

Fluorescent silver nanoclusters (Ag NCs) in metal-organic framework MIL-101(Fe) for catalytic hydrogenation of 4-nitroaniline

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Catalytic hydrogenation of 4-nitrophenol

In catalytic hydrogenation of 4-NP, 15 mL of 4-NP aqueous solution (0.2 mM) was mixed with 3.5 mL NaBH₄ aqueous solution (0.1 M) in a conical flask under vigorous stirring, that appears bright yellow colouration due to the formation of 4-nitrophenolate as featured by a characteristic UV-visible peak at 400 nm. Addition of 3 mg Ag@MIL-101 (Fe) steers the catalytic reduction that occurs with a gradual decrease in characteristic 400 nm peak of 4-NP and concomitant increase in 4-NA peak at 300 nm. The reaction appears to complete within only 20 min with 1 mg catalyst and a rate constant value of 0.216 min⁻¹ indicating pseudo-first order reaction. We have performed the same catalytic reduction in presence of PVP capped Ag nanoparticles as catalyst without MIL-101(Fe). The rate constant value of PVP stabilized Ag nanoparticles is found to be $k = 0.1 \text{ min}^{-1}$ under the similar reaction conditions. These results are comparable or superior to many of those previously reported catalyst which are in the range of 10⁻¹ to 10⁻³ min⁻¹ under similar reaction condition.¹

