Supporting Information

Surface Chemistry Imposing Selective Reduction of CO_2 to CO over Ta$_3$N$_5$/LaTiO$_2$N Photocatalyst

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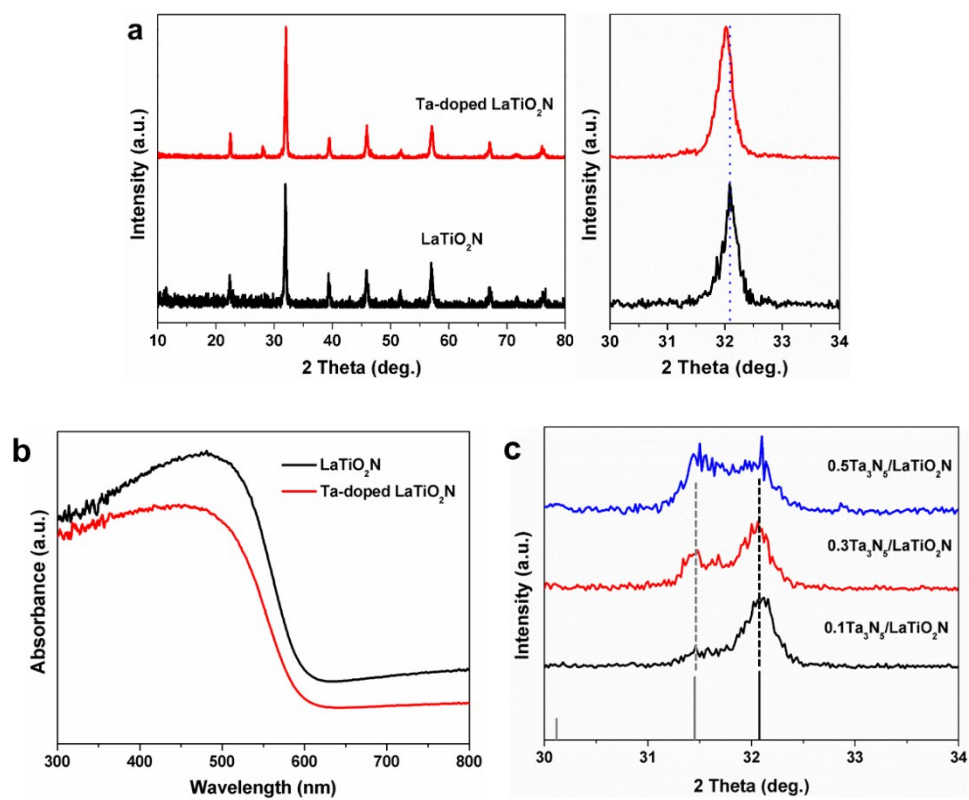
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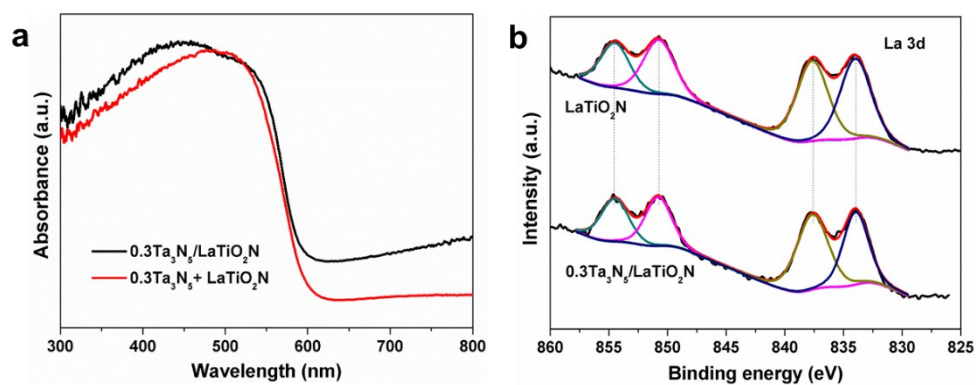
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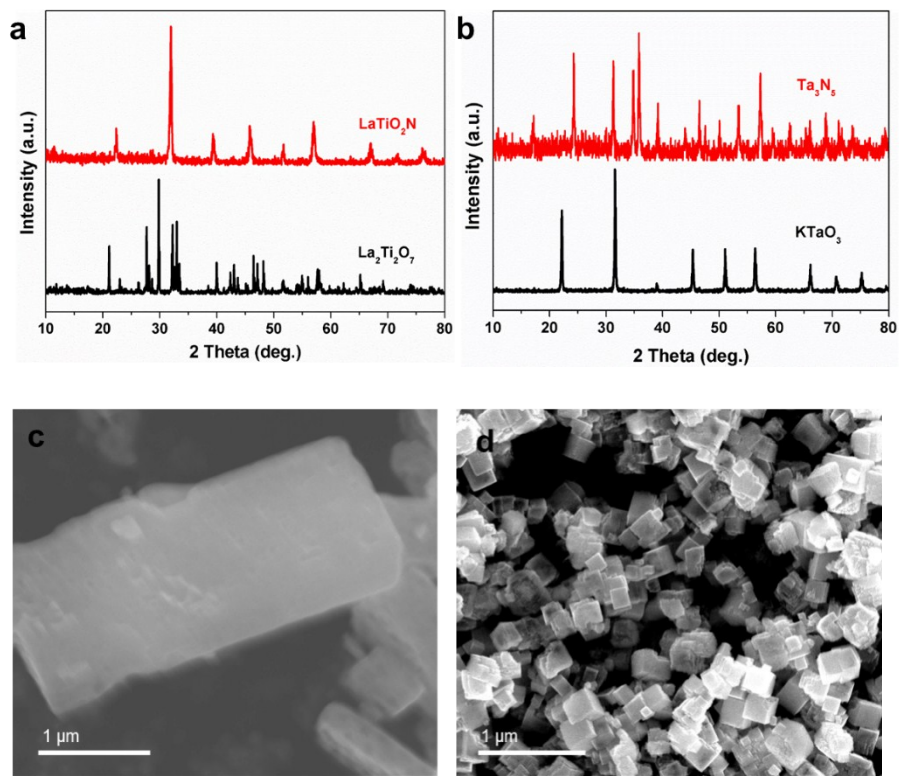
Fig. S1. XRD patterns for as-prepared (a) $La_2Ti_2O_7$ and $LaTiO_2N$, and (b) $KTaO_3$ and Ta_3N_5. SEM image of (c) $La_2Ti_2O_7$ and (d) $KTaO_3$.

