

Metal (Cu, Au)-Modified Silicon Nanowires for High-Selectivity Solvent-Free Hydrocarbon Oxidation in Air (Supporting information)

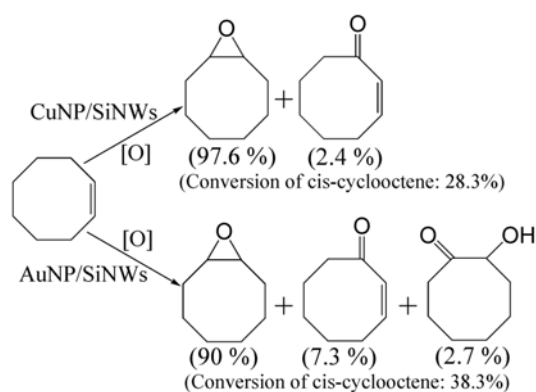
Experimental details.

SiNWs were prepared by the thermal-evaporation oxide-assisted growth method. The oxide layer of the as-grown SiNWs was removed by 5% HF etching for 30 min. Gold nanoparticles (AuNPs) deposition was performed by direct immersion of H-SiNWs into AuCl₃ solution (1×10⁻³ M). The product was then rinsed lightly by deionized water. Copper nanoparticles (CuNPs) deposition was performed similarly by using CuSO₄ solution (1×10⁻³ M) in place of AuCl₃ solution. TEM and EDX characterizations of the samples were performed using a FEI/Philips Techal 12 BioTWIN TEM and EDX attached to the TEM microscope. HR-TEM characterization was carried out with a CM200 FEG TEM. TEM images reveal that AuNPs and CuNPs are randomly deposited on the surface of SiNWs. AuNPs on SiNWs have sizes of 10-90 nm, while CuNPs on SiNWs have sizes of 5-30 nm. The EDX analysis results reveal that Au in AuNPs was 66 wt%, while that of Cu in CuNPs was 50 wt%, which indicated that the metal (Au, Cu) was effectively anchored on the SiNWs surface with high metal content. The XRD patterns were obtained on a Rigaku D/max 2500V PC diffractometer using CuK α radiation. Nitrogen-sorption isotherms of catalyst (SiNWs, AuNPs/SiNWs, and CuNPs/SiNWs) were determined at -196 °C using nitrogen in a conventional volumetric technique by a Micromeritics ASAP2020 sorptometer.

In a typical catalytic experiment, the oxidation of cis-cyclooctene (Sigma-Aldrich, 95%) under mild condition was performed in a 50 ml round bottom flask, which was connected to a water condenser and equipped with a magnetic stirrer. Briefly, 25 mg of AuNPs/SiNWs or CuNPs/SiNWs was dispersed in 10 ml of cis-cyclooctene. Then 0.12 g of tert-butyl hydrogen peroxide (TBHP) (Sigma-Aldrich, 37%, aqueous) was added dropwise to the system free of solvent. The reaction was carried out in air at ambient pressure at 60-80 oC in an oil bath, and the mixture was stirred for 24 h. The sample was extracted from the reaction system every hour in the first 12 hr, followed by every 6 h in the next 12 h. Oxidation of cyclohexene (Sigma-Aldrich, 95%) under mild condition was performed in the 50 ml round bottom flask which connected to a water condenser and equipped with a magnetic stirrer. Briefly, 25 mg of AuNPs/SiNWs or CuNPs/SiNWs were dispersed in 10 ml of cyclohexene. Then 0.12 g of tert-butyl hydrogenperoxide (TBHP) (Sigma-Aldrich, 37%, aqueous) was drop wise added to the system. No solvent was added to the mixture. The

reaction was carried out in the same reaction condition as the selective oxidation of cis-cyclooctene.

Analysis of products was carried out by using gas chromatography-mass spectrometry measurements, performed using an Agilent 6890 GC system coupled to an Agilent 5973 quadrupole mass-selective detector equipped with a HP 5MS column (30 m long, 0.25 mm i.d., 0.25 μ m film thickness).