References

1. J. Lee, J. C. Park and H. Song, *Adv. Mater.*, 2008, **20**, 1523–1528.

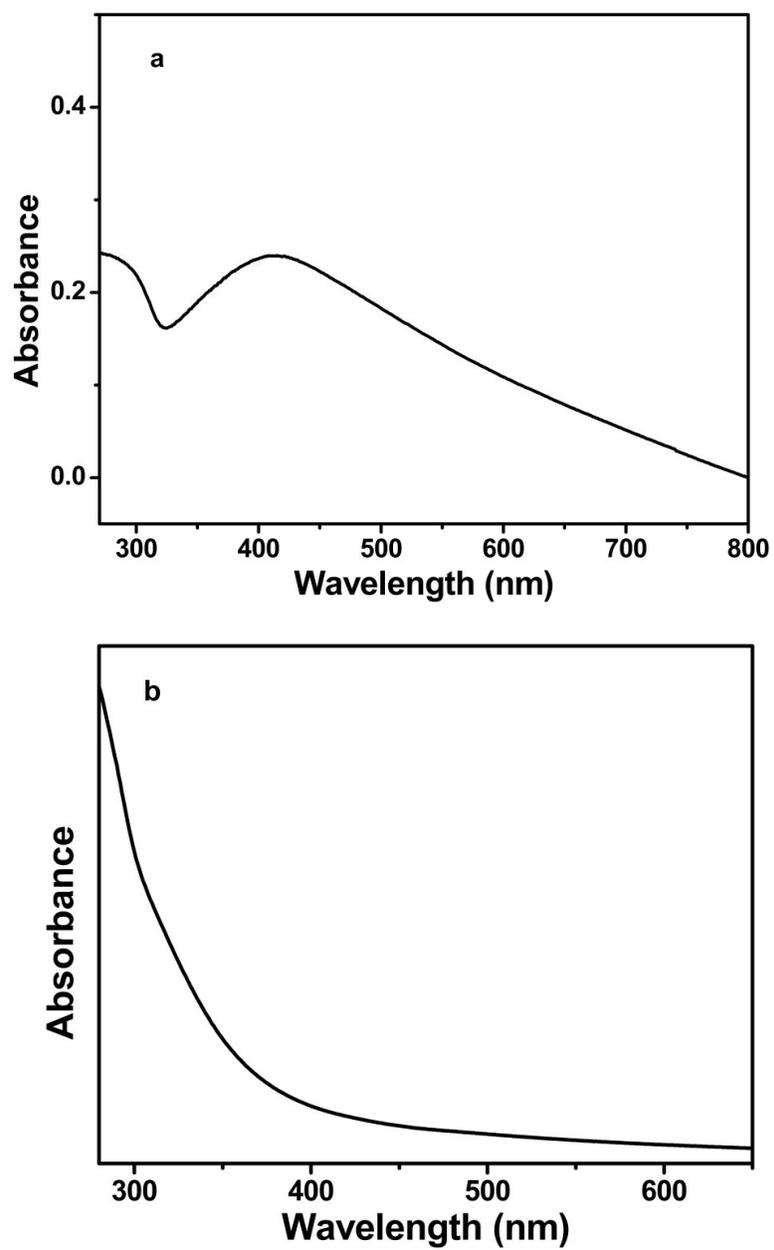


Fig. S1 UV-vis absorption spectrum of Ag nanoclusters showing (a) aggregation after 2 days in aqueous solution (b) high dispersion in CTAB solution after 7 days.

