Supplementary Information

Novel C_3N_4-CdS composite photocatalysts with organic-inorganic heterojunctions: *in suit* synthesis, exceptional activity, high stability and photocatalytic mechanism

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Details for the preparation of N-modified TiO_2 photocatalyst, $0.7C_3N_4$-$0.3TiO_2$ and $0.3CdS$-$0.7TiO_2$ composites:

N-modified TiO_2 was prepared by means of solid-state reaction method using urea as a nitrogen source.[1] P25 TiO_2 (1.0 g) was finely milled with urea (2.0 g) and the mixture was heated at 400 ^{o}C for 2 h. After cooling to the room temperature, the N-modified TiO_2 photocatalyst was obtained.

The $0.7C_3N_4$-$0.3TiO_2$ sample was synthesized by a mixing-heating method.[2] A mixture of P25 TiO_2 (0.3 g) and C_3N_4 (0.7 g) was finely ground and then calcined at 400 ^{o}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 $0.3CdS$-$0.7TiO_2$ photocatalyst, a mixture of $Cd(NO_3)_2 \cdot 4H_2O$

(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_2 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 ^{o}C over night. Finally, the sample was heated to 250 ^{o}C for 1 h and 0.3CdS-0.7TiO_2 sample was obtained.
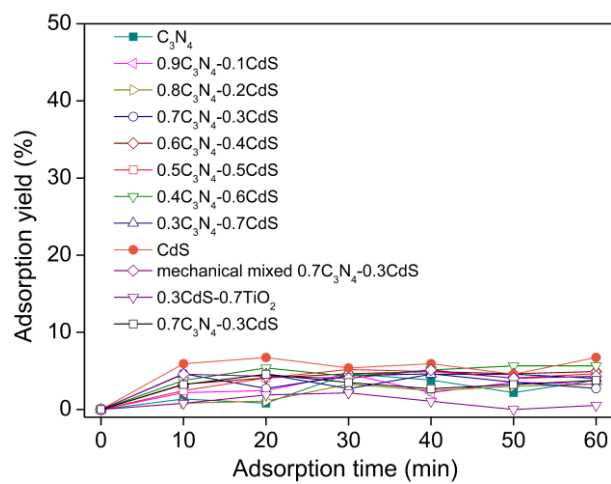
Fig. S1 MO adsorption curves over various photocatalysts in the dark.

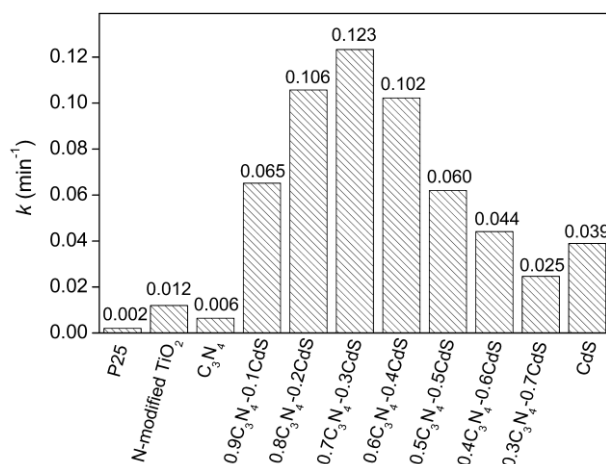**Fig. S2** Kinetic constants (k) for the photodegradation of MO over C_3N_4-CdS composite materials, pure C_3N_4 and CdS, as well as P25 and N-modified TiO_2.

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.
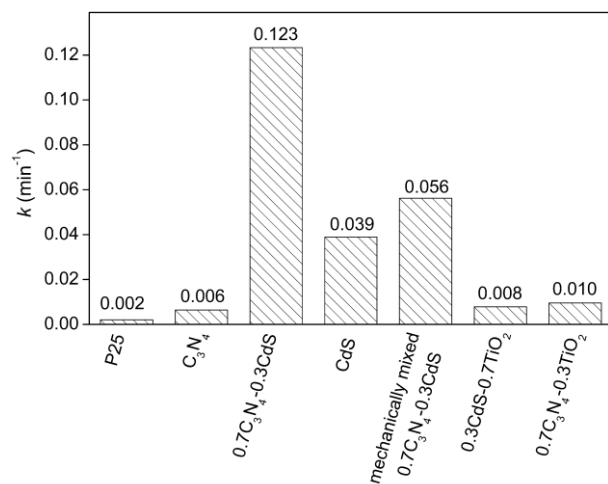
Fig. S3 Kinetic constants (k) for the photodegradation of MO over various photocatalysts.
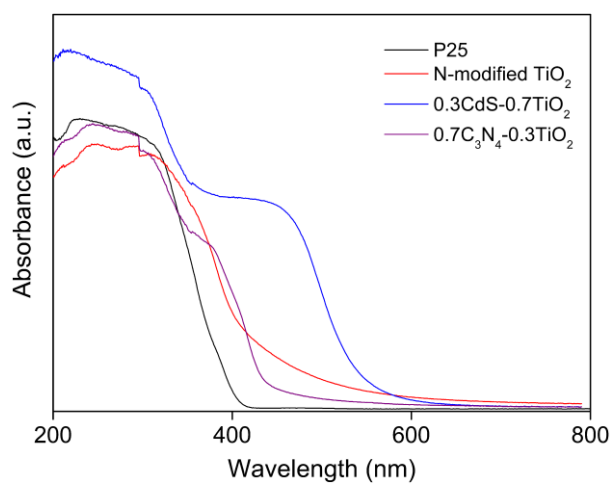
Fig. S4 UV-vis DRS of P25, N-modified TiO$_2$, 0.3CdS-0.7TiO$_2$ and 0.7C$_3$N$_4$-0.3TiO$_2$
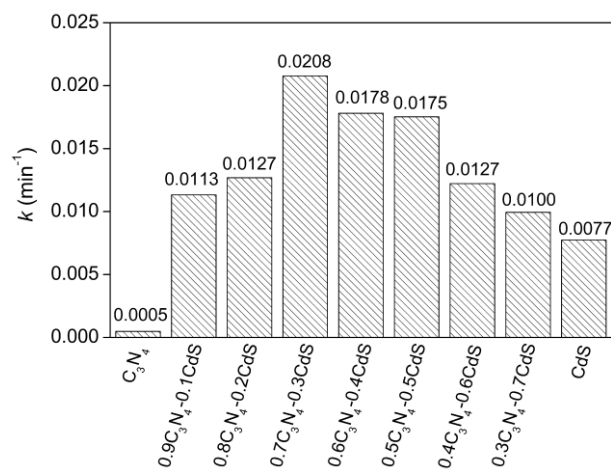
samples.