Fig. S2. (a) XRD patterns and (b) UV-vis absorption spectra for LaTiO$_2$N and Ta-doped LaTiO$_2$N. (c) Enlarged XRD patterns for xTa$_3$N$_5$/LaTiO$_2$N (x = 0.1, 0.3, and 0.5).

Fig. S3. (a) UV-vis absorption spectra for $0.3Ta_3N_5/LaTiO_2N$ and mixtures of Ta_3N_5 and $LaTiO_2N$ with the same mole ratio. (b) La 3d XPS spectra for $LaTiO_2N$ and $0.3Ta_3N_5/LaTiO_2N$.
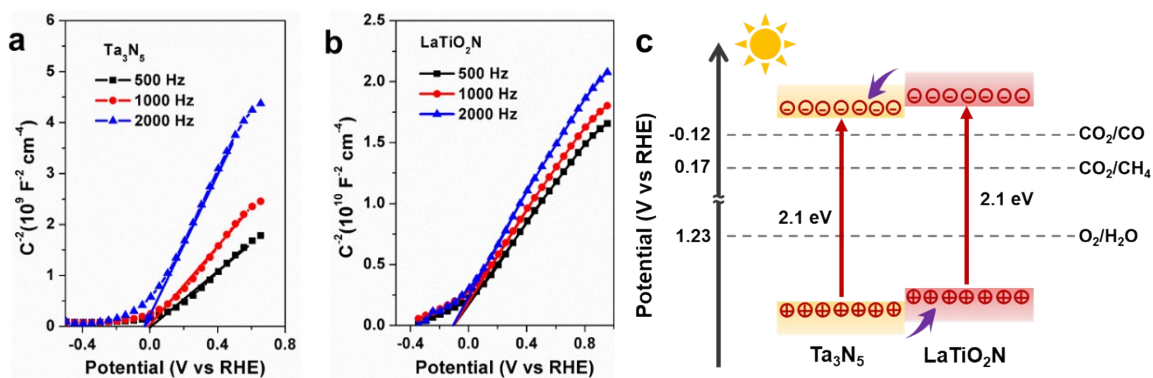
Fig. S4. Mott-Schottky plots for the (a) Ta_3N_5 and (b) $LaTiO_2N$. Electrolyte: 0.5 M Na_2SO_4 solution (pH 7). (c) The relative band positions for Ta_3N_5/$LaTiO_2N$.