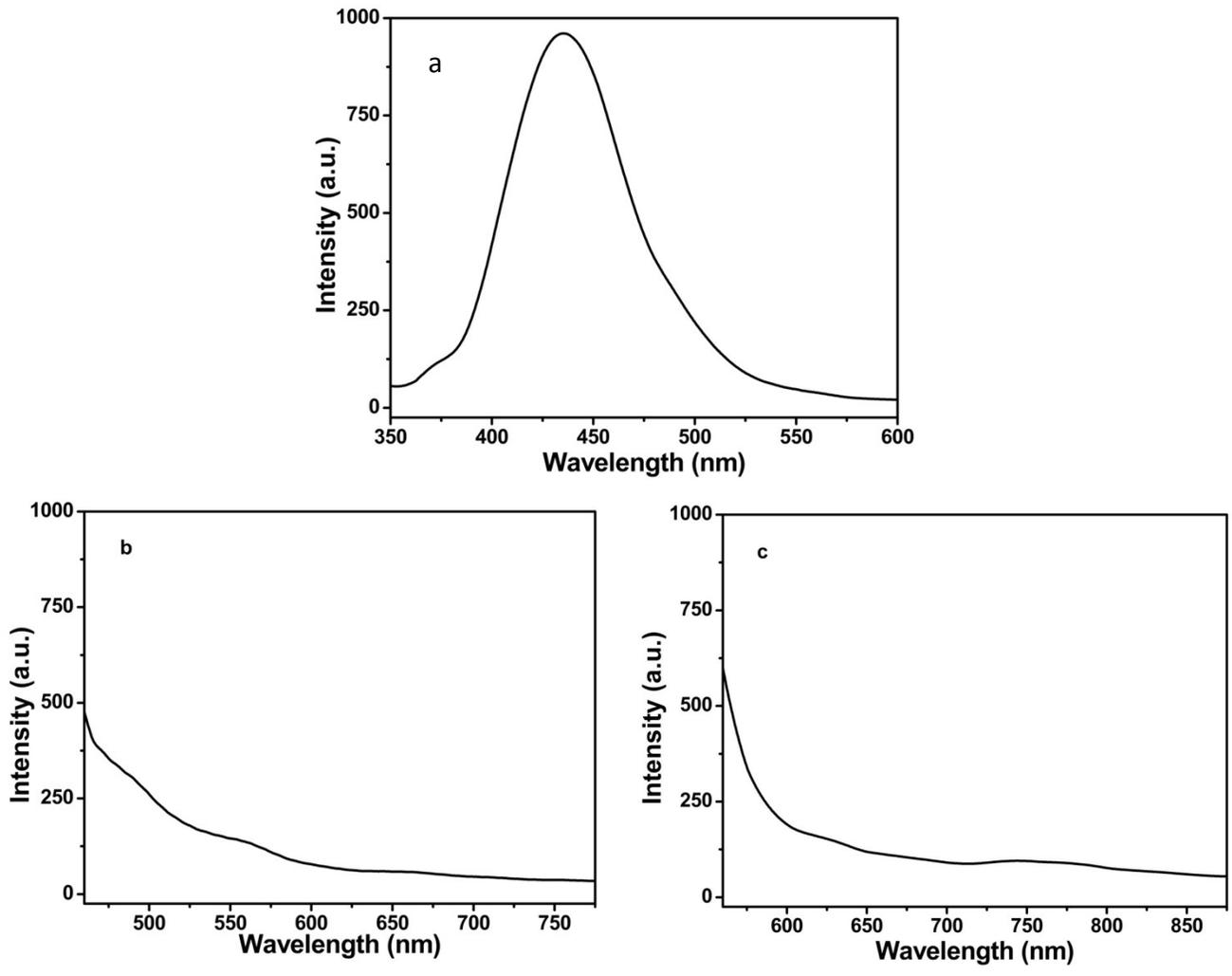


Fig. S2 Emission spectra of Ag nanoclusters after dissolution of host framework with excitation at (a) 330 nm, (b) 420 nm and (b) 520 nm respectively.

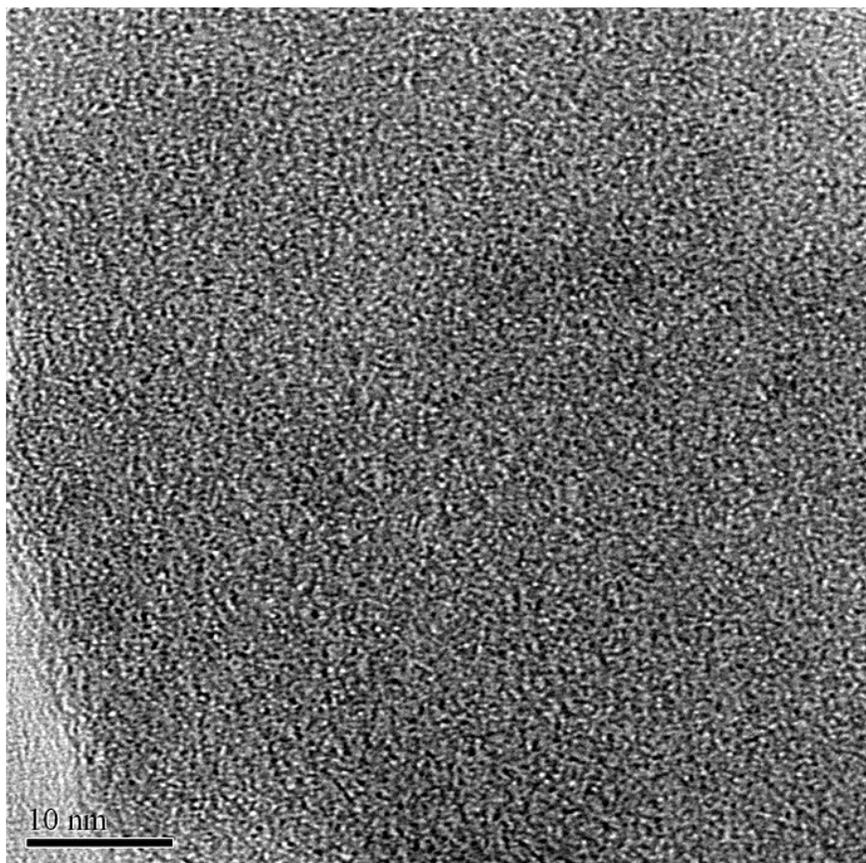


Fig. S3 Large area HRTEM image of AgNC@MIL-101(Fe)