Fig. S5 Kinetic constants (k) for the photodegradation of 4-ABA over C_3N_4-CdS

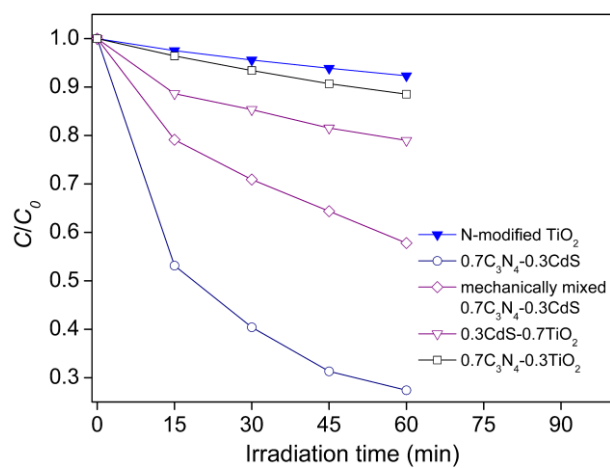composite photocatalysts, pure C_3N_4 and CdS.

Fig. S6 Comparison of photocatalytic properties for the degradation of 4-ABA over

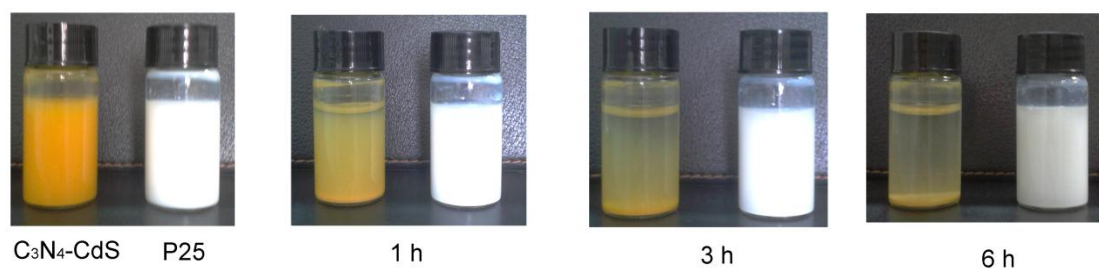various photocatalysts under visible light irradiation (420-780 nm).

Fig. S7 Sedimentation of P25 TiO$_2$ and 0.7C$_3$N$_4$-0.3CdS sample in water.
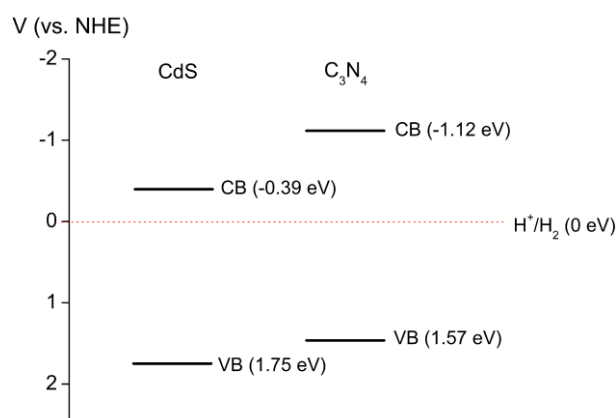
Fig. S8 Proposed energy levels of C_3N_4 and CdS.

The CB and VB edge potentials of C_3N_4 at -1.12 and 1.57 eV are obtained by theoretical calculations as reported in the literature.[3] For CdS, the CB and VB edge potentials are calculated *via* the Mulliken electronegativity theory:[4,5] $E_{VB} = X - E^e + 0.5E_g$, where E_{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^e is the energy of free electrons on the hydrogen scale (*ca.* 4.5 eV); E_g is the band gap of semiconductors, which can be estimated from the onset of the absorption edge (λ_g) using formula $E_g = 1240/\lambda_g$.[6] The CB edge potential can be deduced by $E_{CB} = E_{VB} - E_g$. On the basis of DRS result (Fig. 5), the estimated E_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

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