The relative band positions of Ta_3N_5 and $LaTiO_2N$ were analyzed by combining their Mott-Schottky (M-S) plots and UV-vis results. As shown in **Fig. S4a**, the evaluated flat band potential of the as-prepared Ta_3N_5 was about -0.018 V vs reversible hydrogen electrode (RHE), and the measured flat band potential of the $LaTiO_2N$ was -0.132 V vs RHE **(Fig. 4b)**. Normally, the CB bottom for an n-type semiconductor is about 0.2 V above the flat band potential.[1,2] Then, the corresponding CB positions of the n-type Ta_3N_5 and $LaTiO_2N$ were, respectively, estimated to be -0.218 and -0.332 eV. Based on their band gaps calculated from the UV-vis results **(Fig. 3a)**, the relative VB positions of the Ta_3N_5 and $LaTiO_2N$ were deduced and given in **Fig. S4c**. Obviously, the composite materials showed a typical type-Ⅱ heterojunction structure, in which the photogenerated electrons were expected to transfer from the CB of $LaTiO_2N$ to Ta_3N_5, while the holes were followed by an opposite way. This indicated that the CO_2 reduction would actually take place on Ta_3N_5 surface. Here, it was noted that the measured CB and VB levels of $LaTiO_2N$ were in consistent with the reported value,[3] while the corresponding CB and VB energies of Ta_3N_5 were both lower than the previous reported value.[4] This was possibly resulted from the high content of TaO_x species (13.1%) in the as-prepared Ta_3N_5 **(Fig. 3e)**. Indeed, both the previous theoretical calculations and experimental results confirmed that the oxygen impurity contributed to the downshift of band position due to the lower energy of O 2p orbital than that of N 2p orbital, which composed the valance band of Ta_3N_5.[5,6]
