Electronic Supplementary Information

Mesoporous Au–TiO_2 Nanoparticle Assemblies as Efficient Catalysts for the Chemoselective Reduction of Nitro Compounds

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Calculation method for density of gold edge sites

Assuming spherical-shaped Au nanoparticles, the number of Au nanoparticles was calculated by the following equation:

$$N_p = \frac{m_{Au}}{V \times d} \quad (1)$$

where, m_{Au} is the total weight of Au in each sample, V is the volume of each Au nanoparticle ($V=4/3\pi r^3$) assuming spherical shape and average radius of Au particles r, and d is the mass density of gold (19.3 g cm^{-3}).

Then, the density of edge site of Au atoms (D_{es}) was calculated by dividing the size of the contact area between gold and TiO_2 nanoparticles (derived as $L = N_p \times 2\pi r$) by the size of a single Au atom (d_{Au}=0.33 nm) and the surface area of the titania support (SA=159 m^2g^{-1}) according to the following equation:

$$D_{es} = \frac{N_p \times 2\pi r}{d_{Au} \times SA} \quad (2)$$

Table S1. Comparison of Au-MTA with various Au supported catalysts.

Catalyst	**Reaction conditions: Au/nitroarene/$NaBH_4$**	**Nitro compound**	**Time/yield**	**Ref.**
Au-MTA	0.1/1/6	Several aryl nitro compounds	1-2h / 92-99%	In this work
Au/NAP-MgO[a]	1/1/50	Several aryl nitro compounds	1-7h / 80-98%	[30]
Au/PNIPA[b]	6.25/1.1/1000	4-Nitrophenol, Nitrobenzene	40min (15 °C)/ ~85% (4NP), <20% (NB) conv.	[31]
Au/PVP[c]	0.5/1/15	4-Nitrophenol	20 min	[32]
Au/PMMA[d]	1/15/22500	4-Nitrophenol	10 min / almost complete conv.	[33]
Au/PAA/PAH[e]	-/1/100	Several aryl nitro compounds	73-99%[f]	[34]

[a] Nano active magnesium oxide plus, [b] Polystyrene (PS)-poly(N-isopropylacrylamide), [c] Poly-vinylpyrrolidone, [d] Poly(methyl methacrylate). [e] Poly(acrylic acid)/poly(allylamine hydrochloride), [f] Reaction under 0.015 mL/cm·s flux of nitro compound.

