

Supporting information

Photo-reduced Cu/CuO nanoclusters on TiO₂ nanotube arrays as highly efficient and reusable catalyst

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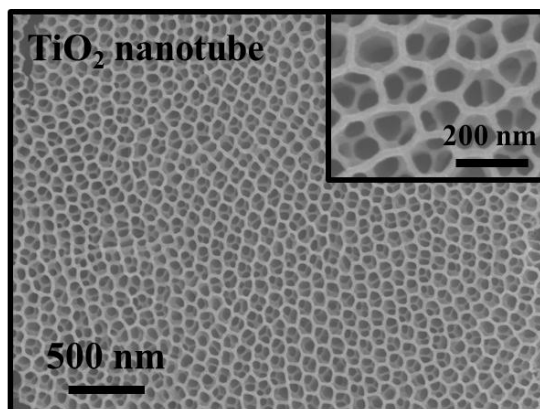


Figure S1. SEM characterization of TiO₂ nanotube arrays without Cu/CuO decoration. Inset shows the high magnification image.

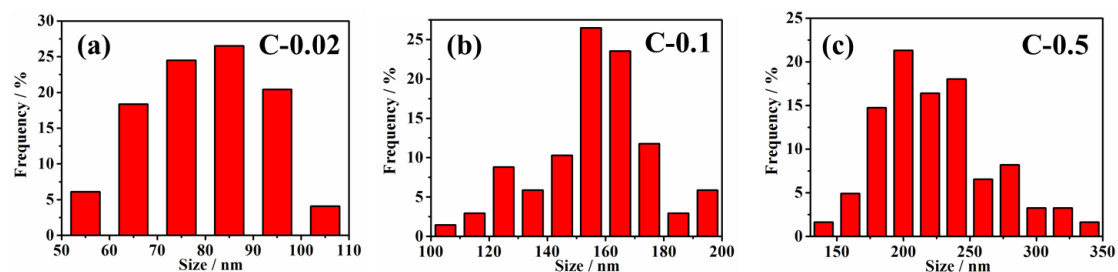


Figure S2. Cu/CuO nanoclusters size distributions of different catalysts: (a) C-0.02, (b) C-0.1 and (c) C-0.5 with average size of 81 nm, 158 nm and 223 nm, respectively.

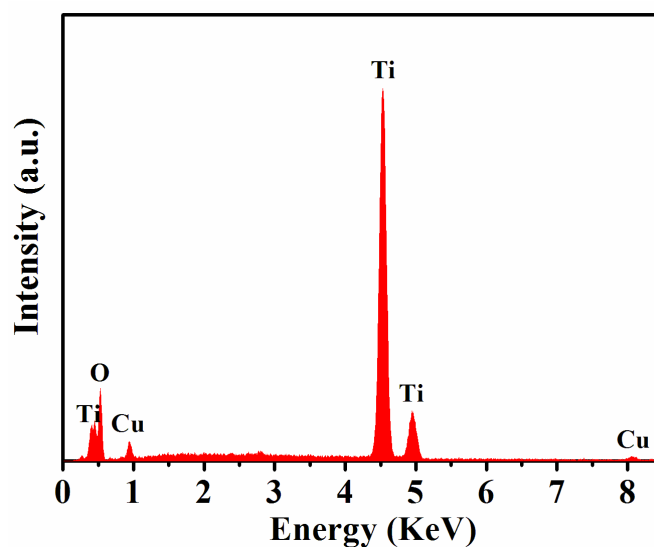


Figure S3. EDS spectrum of catalyst C-0.1.

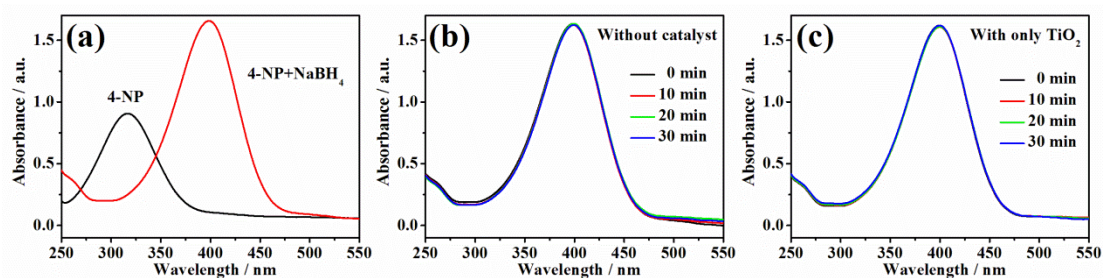


Figure S4. (a) UV-vis absorption spectra of 4-NP with and without NaBH₄; Time-dependent UV-vis absorption spectra of 4-NP with NaBH₄ but without catalyst (b) and with TiO₂ substrate (c).