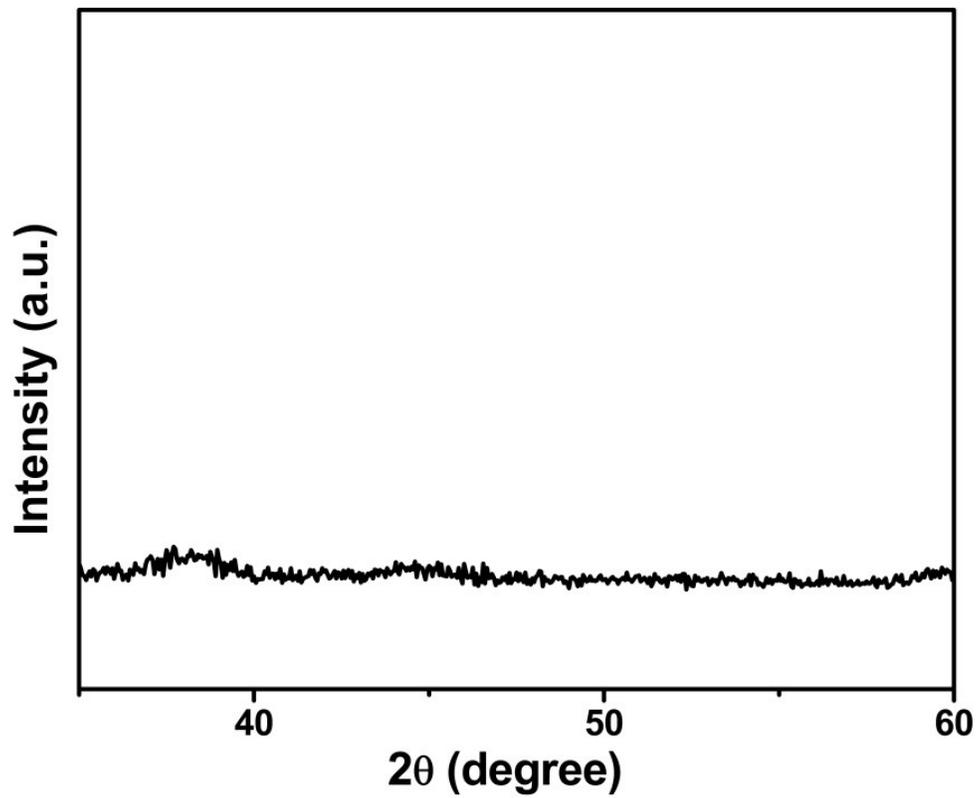


Fig. S4 Wide angle powder XRD pattern of Ag NCs@MIL-101(Fe) showing a very weak Ag (111) traces.

