A novel visible-light-driven isocyanate silver photocatalyst: superior stability enhanced by intrinsic resonance effect

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Figure S1. XPS spectrum of the as-prepared AgNCO sample



Figure S2. UV-Vis absorption spectroscopy of RhB dye degradation over AgNCO sample



Figure S3. Dynamic curves of photodegradation (a), plots of $\ln(C_0/C)$ versus time (b) and rate constant *k* (c) for MB solutions over AgNCO and N-TiO₂ samples under visible light, absorption spectrum of the photodegradation the MB solution (d) over AgNCO sample



Figure S4. Dynamic curves of RhB (a) and MB (b) degradation over AgNCO added radical scavengers under the visible-light with $\lambda \ge 400$ nm (a: added 3 ml DMSO, b: added 10^{-4} mol L⁻¹ BQ or AO, c: added 10^{-4} mol L⁻¹ AO or BQ d: without radical scavenger).

We explore the dominant effect of the different kinds of activated species based on suppressive degree of degradation rate of them in photoreaction process. The degradation efficiency of RhB decreases significantly from about 90% to 15% when BQ as $\cdot O^{2-}$ radicals trapping agents is added into the photocatalytic reaction system compared with that of without radicals scavengers in Fig. S4(a). We conclude the $\cdot O^{2-}$ radicals are key factors in photooxidation process of RhB, and corresponding photogenetated holes and $\cdot OH$ radicals are insignificant. In contrast, the degradation efficiency of RhB still reaches up to 77% and 79% when DMSO and AO as $\cdot OH$ radicals and photogenetated holes trapping agents are present in the reaction systems, respectively. And it reveals $\cdot O^{2-}$ radicals play a more important role than $\cdot OH$ radicals and holes in oxidation process of RhB. Taking the same methods, the degradation efficiency of MB decreases from 90% to 14% when adding DMSO in Fig. S4(b) compared to that with free of radicals scavengers. Meanwhile, after adding AO and BQ, the degradation efficiency of MB still reaching to 69% and 88% clarifies that $\cdot OH$ radicals are more crucial roles than $\cdot O^{2-}$ radicals and photogenetated holes in the same method in Fig. S4(b) compared to that with free of radicals scavengers. Meanwhile, after adding AO and BQ, the degradation efficiency of MB still reaching to 69% and 88% clarifies that $\cdot OH$ radicals are more crucial roles than $\cdot O^{2-}$ radicals and photogenetated holes in the

degradation process of MB.



Figure S5. Dynamic curves of RhB and MB degradation over AgNCO under visible-light with different monochromatic central wavelength (a: RhB with λ =550 nm, b: RhB with λ =420 nm c: MB with λ =420 nm)

The relevant degradation experiment of RhB and MB over AgNCO is performed under visible light with different monochromatic central wavelength irradiation conditions. It is carried out to ascertain the degradation pattern is self-oxidation or the possibly evolved effects of photosensitization. It is well known that RhB is mainly excited by a wavelength of 554 nm in visible-light regions, whereas AgNCO can be excited only by a wavelength shorter than 530 nm on account of absorption edge of AgNCO from UV-vis absorption spectrum in Fig. 5. Therefore, as shown in Fig. S5 monochromatic central wavelength with 550 nm ($\lambda = \pm 15$ nm) visible-light is used to excite RhB molecules rather than AgNCO. The result exhibits that RhB molecules are only decomposed less than 15% after 270 min, proving that the effect of photosensitization during degradation processes of RhB molecules over AgNCO is extraessential. Monochromatic central wavelength with 420 nm ($\lambda = \pm 15$ nm) visiblelight is used to excite AgNCO instead of RhB molecules. The degradation efficiency of RhB molecules reaches up to approximate 55% after 270 min, which further determines that degradation of RhB is mianly attributed to intrinsically strong photooxidation ability of AgNCO. Moreover, the same method is performed to investigate degradation pattern of MB, which also verifies the self-oxidation ability of AgNCO photocatalyst. In conclusion, it remarkably proves that the degradation pattern of AgNCO photocatalyst is mainly self-oxidation rather than the sensitization effect of MB and RhB.



Figure S6. Total density of states (DOS) of AgNCO sample

Calculation method of theory

The band structure and the density of states (DOS) calculation were performed using the CASTEP code program package.3-4 The CASTEP calculation includes the plane-wave pseudopotential total energy method based density functional theory (DFT). The GGA (generalized gradient approximation) function of PBE (Perdew, Burke and Ernzerhof) 5 was applied to the exchange correlation potential. The kinetic energy cutoff with 340.0 eV, ultrasoft pseudopotential, convergence tolerance with 5.0×10^{-6} eV/atom, and band energy tolerance with 1.0×10^{-5} eV were adopted in calculation. The Monkhorst-Pack k-points were sampled at $5 \times 4 \times 7$ for AgNCO.