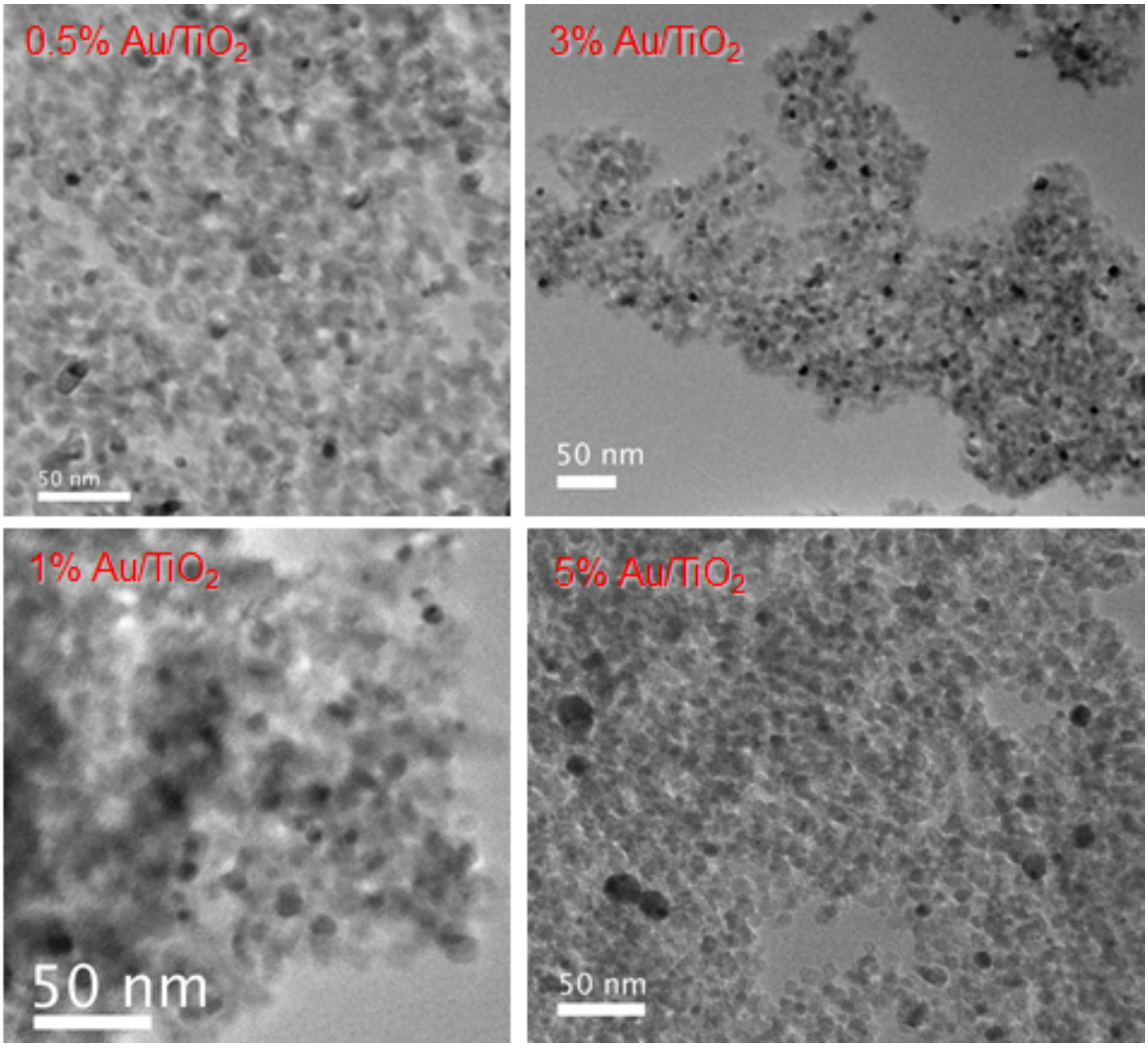

Figure S1. Typical TEM images of mesoporous Au-MTA samples.

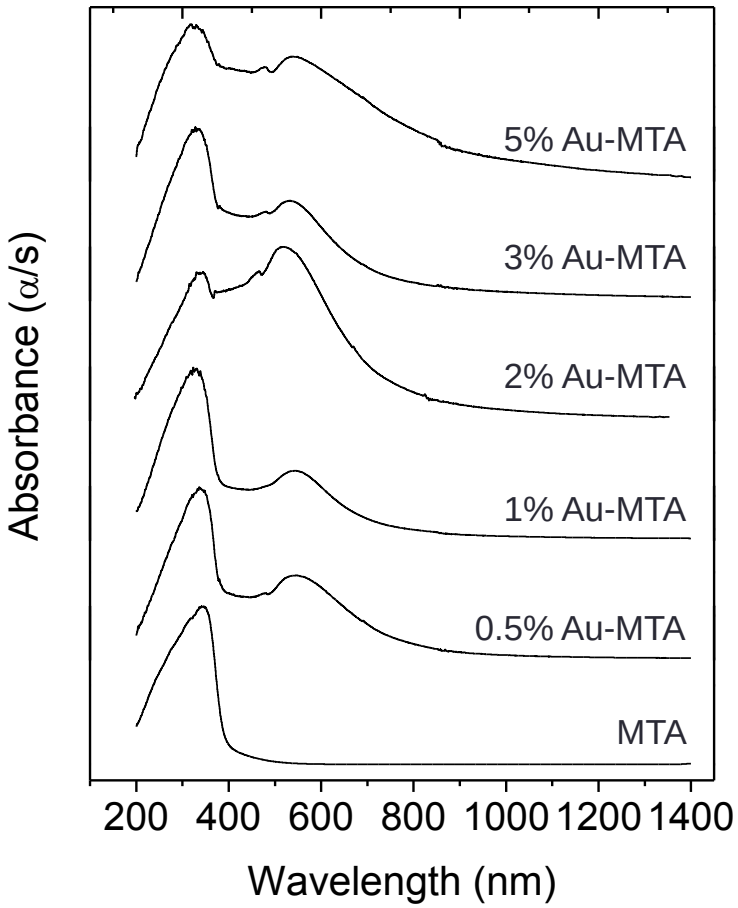

Figure S2. Diffuse reflectance UV–vis spectra of mesoporous MTA and Au-MTA materials.

