Supplementary Information for

Mechanism of Supported Gold Nanoparticles as Photocatalysts under Ultraviolet and Visible Light Irradiation

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Experimental Details

Preparation and characterization of catalysts. Gold nanoparticles (about 8% of the overall catalyst mass) were loaded to the supports by the impregnation method. A $HAuCl_4$ aqueous solution of 50 ml H_2O and 200 mg $HAuCl_4$ was prepared and its pH was adjusted to 8-10 with 0.1M NaOH solution. Then, 2 g of support powder was dispersed into the $HAuCl_4$ solution, the resulting suspension was stirred for 2 hours at 80°C. The solid in the suspension was separated, washed extensively with deionized water, dried overnight at 80°C and heated at 300°C for 4 hours. Transmission electron microscopy (TEM) images were taken with a JEOL 2010 microscope employing an accelerating voltage of 200 kV. The UV-visible spectra were examined by Cary5000, Stheno. Energy dispersive X-ray spectroscopy (EDS) experiment was attached on FEI Quanta 200 Environmental SEM. X-ray photoelectron spectroscopy (XPS) test was attached on Kratos Analytical Axis Ultra X-ray photoelectron spectrometer.

Surface photocurrent (SPC) and transient photovoltage (TPV). The SPC measurements were performed on the system constituted of a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), and a photovoltaic cell. A 500 W xenon lamp (CHFXQ500W, Global xenon lamp power) and a double-prism monochromator (Hilger and Watts, D300) provide monochromatic light. A comb-like ITO electrode with an external bias (10.0 V) on its two sides was used. The sample chamber for TPV measurements consists of ITO electrode, a 10 μm thick mica spacer as electron isolator, and a platinum wire gauze electrode (with a transparency of about 50%). The construction is a sandwich-like structure of ITO electrode-sample-mica-gauze platinum electrode. During the measurement, the gauze platinum electrode was connected to the core of a BNC cable which input signals to the oscilloscope. The samples were excited from platinum wire gauze electrode with a laser radiation pulse (wavelength of 532 nm and pulse width of 5 ns) from a third-harmonic Nd:YAG laser (Polaris II, New Wave Research, Inc.). The intensity of the pulse was regulated with a neutral gray filter and determined with an EM500 single-channel joulemeter (Molectron, Inc.). The TPV signals were registered with a 500 MHz digital phosphor oscilloscope (TDS 5054, Tektronix).

Photocatalytic tests. The photocatalytic activity of the catalysts for decomposing sulforhodamine-B (SRB) and phenol in aqueous solution at 25 °C was tested in similar procedure. For example, 50 mg of photocatalyst powder was dispersed in aqueous suspension of SRB (50 mL, 2×10^{-5} M). The catalyst concentration was 1.0 g/L. pH of the suspension was adjusted to 3 by 0.1M HNO_3 and then the suspension was placed in a chamber with 6 light tubes (18 W/tube, from Philips, light intensity was 0.17 W/cm^2) as the light source. The vessel is in a chamber with 6 blue light tubes (18 W/tube, from Philips) or 6 UV light tubes (20 W/tube, light intensity was 0.19 W/cm^2, wavelength around 365 nm) as the light source. In order to study the effect of light intensity to SRB photodegradation, the same experiments were conducted except turning off 2 or 4 blue light tubes (the light intensity was reduced to 0.13 and 0.08 W/cm^2, respectively). An air condition was installed in the chamber to maintain the temperature at 25 °C as the light illumination could cause an increase in temperature of the vessel. The suspension was magnetically stirred in the dark for 30 min prior to irradiation to establish adsorption/desorption equilibrium between the dye and the surface of the catalyst under ambient air-equilibrated conditions. At given irradiation time intervals, 4 mL aliquots were collected, centrifuged, and then filtered through a Millipore filter (pore size 0.45 μm) to remove the catalyst particulates. The filtrates were analysed at the wavelength of maximal absorption (565 nm) in the UV-vis spectra of SRB using Varian 5000. The data shown in Table 1 were obtained after 1 hour of irradiation. For comparison we also prepared nitrogen-doped TiO_2 by annealing TiO_2 at 550°C in N_2 gas for 4 hours, and the activity of this sample for SRB photodegradation was tested in the same procedures used for the Au-NPs photocatalysts. In the photocatalytic phenol degradation experiment, aqueous suspensions of organic compounds (100 mL, 1 mM) and 100 mg of gold photocatalyst powders were placed in the vessel. Then the vessel was in a chamber with 6 UV light tubes as the light source. The filtrates were analysed at 270nm in the UV-vis spectra using the Varian 50.

