Supplementary Information for

Tuning the reduction power of supported gold nanoparticle photocatalyst for selective reductions by manipulating wavelength of visible light irradiation

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Experimental Details

Catalyst preparation: 2.5 g of CeO_2 fine powder (particles size < 100 nm) was dispersed into 100 ml of a given concentration of $HAuCl_4$ solution. Subsequently, 20 ml of 0.53 M lysine was added to the mixture which was vigorously stirred for 30 min. To this suspension, 10 ml of 0.35 M $NaBH_4$ solution was added gradually, followed by 10 ml of 0.3 M hydrochloric acid (to achieve a pH = 9.5). The mixture was stirred for 1 h and aged for 24 h. The solid was separated, washed firstly with deionized water and finally with ethanol, and dried at 60°C for 16 h. The dried solid was used directly as photocatalyst. The samples of different size and dispersion of the Au-NPs were obtained by varying the ratios of sodium borohydride to $HAuCl_4$, and $HAuCl_4$ to CeO_2 support.

Photocatalytic reduction test: Catalytic deoxygenation of epoxides to alkenes was conducted under an argon atmosphere at 25°C. Typically, 3 mmol of styrene oxide was dissolved into 30 ml isopropanol, and 3 ml of 0.1 M KOH solution in isopropanal and 100 mg of the catalyst were added into the mixture. The mixture was stirred by a magnetic stirrer during reaction and illuminated with an incandescent light.

Catalytic reduction of ketones to alcohols was conducted under an argon atmosphere at 30°C. Typically, 3 mmol acetophenone was dissolved into 30 ml isopropanol, and 3 ml solution of 0.1 M KOH in isopropanal and 100 mg of the catalyst were added into the mixture that was then stirred by a magnetic stirrer during reaction and illuminated with incandescent light.

To hydrogenate azobenzene, generally 2 mmol azobenzene was dissolved into 20 ml isopropanol in a 50 ml round bottom flask. 100 mg of the photocatalysts and 2 ml solution of 0.1 M KOH in isopropanol was then added. After that, air in the flask was eliminated with argon. The reaction was conducted at 30°C under the illumination of incandescent light and the reaction mixture was stirred by a magnetic stirrer.

During these reactions, 0.5 ml aliquots were collected at given irradiation time intervals and filtered through a Millipore filter (pore size 0.45 μm) to remove the catalyst particulates. Then flask was purged with argon again for more than 3 min to remove air and then sealed. The filtrates were analyzed by an Agilent 6890 gas chromatograph with HP-5 column. An Agilent HP5973 mass spectrometer was used to determine and analyze the product compositions.

Characterization: TEM images were taken with a Philips CM200 transmission electron microscope employing an accelerating voltage of 200 kV. The specimens were sample powders deposited onto a copper microgrid coated with a holey carbon film. The element composition of some samples was determined by energy-dispersive X-ray spectroscopy attached on an FEI Quanta 200 scanning electron microscopy. The diffuse reflectance UV-Visible spectra of the samples were recorded on a Cary 5000 spectrometer.

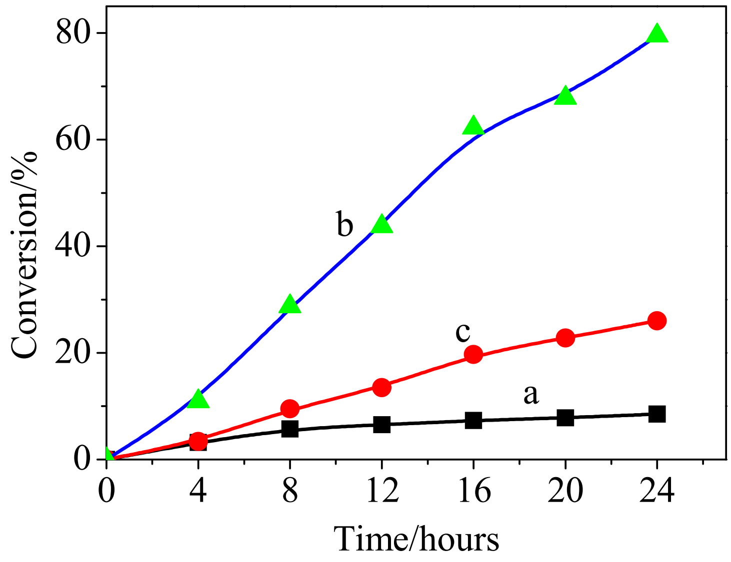

Figure S1. Reduction of styrene oxide with supported Au-NPs of different sizes: a) 2 nm, b) 5 nm, and c) 8 nm.