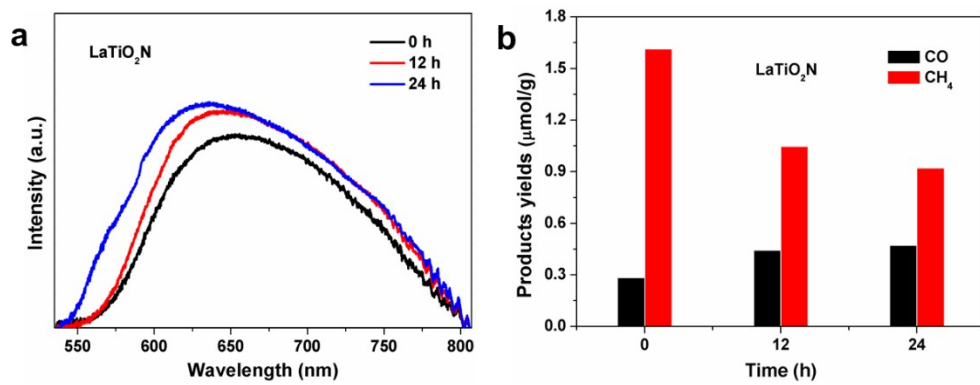
Fig. S5. (a) PL patterns and (b) according CO_2 reduction products for $LaTiO_2N$ with different annealing time under air.
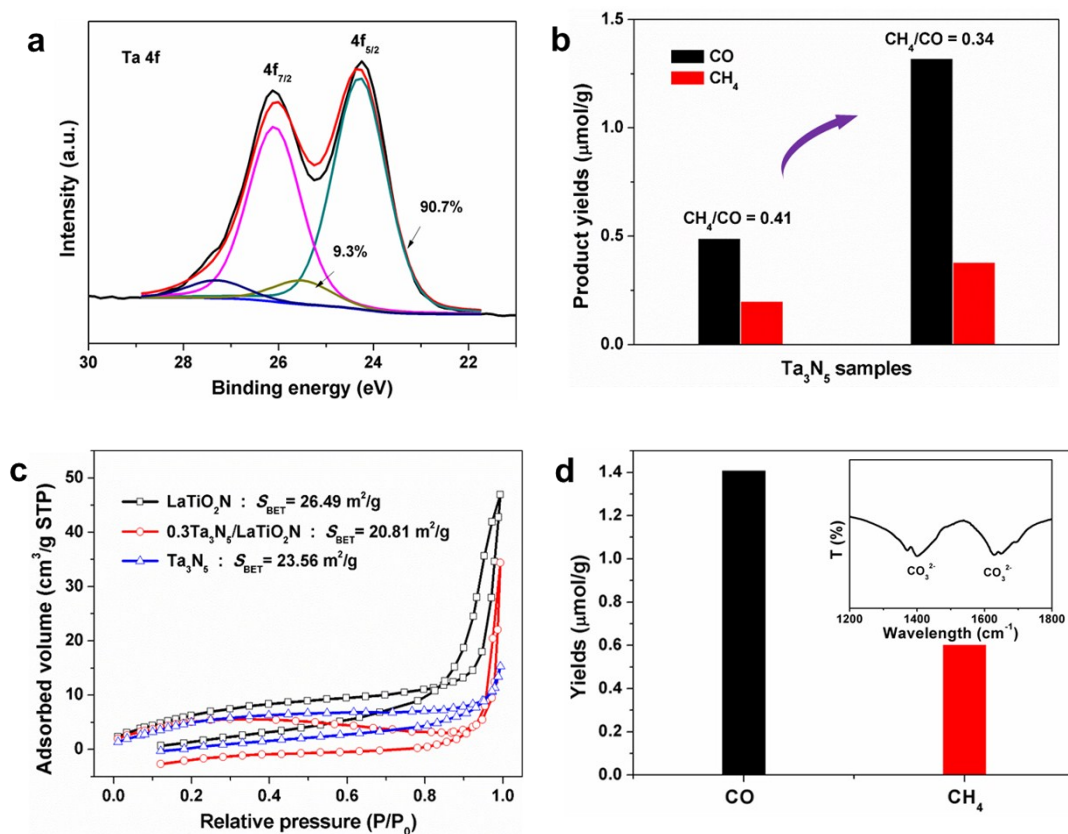
Fig. S6. (a) Ta 4f XPS peaks for Ta_3N_5 by nitriding $KTaO_3$ at 1223 K for 8 h under 500 mL/min NH_3. (b) CO_2 reduction products for Ta_3N_5 samples from $KTaO_3$ with different nitridation process. (c) N_2 adsorption-desorption isotherms for $LaTiO_2N$, Ta_3N_5, and $0.3Ta_3N_5/LaTiO_2N$ samples. (d) The CO_2 reduction products over KOH modified (020) Ta_3N_5 under the visible light irradiation for 8 h. The inset shows the FT-IR spectrum.
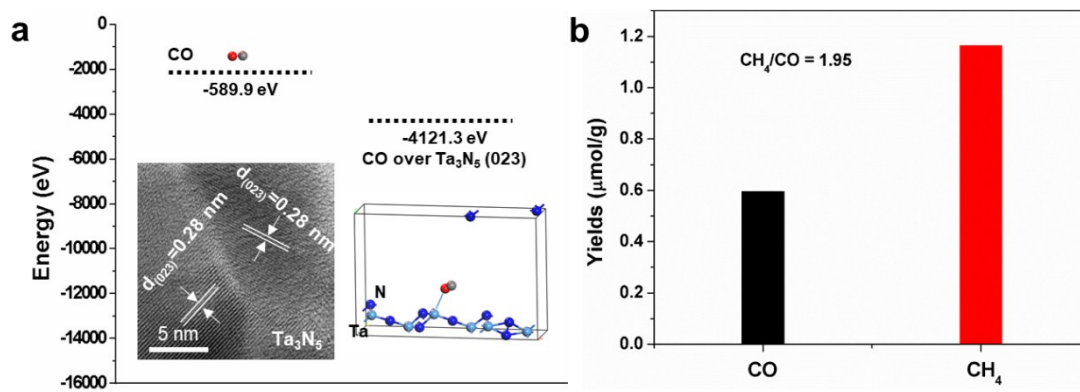
Fig. S7. (a) The adsorbed energy for CO on Ta_3N_5 (023) facet. The calculated energy for Ta_3N_5 (023) facet was -3528.7 eV. (b) CO_2 reduction products over polycrystalline Ta_3N_5 prepared by direct nitriding of Ta_2O_5 at 1123 K for 8 h under 500 mL/min NH_3. The inset in Fig. S7a shows the TEM image of polycrystalline Ta_3N_5.

REFERENCES

1. Y. Qi, S. Chen, M. Li, Q. Ding, Z. Li, J. Cui, B. Dong, F. Zhang and C. Li, *Chem. Sci.*, 2017, **8**, 437.

2. S. Chen, S. Shen, G. Liu, Y. Qi, F. Zhang and C. Li, *Angew. Chem. Int. Ed.*, 2015, **54**, 3047.

3. E. Watanabe, H. Ushiyama and K. Yamashita, *ACS Appl. Mater. Inter.*, 2017, **9**, 9559.

4. T. Minegishi, N. Nishimura, J. Kubota and K. Domen, *Chem. Sci.*, 2013, **4**, 1120.

5. Y. He, J. Thorne, C. Wu, P. Ma, C. Du, Q. Dong, J. Guoa and D. Wang, *Chem*, 2016, **1**, 640.

6. J. Wang, T. Fang, L. Zhang, J. Feng, Z. Li and Z. Zou, *J. Catal.*, 2014, **309**, 291.