Supplementary Material for

Tuning Selectivity in Propylene Epoxidation by Plasmon Mediated Photo-Switching of Cu Oxidation State

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Tuning selectivity in propylene epoxidation by plasmon mediated photo-switching of Cu oxidation state
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Materials and Methods
Section S1. Preparation of catalyst: Copper nanoparticles catalysts were prepared using (water in oil) micro emulsion synthesis method reported previously (30). n-heptane (99% purity, Sigma-Aldrich Cat. No. 246654), polyethylene glycol-dodecyl ether (average M_n ~362, Sigma-Aldrich Cat. No. 235989), copper nitrate (99.999%, Sigma-Aldrich Cat. No. 229636) and hydrazine (98% purity, Sigma-Aldrich Cat. No. 215155) were used as continuous oil phase, surfactant, copper precursor and reducing agent, respectively. Water to surfactant (molar) ratio of 30 and reducing agent to precursor ratio of 10 were used for the synthesis. Briefly, an aqueous solution of copper precursor (0.1 M Cu(NO3)_2) was added to the mixture of n-heptane and surfactant (16.54 wt%) under inert atmosphere (argon). After the mixture was equilibrated, an aqueous solution of reducing agent (1 M hydrazine) was added drop by drop to the mixture and the microemulsion was kept under continuous stirring in inert atmosphere (argon) at room temperature for the complete reduction of copper precursor. A known amount of support material, SiO_2, (Surface area ~80-100 m^2/g, Alfa Aesar, Product No. 42737) was then added under stirring to the microemulsion containing copper nanoparticles to prepare catalyst with final composition of ~2 wt % Cu/SiO_2. Acetone was then added to the mixture under stirring to break the microemulsion and remove the surfactant. The catalyst was further washed with water and ethanol by centrifugation and dried in argon at room temperature. The scanning electron microscope (SEM) images of the copper nanoparticles synthesized showed that the particles are quasi-spherical in shape with average size of 41 ± 9 nm. A representative SEM image of the
copper nanoparticles is shown in Figure S1. Micrographs were obtained using an FEI Nova 200 Nanolab and the accelerating voltage used for the imaging was 10 kV.

**Section S2. Reactor studies:** The reactions were performed in a vertically oriented packed bed reactor (Harrick High Temperature Reaction Chamber) that allowed both temperature control through electrical heating at the bottom and light illumination through 1 cm² silica window at the top of the reactor (8). The light source (Dolan-Jenner Fiber-Lite 180 Model illuminator with single gooseneck fiber optics) used for the photothermal studies (light on) was a broadband visible light source with a maximum spectral intensity at ~580 nm (Figure S2). The source intensity was varied by controlling the source power and the total light intensity was measured using the combination of UV intensity meter (OAI Instruments) and CCD camera (Avantes AvaSpec-2048). For the wavelength dependent photothermal experiments, optical filters (Edmund Optics) were used to control the wavelength of light reaching the catalyst from the light source and the total intensity of light reaching the catalyst surface was kept constant (~ 550 mW/cm²) for all experiments by adjusting the power to the light source. The catalyst (packed) bed was prepared by loading 10 mg of inert silica beads (Silica gel, Sigma-Aldrich Cat. No. 214418) to the bottom of the reactor and 12 mg of 2 wt% Cu/SiO₂ catalysts on top of the layers of silica beads. For all reactions reported here, the catalysts were pre-reduced at 523K for 1 hr in 20% hydrogen (remaining helium) at a total flow rate of 100 cm³/min before starting the reactions. For propylene epoxidation reaction, the reactants with a composition of 50% propylene and 50% oxygen at a total flow rate of 100 cm³/min were delivered from the top of the catalyst bed under specified reaction conditions. The reactants and products were analyzed online using a gas chromatograph (Varian CP 3800) equipped with thermal conductivity and flame ionization detectors.