The selective oxidation of benzyl alcohol to benzaldehyde was conducted in a toluene solution under UV irradiation. 50 mg of gold photocatalyst powder was dispersed in toluene solution of benzyl alcohol (10%). Then the suspension was placed in a chamber in which 6 UV light tubes as the light source and the temperature was maintained at 25 °C with an air condition. 30 mg NaOH was added into the suspension and the air in the container of the suspension was replaced with pure oxygen. Prior to light irradiation the suspension was magnetically stirred in the dark for 30 min. At given irradiation time intervals, 2 mL aliquots were collected, centrifuged, and then filtered through a Millipore filter (pore size 0.45 μm) to remove the catalyst particulates. The filtrates were analysed in a Gas Chromatography (HP6890 Prometheus) to measure concentration change of benzyl alcohol.

To degrade HCHO, the coated slides were placed in a glass vessel of about 6 liters. The vessel is in a chamber with 6 light tubes (18 W/tube, from Philips) as the light source. An air condition was installed in the chamber to maintain the temperature at 25 °C. The vessel was filled with air and sealed after the coated glass slides were mounted. Small amount of HCHO was injected into the vessel and a fan installed in the vessel assisted in evaporating HCHO into gas phase. The gaseous specimens were taken from the vessel and analyzed by a gas chromatograph (Shimadzu GC-2014) used specially for this experiment. The gaseous specimens were sampled during the reaction course with light on to monitor the changes in the HCHO content.

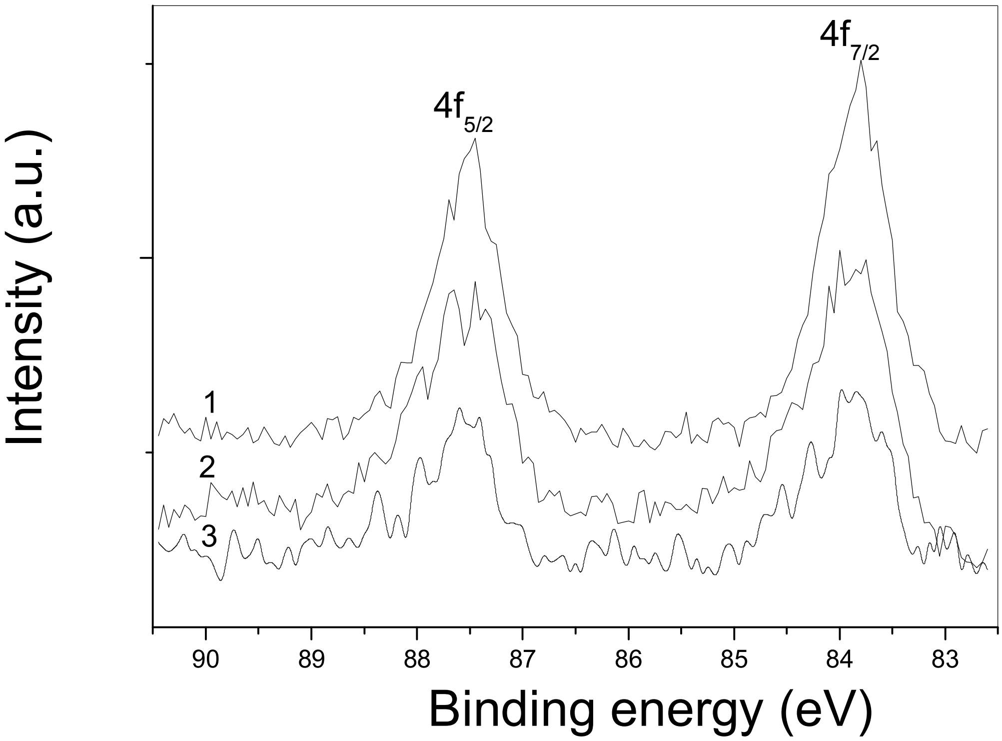

Figure S1 Binding energy of Au $4f_{5/2}$ and Au $4f_{7/2}$ for gold photocatalysts. (1) Ay/Zeolite Y; (2) Ayg/ZrO_2; (3) Ay/SiO_2.