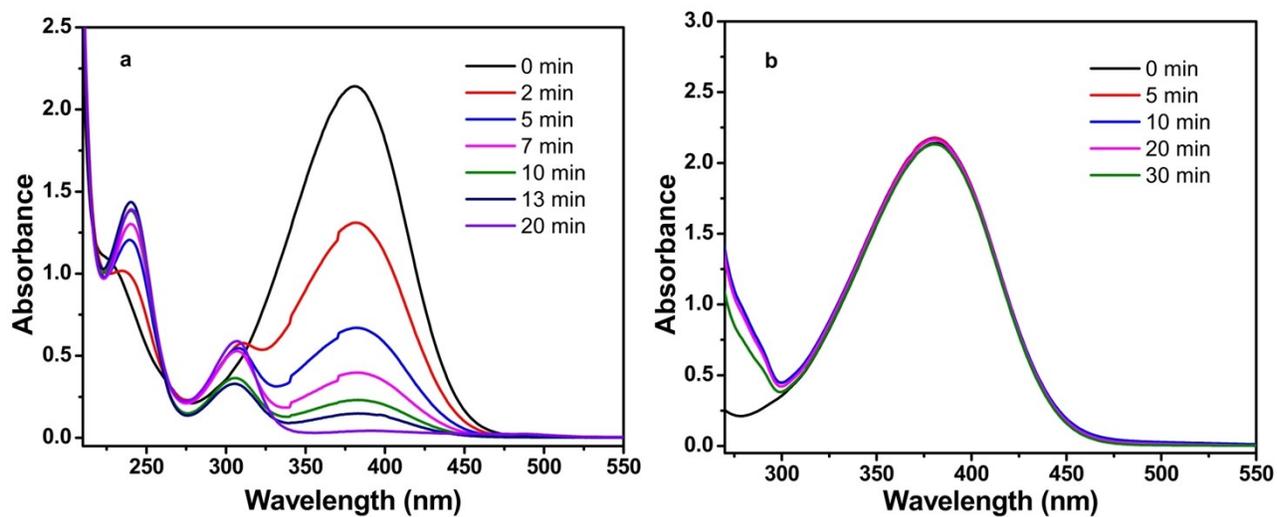


Fig. S5 UV-vis absorption spectra recorded on systematic catalytic reduction of 4-nitroaniline with NaBH_4 in presence of (a) PVP stabilized Ag nanoparticles and (b) MIL-101(Fe) as a catalyst.