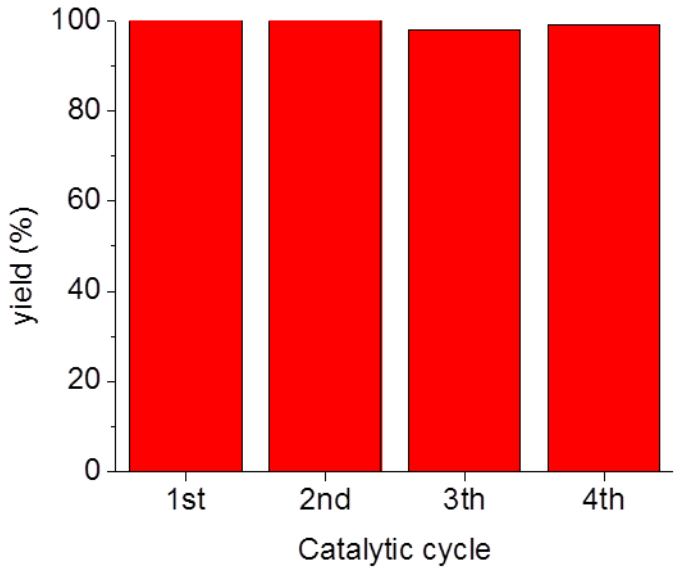

Figure S3. Recycling study of the mesoporous 2% Au-MTA catalyst (*experimental conditions: 0.2 mmol of p-nitrotoluene, 20 mg of catalyst, 6 mmol of $NaBH_4$ 2 mL of ethanol, room temperature, 2 h*).

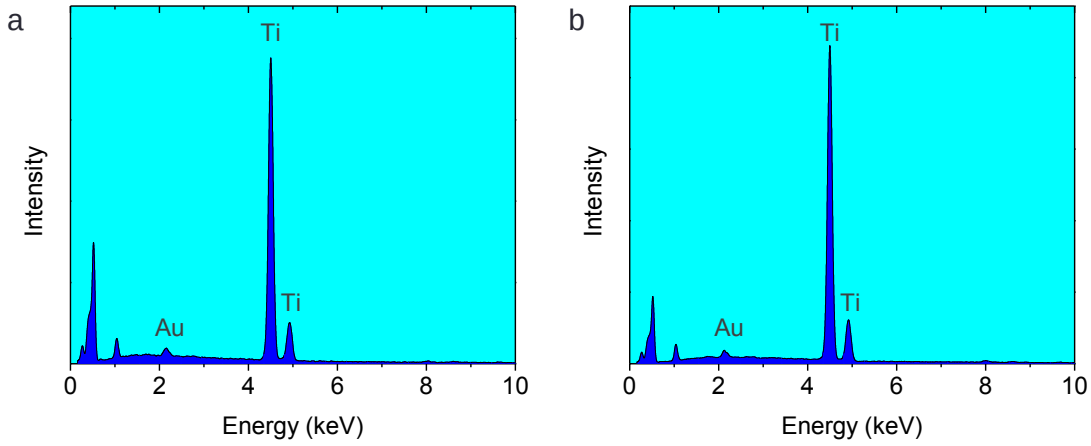

Figure S4. Typical EDS-SEM microanalysis spectra obtained from the 2% Au-MTA sample (a) before and (b) after catalytic reactions. The EDS spectra show an average Au/Ti atomic ratio of ~0.85:99.15 and ~0.84:99.16 that correspond to a gold loading of ~2.07 and ~2.04 wt.% for fresh and four-times reused 2% Au-MTA catalyst, respectively.

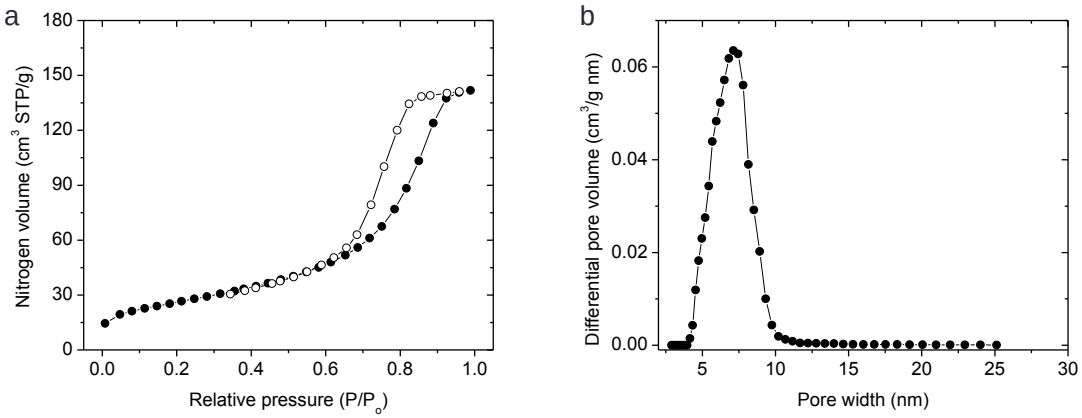

Figure S5. (a) Nitrogen adsorption-desorption isotherms at 77K of four-times reused 2% Au-MTA catalyst. Analysis of the adsorption branch with the BET method gives surface area of 96 m^2g^{-1} and total pore volume of 0.22 cm^3g^{-1}. (b) NLDFT pore size distribution calculated from the adsorption branch, indicating mesopore diameter of 7.3 nm.