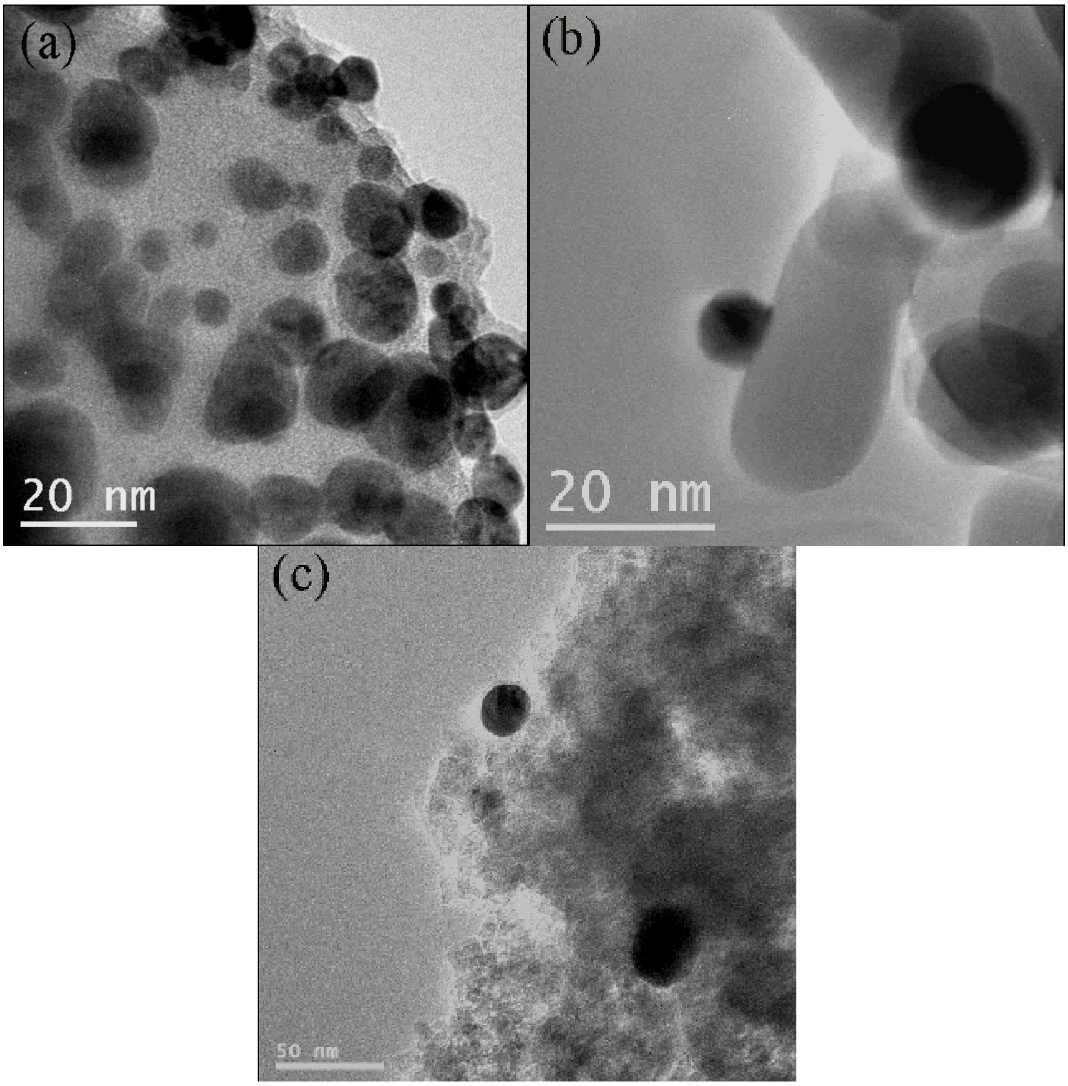

Figure S2 The transmission electron microscope images of the photocatalysts of gold nanoparticles on supports. (a) gold on zeolite Y, Au/zeolite Y, (b) gold on zirconia, Au/ZrO_2 and (c) gold on silica, Au/SiO_2.

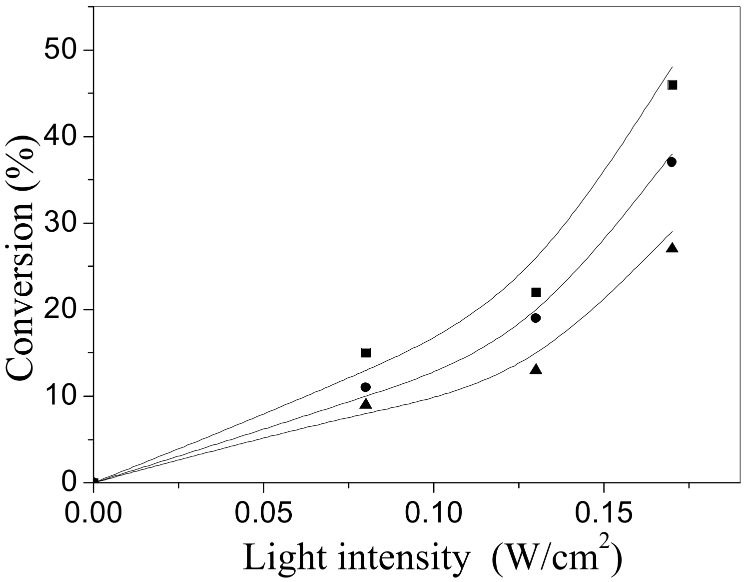

Figure S3 The relationship between SRB conversion and the light intensity. The symbols ■, ● and ▲ represent the results obtained over Au/ZrO_2, Au/zeolite Y and Au/SiO_2, respectively.

Table s1 Gold content of the gold nanoparticles on various oxides analysed by EDS

	Au-Zeolite Y	Au-ZrO_2	Zu-SiO_2
Gold content (wt%)	8.06	8.21	8.22