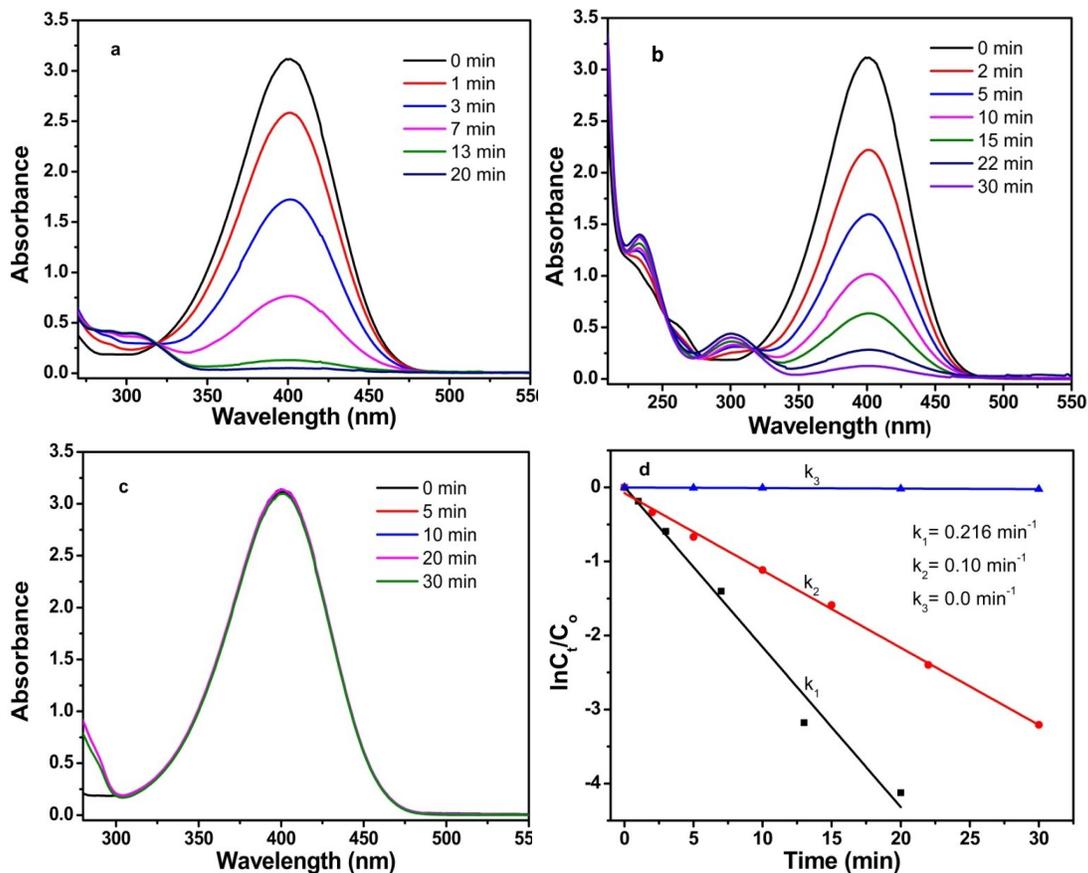


Fig. S6 UV-vis absorption spectra showing catalytic reduction of 4-nitrophenolate with NaBH_4 in presence of (a) Ag NCs@MIL-101(Fe), (b) PVP stabilized Ag nanoparticles and (c) MIL-101(Fe) and (d) Plot of $\ln(C_t/C_0)$ versus reaction time in minutes ($k_1 = 0.216 \text{ min}^{-1}$), PVP stabilized Ag nanoparticles ($k_2 = 0.10 \text{ min}^{-1}$) and MIL-101(Fe) ($k_3 = 0.0 \text{ min}^{-1}$)

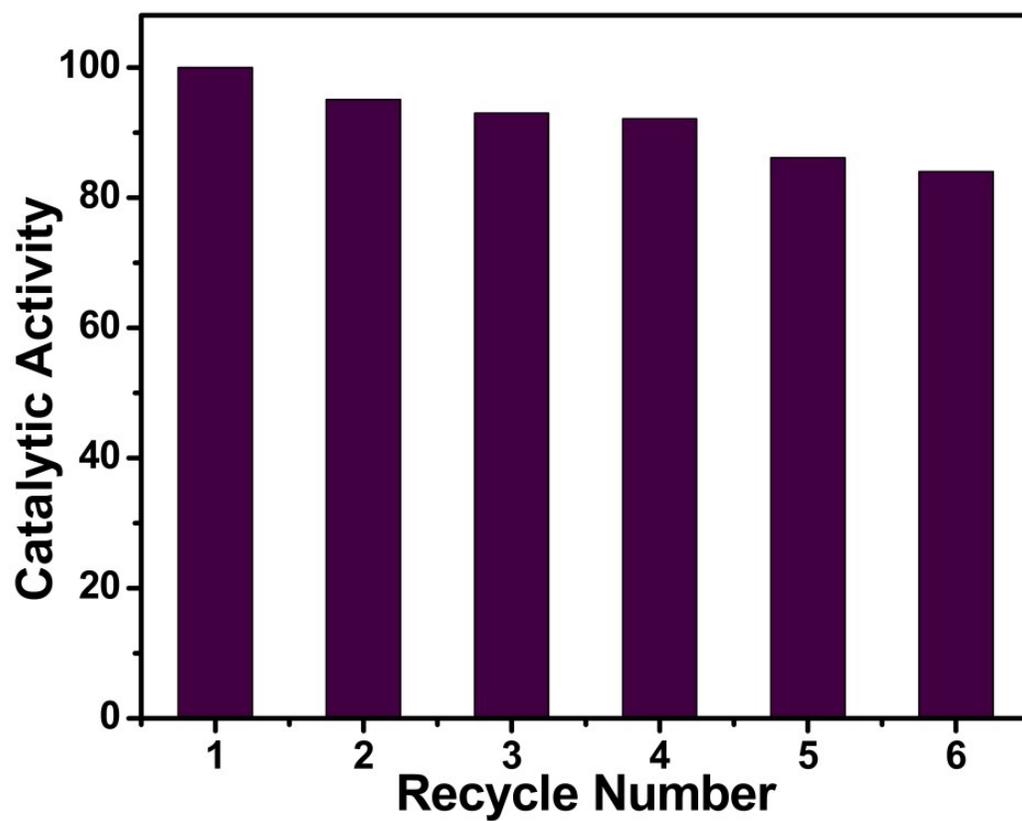


Fig. S7 (a) The stability of Ag NCs@MIL-101(Fe) catalyst with six successive reuse cycles of the green reduction of 4-nitrophenolate at 7 minutes.