

## Supplementary Information

Novel C<sub>3</sub>N<sub>4</sub>-CdS composite photocatalysts with organic-inorganic heterojunctions: *in situ* synthesis, exceptional activity, high stability and photocatalytic mechanism

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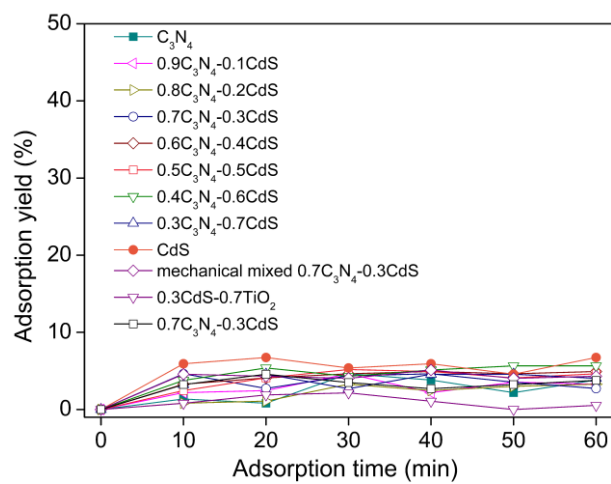
### **Details for the preparation of N-modified TiO<sub>2</sub> photocatalyst, 0.7C<sub>3</sub>N<sub>4</sub>-0.3TiO<sub>2</sub> and 0.3CdS-0.7TiO<sub>2</sub> composites:**

N-modified TiO<sub>2</sub> was prepared by means of solid-state reaction method using urea as a nitrogen source.<sup>1</sup> P25 TiO<sub>2</sub> (1.0 g) was finely milled with urea (2.0 g) and the mixture was heated at 400 °C for 2 h. After cooling to the room temperature, the N-modified TiO<sub>2</sub> photocatalyst was obtained.

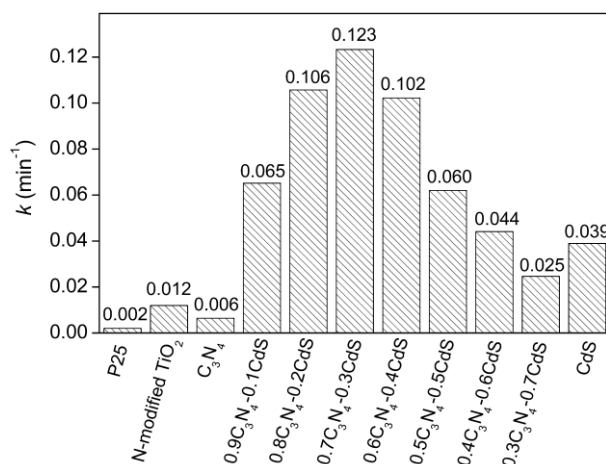
The 0.7C<sub>3</sub>N<sub>4</sub>-0.3TiO<sub>2</sub> sample was synthesized by a mixing-heating method.<sup>2</sup> A mixture of P25 TiO<sub>2</sub> (0.3 g) and C<sub>3</sub>N<sub>4</sub> (0.7 g) was finely ground and then calcined at 400 °C for 2 h. After cooling to the room temperature, the resultant product was collected and crushed to a powder for further use.

For the synthesis of 0.3CdS-0.7TiO<sub>2</sub> photocatalyst, a mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O

(0.64 g) and thiourea (0.32 g) was dissolved in 50 mL of distilled water and stirring for 30 min. Then, 0.7 g of P25 TiO<sub>2</sub> was added to the above solution and stirred for another 3 h. The pH of resulting suspension was carefully adjusted to 10 with a 0.5 M NaOH solution. After stirring for 12 h, the precipitate was collected by filtration, washed with distilled water, and dried at 60 °C over night. Finally, the sample was heated to 250 °C for 1 h and 0.3CdS-0.7TiO<sub>2</sub> sample was obtained.

