Ta/U precursors ( $R_{U/Ta} = 2.0$  and 7.0) at 700 and 775 °C. At 700 °C, only amorphous products are received in the absence of  $Sr^{2+}$ , and the higher temperature of 775 °C is required to fabricate crystallized Ta-based (oxy)nitrides, which is well consistent with the TGA/DSC results (Figure 5a in manuscript and Figure S6 in SI).



**Fig. S10** XRD patterns of the products obtained with a varied Sr/Ta ratios ( $R_{Sr/Ta}$ ) of 0.5, 1.0 and 2.0, as a  $R_{U/Ta}$  of (a) 2.0 and (b) 7.0 is adopted, which clearly show the influenced nitridation by controlling strontium tantalate intermediates. In the case with the  $R_{U/Ta}$  of 2.0 (a), TaON is received at  $R_{Sr/Ta} = 0.5$  and 1.0, while,  $SrTa_4O_{11}$  is mainly harvested at  $R_{Sr/Ta} = 2.0$ . The presence of  $SrTa_4O_{11}$  is associated with the inadequate urea for nitridation ( $R_{U/Ta} = 2.0$ ). This indicates the suitable  $R_{Sr/Ta}$  between 0.5 ~ 1.0 for the controlled generation of TaON. In another case with the  $R_{U/Ta}$  of 7.0 (b), a varied evolution is observed, which can be ascribed to the sufficient nitrogen source of urea. With the low  $R_{Sr/Ta}$  of 0.5, a mixture of  $Ta_3N_5$  and TaON is obtained due to insufficient  $Sr^{2+}$ , and  $Ta_3N_5$  is fabricated as  $R_{Sr/Ta}$  is 1.0. With the high  $R_{Sr/Ta}$  of 2.0, TaON is received because the controlled nitridation is further enhanced by excessive  $Sr^{2+}$ .

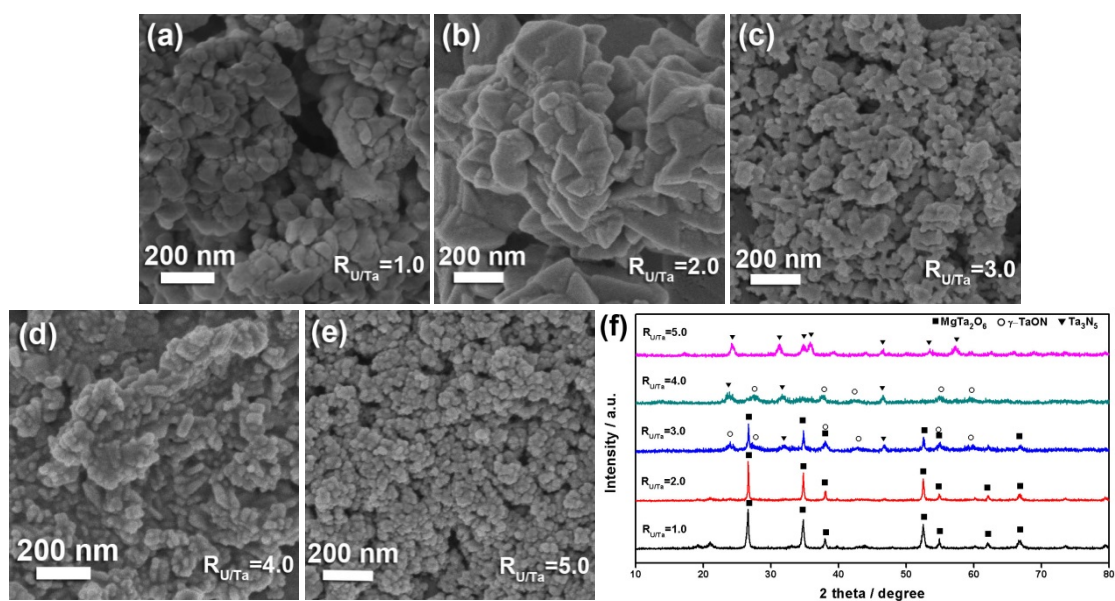


**Fig. S11** (a-e) SEM images and (f) XRD patterns of products synthesized via  $Ba^{2+}$ -mediated ionothermal method with the  $R_{U/Ta}$  from 1.0 to 5.0.



**Fig. S12** (a-e) SEM images and (f) XRD patterns of products synthesized via  $Ca^{2+}$ -mediated ionothermal method with the  $R_{U/Ta}$  from 1.0 to 5.0.





**Fig. S13** (a-e) SEM images and (f) XRD patterns of products synthesized via  $\text{Mg}^{2+}$ -mediated ionothermal method with the  $R_{\text{U/Ta}}$  from 1.0 to 5.0.

**Table S2** Hydrogenation of NB over supported Au with a varied loading amount.<sup>a</sup>

Entry	Catalysts	Conv.(%)	Sel. (%)	
			PHA	AN
1	0.5%Au/Ta <sub>2</sub> O <sub>5</sub>	36	>99	0
2	0.5%Au/TaON	39	85	15
3	0.5%Au/Ta <sub>3</sub> N <sub>5</sub>	37	>99	0
4	1.3%Au/Ta <sub>2</sub> O <sub>5</sub>	60	42	58
5	1.3%Au/TaON	>99	29	71
6	1.4%Au/Ta <sub>3</sub> N <sub>5</sub>	67	58	42
7	1.8%Au/Ta <sub>2</sub> O <sub>5</sub>	77	67	33
8	1.7%Au/TaON	>99	27	73
9	1.7%Au/Ta <sub>3</sub> N <sub>5</sub>	96	37	63

[a] Typical conditions: NB (0.5 mmol), catalysts (40 mg), FA (6.0 mmol), EtOH (5.0 mL), H<sub>2</sub>O (5.0 mL), N<sub>2</sub> (0.5 MPa), 80 °C, 2.5 hours.

**Table S3** Catalytic decomposition of formic acid over supported Au.<sup>a</sup>

Catalysts	Conv. (%)	CO <sub>2</sub> Sel. (%)
0.9%Au/Ta <sub>2</sub> O <sub>5</sub>	44	>99
0.8%Au/TaON	49	>99
0.9%Au/Ta <sub>3</sub> N <sub>5</sub>	52	>99

a: Typical reaction conditions: 6 mmol of HCOOH, 40 mg of catalyst, 0.5 MPa N<sub>2</sub>, 80 °C, 2.5 hours. The liquid and gas products were analyzed by HPLC and GC, respectively.

**Table S4** Catalytic hydrogenation of phenylhydroxylamine (PHA) over supported Au.<sup>a</sup>

Catalysts	Conv.(%)	Sel. <sub>AN</sub> (%)
0.9%Au/Ta <sub>2</sub> O <sub>5</sub>	79	> 99
0.8%Au/TaON	78	> 99
0.9%Au/Ta <sub>3</sub> N <sub>5</sub>	72	> 99

[a] Typical conditions: PHA (0.5 mmol), catalysts (40 mg), FA (6.0 mmol), EtOH (5.0 mL), H<sub>2</sub>O (5.0 mL), N<sub>2</sub> (0.5 MPa), 80 °C, 2.5 hours.

## References

[1] B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Muller, W. Schnick, *J. Am. Chem. Soc.* **2003**, *125*, 10288.