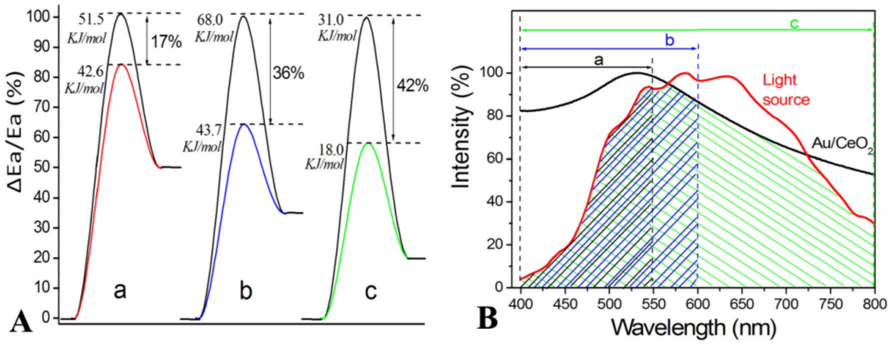

Figure S2. Comparison between the activation energies (Panel A) for photocatalytic reduction (black lines) and thermal reduction (color lines): deoxygenation of styrene oxide (a); reduction of acetophenone (b) and hydrogenation of azobenzene (c). Activation energy of these demonstrated reactions and the useable wavelength regions. Relative reduction in the activation energy due to the light irradiation, $\Delta E_a/E_a$ (%), for each reaction is given. The intensity of the light irradiation against the wavelength is illustrated in (B). From the dashed area the light energy absorbed by the Au-NPs are estimated. When no filter was used, the energy absorbed is in proportional to the whole dashed area. When a filter was used to filter out the irradiation with wavelengths shorter than 550 nm, the energy absorbed by the photocatalyst is in proportional to the dashed area in the range between 550 nm and 800 nm.

Table S1. Influences of cut-off threshold wavelength on these demonstrated reactions

Cut-off threshold wavelength (nm)	Full wavelength	420	550	600	650
Emission energy from light source (%)	100	90.2	75.1	57.6	40.0
Deoxygenation of styrene oxide (%)	21.3	19.7	-	-	-
Reduction of acetophenone (%)	34	31	9	-	-
Hydrogenation of azobenzene (%)	41	40	22	20	-

Table S2. Influences of light intensity on these demonstrated reactions

Light Intensity (W/cm^2)	0.40	0.30	0.15
Deoxygenation of styrene oxide (%)	19.7	9.6	5.2
Reduction of acetophenone (%)	31	13	8
Hydrogenation of azobenzene (%)	40	31	13

Table S3. Influences of supports on reduction of styrene oxide with supported Au-NPs

Catalysts	Experimental conditions	Conversion (%)	Selectivity (%)
Au/CeO_2	light illumination	19.7	87.5
Au/ZrO_2	light illumination	17.4	72.3
Au/TiO_2	light illumination	22.5	73.4

The formation and reaction of surface Au-H species

Isopropanol is a hydrogen donor. Under visible light irradiation, the Au-NPs are able to abstract hydrogen from isopropanol forming the transient Au-H species.[1] The active Au-H species attack the double bonds (C=O, N=N) or epoxide bond leading to the hydrogenation or deoxygenation, in which the hydrogen of Au-H species is consumed and the final reductive products form without releasing hydrogen molecules. To confirm the formation of the surface Au-H species on Au-NPs, an efficient hydrogen-abstracting reagent, 2,2',6,6'-tetramethylpiperidine N-oxyl (TEMPO)—can abstract hydrogen from the surface of gold and other metals to form hydroxylamine—was added into the reaction system while other experimental conditions were unchanged.[2] No final reductive products were detected. This confirms the important role of the surface Au-H species in the reductions.

The SPR effect also enhances the local electromagnetic fields near rough surfaces of the Au-NPs [3,4] and this could assist activation of the double bonds or epoxide bond when the reactant molecules are adsorbed on the surface of Au-NPs. The ability of the Au-H species to react with the double bonds (C=O, N=N) or epoxide bond should also depend on the energy of the excited electrons in Au-NPs, which is higher when the irradiation wavelength is shorter as discussed previously.

References:

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