Scheme S1. Reaction schemes of cis-cyclooctene epoxidation catalyzed by Cu- and Au-modified SiNWs at 60-80 °C for 24 h.

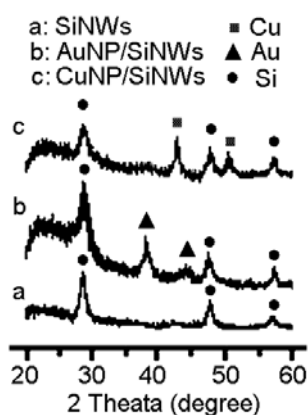


Figure S1 The XRD patterns of SiNWs (a), AuNP/SiNWs(b), and CuNP/SiNWs(c).

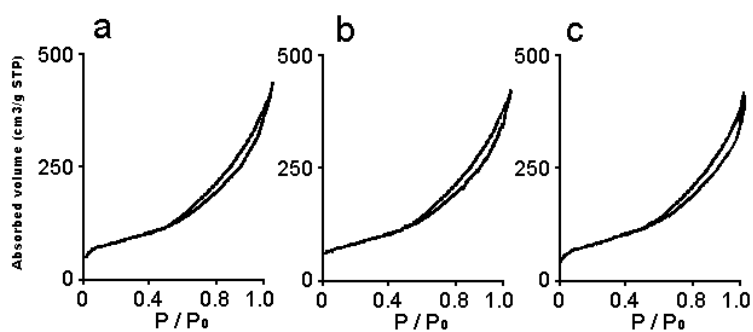







Figure S2 The nitrogen adsorption/desorption isotherms of SiNWs (a), AuNPs/SiNWs(b), and CuNPs/SiNWs (c).

Table S1. Cis-Cyclooctene (10 ml) oxidation with molecular oxygen and free radical initiator TBHP (0.12 g) in the absence of solvent (25 mg catalyst) after 24 h.




Catalyst	Selectivity (%)					Conversion (%)	$\Sigma_{\text{sel}}\text{C}_8^{\S}$
							
Au/SiNWs	90	7.3	2.7	--	--	38.3	100
Cu/SiNWs	97.6	2.4	--	--	--	28.3	100
H-SiNWs	100	--	--	--	--	8.2	100
Au/C*	81.2	4.1	--	9.3	0.5	7.9	95.1

[§]Total selectivity of C₈ partial oxidation products. *Data taken from Ref 2a, mass of Au/C = 0.12 g, mass of TBHP = 0.12 g.

Table S2. Oxidation of cyclooctene with Au/SiNWs and Au/C as catalysts (different metal loading) under the same condition (reaction time 24 h; catalyst mass 50mg; cyclooctene, 20ml; free radical initiator TBHP, 0.12 g).

	Au/SiNWs	Au/C	Au/SiNWs	Au/C	Au/SiNWs	Au/C	Au/SiNWs	Au/C
	Au,1%	Au,1%	Au,3%	Au,3%	Au,10%	Au,10%	Au,20%	Au,20%
Conversion (cyclooctene)	13%	3%	21%	5%	29%	9%	37%	14%
Selectivity (epoxycyclooctane)	96%	81%	95%	81%	95%	78%	93%	79%

Table S3. Cyclohexene (10 ml) oxidation with molecular oxygen and free radical initiator TBHP (0.12 g) in the absence of solvent (25 mg catalyst) after 24 h.

Catalyst	Selectivity (%)			Conversion (%)	$\Sigma_{\text{sel}}\text{C}_6^{\S}$
					
Au/SiNWs	0.2	24.9	74.9	92.8	100
Cu/SiNWs	0.1	46.3	53.7	98.4	100
Au/C*	50.2	tr	26.3	29.7	76.5

[§]Total selectivity of C₆ partial oxidation products.*Data taken from Ref 2a, mass of Au/C = 0.22 g, C₆H₁₀ (0.012 mol), 1,2,3,5-tetramethyl-benzene (20ml), TBHP (5 mol% based on C₆H₁₀), 80 °C, 24 h.