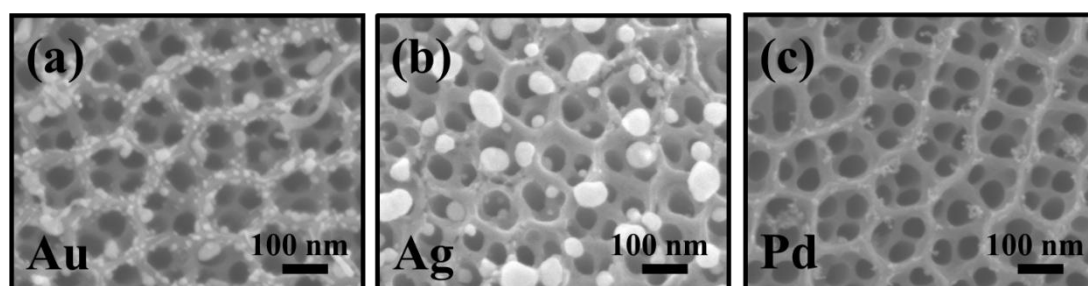


Figure S5. SEM images of TiO₂ substrate with different metal nanoparticles: (a) Au-TiO₂; (b) Ag-TiO₂ and (c) Pd-TiO₂;

Table S1. Comparison of different catalysts for 4-NP reduction.

Catalyst	4-NP(M)	NaBH ₄ (M)	K(s ⁻¹)	Ref.
C-0.1	1.0×10 ⁻⁴	1.0×10 ⁻²	13.6×10 ⁻³	This work
Au-TiO ₂	1.0×10 ⁻⁴	1.0×10 ⁻²	1.5×10 ⁻³	This work
Ag-TiO ₂	1.0×10 ⁻⁴	1.0×10 ⁻²	1.3×10 ⁻³	This work
Pd-TiO ₂	1.0×10 ⁻⁴	1.0×10 ⁻²	2.7×10 ⁻³	This work
SiNWAs-Cu	1.0×10 ⁻⁴	1.1×10 ⁻²	10.5×10 ⁻³	26
Au-PMMA	-	-	1.6×10 ⁻³	8
Ag-PMMA	-	-	0.8×10 ⁻³	8
Porous Cu	1.0×10 ⁻³	1.0×10 ⁻¹	8.9×10 ⁻³	36
Porous Cu/Ag	1.0×10 ⁻³	1.0×10 ⁻¹	19.0×10 ⁻³	36
PAu	2.0×10 ⁻³	2.0×10 ⁻¹	0.5×10 ⁻³	10
Pd-dendrite/PAu	2.0×10 ⁻³	2.0×10 ⁻¹	1.0×10 ⁻³	10

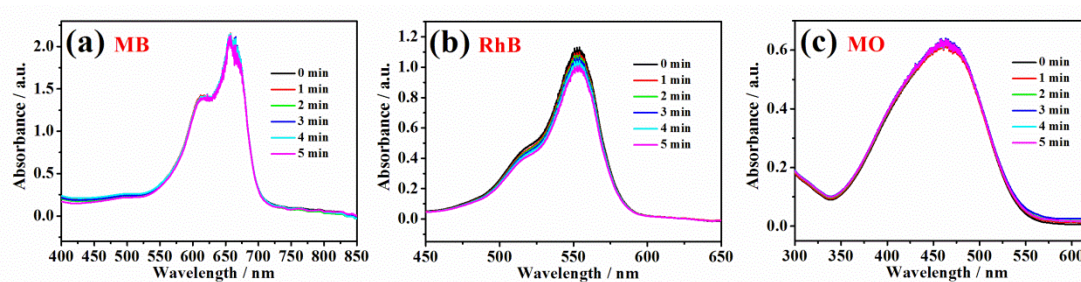


Figure S6. Time-dependent UV-vis absorption spectra for (a) MB; (b) RhB and (c) MO without catalysts.

Calculation of turnover frequency (TOF):

TOF is defined as the moles of reduced 4-NP molecules per mole of catalyst atom per hour. The total mass of Cu on C-0.1 is calculated as 0.0024 mg according to the inductively coupled plasma-optical emission spectrophotometry (ICP-OES). Hence, the molar ratio of 4-NP/Cu is about 6.7. The reaction time for C-0.1 is nearly 3.5 min. As a result, the final TOF is calculated as 115 h^{-1} .