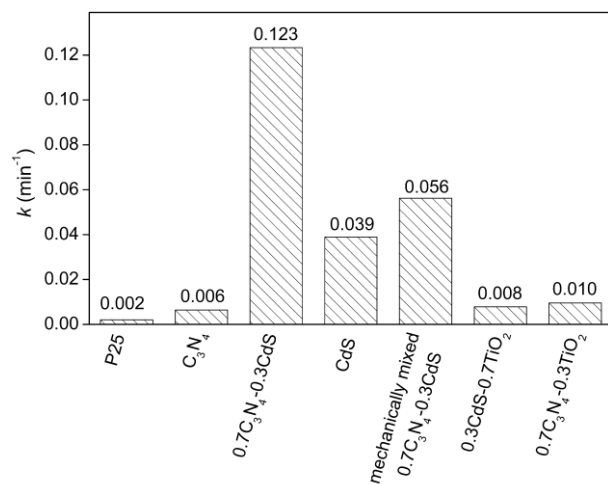


**Fig. S1** MO adsorption curves over various photocatalysts in the dark.

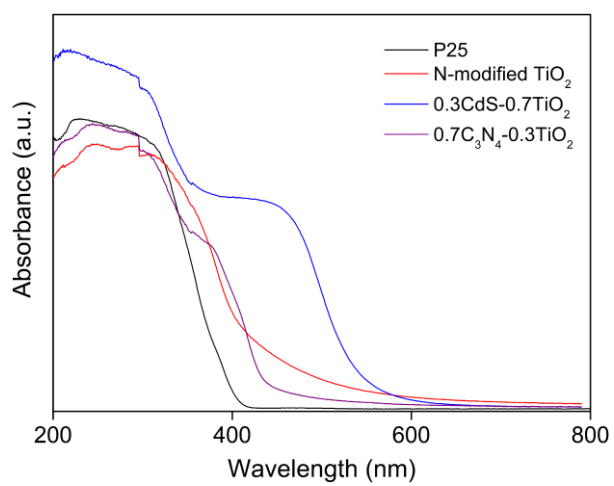


**Fig. S2** Kinetic constants ( $k$ ) for the photodegradation of MO over  $\text{C}_3\text{N}_4$ -CdS composite materials, pure  $\text{C}_3\text{N}_4$  and CdS, as well as P25 and N-modified  $\text{TiO}_2$ .

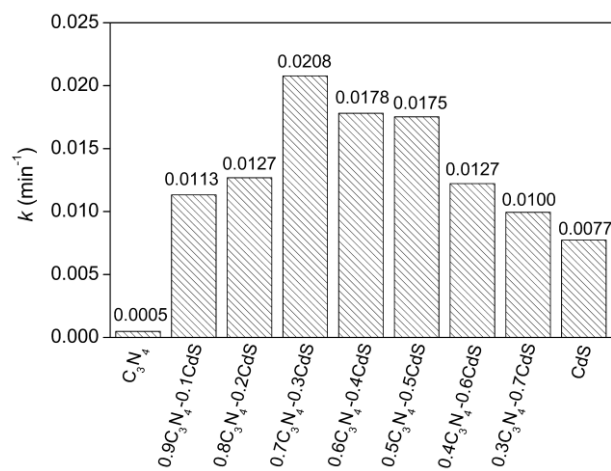
The  $k$  values were obtained by fitting the experimental data using the first-order model,  $\ln(C_0/C)=kt$ , where  $C_0$  and  $C$  are the concentrations of MO solution at times 0 (after stirring in the dark for 30 min) at  $t$ , respectively, and  $k$  is the first-order constant.



**Fig. S3** Kinetic constants ( $k$ ) for the photodegradation of MO over various photocatalysts.

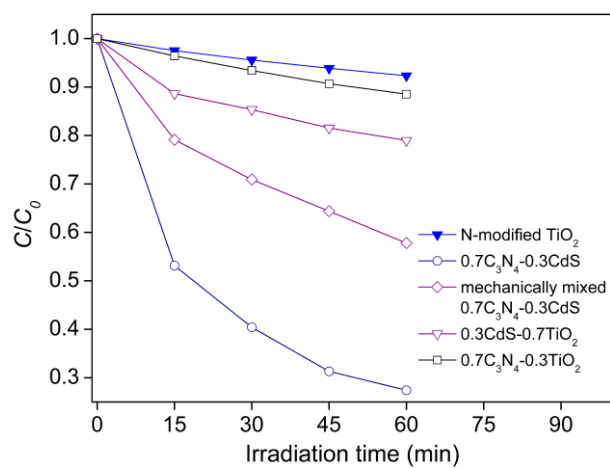


**Fig. S4** UV-vis DRS of P25, N-modified TiO<sub>2</sub>, 0.3CdS-0.7TiO<sub>2</sub> and 0.7C<sub>3</sub>N<sub>4</sub>-0.3TiO<sub>2</sub> samples.