The rate and selectivity results reported here for thermal (light off) and photothermal (light on) conditions were measured in a differential reactor set-up in the regime limited by the reaction kinetics under steady state reaction conditions. Propylene oxide (PO), acrolein (Acr) and carbon dioxide (CO₂) were observed as the principal products. The reaction rates were calculated using the formula, \((\frac{C_{PO}+C_{Acr}+C_{CO2}/3}{W})\), where, \(C_{PO}\), \(C_{Acr}\), \(C_{CO2}\) and \(W\) denote the measured concentration of the products- PO, acrolein and CO₂, and the weight of the catalyst, respectively. The PO, acrolein and CO₂ selectivity were calculated using the formulae- \(C_{PO}/(C_{PO}+C_{Acr}+C_{CO2}/3)\), \(C_{Acr}/(C_{PO}+C_{Acr}+C_{CO2}/3)\) and \((C_{CO2}/3)/(C_{PO}+C_{Acr}+C_{CO2}/3)\), respectively. The reaction rate and selectivity data shown in the figures represent the average values of the results obtained from multiple independent experiments and the error bars in the data represent the standard deviations. The selectivity to all carbon-based reaction products at \(T = 473\) K as a function of light intensity is shown in figure S3. The selectivity of all carbon-based products as a
function of temperature at light intensity of 550 mW/cm² is shown in figure S4. The selectivity to all carbon-based products as a function of temperature for non-illuminated catalysts is shown in figure S5.

Section S3. Characterization of catalyst: UV-Vis extinction spectra of the catalysts were measured using Thermo Scientific Evolution 300 UV-Vis Spectrophotometer with a Harrick Praying Mantis Diffuse Reflection Accessory. Harrick High Temperature Reaction Chamber used to carry out reactions under thermal and photothermal conditions is equipped with silica windows which allow recording of the UV-Vis spectra of the catalyst under in situ conditions. All in situ UV-Vis measurements were acquired under inert atmosphere (100 cm³/min of helium) at specified temperature. For in situ UV-Vis measurements under photothermal conditions (light on), the experiments were first carried out as described in the previous section. Before measuring the UV-Vis spectrum, the flow of reactants (100 cm³/min) was exchanged for helium (100 cm³/min) for ~15 minutes. The light source used for the photothermal experiments was then turned off and the UV-Vis spectrum was measured in inert atmosphere (100 cm³/min of helium). The identical procedure was followed for measuring the in situ UV-Vis spectra of the catalysts under thermal conditions.

X-ray diffraction (XRD) patterns of the used catalysts were acquired using Rigaku Miniflex DMAX-B rotating anode X-ray diffractometer with Cu-Kα radiation source operated at 30 kV and 15 mA.

Section S4. Finite-difference Time-domain (FDTD) simulation: Finite-difference time-domain (FDTD) optical simulations were performed to simulate the extinction cross section of the copper nanoparticle as a function of wavelength of incident light. Drude-Lorentz model was used to represent the optical properties. The empirical optical constants of copper metal were taken from Palik (31). The periodic boundary conditions were used in x- and y-directions, while the perfectly matched layer (PML) boundary condition was used in the z-direction. The extinction cross sections as a function of wavelengths were calculated using the total-field/scattered-field (TFSF) formalism. The incident light source used for the simulation was 400-1000 nm Gaussian source.
Fig. S1. Top: SEM image of copper nanoparticles dispersed on SiO₂ support. Smaller particles are Cu. Bottom: SEM image of copper nanoparticles deposited on a silicon wafer.
Fig. S2. Spectrum of the light source used in the photothermal studies.
Fig. S3. Selectivity to PO, acrolein and CO₂ under photothermal conditions at 473K as a function of light intensity. The selectivity data shown in the figure represent the average values of the data obtained from five independent experiments and the error bars represent the standard deviations.
Fig. S4. Selectivity to PO, acrolein and CO$_2$ for photothermal (light on) process as a function of temperature. The light intensity used for the photothermal studies was 550 mW/cm$^2$. The selectivity data shown in the figure represent the average values of the data obtained from three independent experiments and the error bars represent the standard deviations.
**Fig. S5.** Selectivity to PO, acrolein and CO$_2$ under thermal conditions (light off) as a function of temperature. The selectivity data shown in the figure represent the average values of the data obtained from three independent experiments and the error bars represent the standard deviations.
Fig. S6. Extinction spectrum of copper spherical nanoparticle (41 nm) calculated from FDTD simulation.
References and Notes


