Photo-assisted cyanation of transition metal nitrates coupled with room temperature C-C bond cleavage of acetonitrile

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Material Synthesis:
M(CN)x (M=Ag,Zn,Ni,Yb,etc.) was synthesized as follows: 1mmol M(NO3)x was dispersed in 5ml acetonitrile under stirring. (To avoid producing CH3ONO2, 100ul 1M HNO3 was also added.) UV irradiation was supplied by a 300 W high-pressure mercury lamp. After 24 h reaction, the solid product was obtained by centrifuging, washed with deionized water. Finally, the precipitate was dried in air at 90 ºC.

AgNPs is synthesized according to Zheng’s paper (J. Am. Chem. Soc., 2006, 128, 6550): Typically, 0.50mmol of CH3COOAg was dissolved in 50mL of toluene containing 0.250mL of dodecanethiol to form a yellow cloudy solution which was further stirred at 75 ºC for 10 minutes. After 5.0 mmol tert-butylamine-borane powders were added, the mixture was kept stirring at 75ºC for 5 hours before it was cooled down. AgNPs were precipitated out from the reaction mixture as black solid powders by addition of 50 mL of ethanol. The precipitate was separated by centrifuge, washed with ethanol. Finally, the precipitate was dried naturally.

AgNPs/SiO2: AgNPs was loaded into SiO2 supports by a colloid deposition method. Desired amount of AgNPs were dissolved in 25 ml of chloroform. To this solution, desired amount of SiO2 was added. After 30min stirring, the solid product was centrifuged and dried in air. The AgNPs/SiO2 was calcined at 350 ºC for 5 h (in 5% H2/Ar) to remove organic residues.

AgCN/SiO2 was synthesized via the reaction of AgNPs/SiO2, KNO3 and CH3CN: 100mg AgNPs/SiO2 as well as 100 mg KNO3 was added into 5 ml acetonitrile. After 24h UV-irradiation, the precipitate was separated by centrifuge, washed with deionized water. Finally, the precipitate was dried in air at 90 ºC.

DFT calculation: The 6-311G(d,p) basis set was used for C, N, O, and H atoms, and LanL2DZ and valence double zeta basis set was used of Ag atom. The B3LYP functional was employed implemented in Gaussian 03W software.

Material characterization: Wide-angle XRD patterns were recorded on a Bruker D8 diffractometer using CuKα radiation. UV/Vis adsorption spectra were measured with a UNIC UV-2802 spectrophotometer in the diffuse/reflectance mode. 1H-NMR spectra were recorded on a BRUKER Advance2B\400MHz Spectrum using CDCl3 as solvent.
**Figure S1.** $^1$H-NMR of reaction solution (reaction time=24h). The red line represents the reaction solution ($\text{AgNO}_3$ and $\text{CH}_3\text{CN}$ react under UV-irradiation for 24h) while the black one represents the blank sample that only $\text{CH}_3\text{CN}$ exists.
**Figure S2** The absorption at $\lambda=273$ nm and the Ag$^+$ concentration detected by ICP of the reaction solution.
Figure S3 TEM of photolyzed Ag\textsubscript{1}NO\textsubscript{3} (reaction time=4h).
Figure S4 XRD patterns of the reaction product of AgNps/SiO₂, KNO₃ and CH₃CN.
Figure S5. XRD patterns of samples obtained by reaction of A) Zn(NO$_3$)$_2$+CH$_3$CN (Zn(CN)$_2$-S); C) Yb(NO$_3$)$_2$+CH$_3$CN(Yb(CN)$_2$-S); D) Ni(NO$_3$)$_2$+CH$_3$CN(Ni(CN)$_2$2H$_2$O-S) (Some amorphous SiO$_2$ was added in order to facilitate the XRD test.); B) FT-IR spectroscopy of Zn(CN)$_2$-S and Zn(CN)$_2$-C(commercial Zn(CN)$_2$).