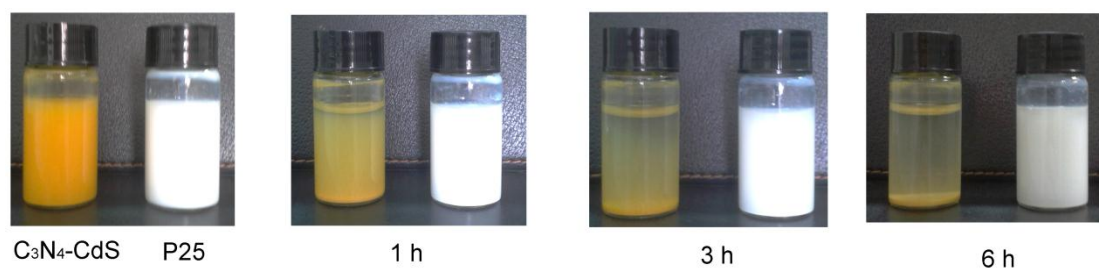
**Fig. S5** Kinetic constants ( $k$ ) for the photodegradation of 4-ABA over  $\text{C}_3\text{N}_4$ -CdS

composite photocatalysts, pure  $\text{C}_3\text{N}_4$  and CdS.

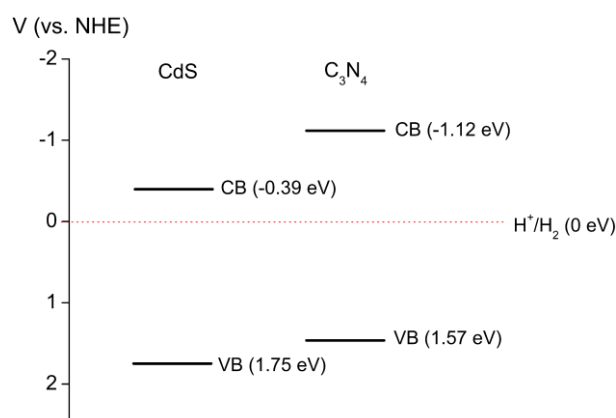


**Fig. S6** Comparison of photocatalytic properties for the degradation of 4-ABA over various photocatalysts under visible light irradiation (420-780 nm).





**Fig. S7** Sedimentation of P25  $TiO_2$  and  $0.7C_3N_4-0.3CdS$  sample in water.



**Fig. S8** Proposed energy levels of C<sub>3</sub>N<sub>4</sub> and CdS.

The CB and VB edge potentials of C<sub>3</sub>N<sub>4</sub> at -1.12 and 1.57 eV are obtained by theoretical calculations as reported in the literature.<sup>3</sup> For CdS, the CB and VB edge potentials are calculated *via* the Mulliken electronegativity theory:<sup>4,5</sup>  $E_{\text{VB}} = X - E^{\circ} + 0.5E_{\text{g}}$ , where  $E_{\text{VB}}$  is the VB edge potential;  $X$  is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms;  $E^{\circ}$  is the energy of free electrons on the hydrogen scale (*ca.* 4.5 eV);  $E_{\text{g}}$  is the band gap of semiconductors, which can be estimated from the onset of the absorption edge ( $\lambda_{\text{g}}$ ) using formula  $E_{\text{g}} = 1240/\lambda_{\text{g}}$ .<sup>6</sup> The CB edge potential can be deduced by  $E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}}$ . On the basis of DRS result (Fig. 5), the estimated  $E_{\text{g}}$  of CdS is 2.14 eV. Thus the VB and CB edge potentials of CdS are calculated to be 1.75 and -0.39 eV.

## References

- 1 D. Mitoraj and H. Kisch, *Angew. Chem. Int. Ed.*, 2008, **47**, 9975.
- 2 L. Ge, C. Han and J. Liu, *Appl. Catal. B: Environ.*, 2011, **108–109**, 100.
- 3 X. Wang, K. Maeda, A. Thomas<sup>1</sup>, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76.
- 4 M. A. Butler and D. S. Ginley, *J. Electrochem. Soc.*, 1978, **125**, 228.
- 5 Y. Xu and M. A. A. Schoonen, *Am. Mineral.* 2000, 85, 543.
- 6 A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253.