Electronic Supplementary Information for

Selective Growth of Palladium Nanocrystals on (100) facets of Truncated Octahedral Cu_2O for UV Plasmonic Photocatalysis

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MATERIALS AND METHODS

Synthesis of Cu_2O truncated octahedron and pristine Pd nanoparticles.

All of the chemical reagents used in the experiments were of analytical grade and used without further purification. Typically, to 1.0 mL of 10 mM copper chloride aqueous solution 1.76 g of polyvinylpyrrolidone (PVP, 55,000) was added. Afterwards, 10 mL of 2.0 M NaOH aqueous solution was added into the above mixed solution with stirring and heated to 55 ℃. After stirring for 0.5 h, 10 mL of 0.6 M ascorbic acid aqueous solution was added into the above solution and continued to react for 3 h. A brick red solution was finally formed. The products were purified by centrifugation and washing with distilled water and absolute ethanol, and finally redispersed in ethanol. The synthesis of pristine Pd NCs followed an earlier method [1].

Selective deposition of Pd/(100) Cu_2O and NiO/Cu_2O heterostructures.

In a typical synthesis of Pd/truncated octahedral Cu_2O, 0.04 mL of 2.5 mg/mL Na_2PdCl_4 aqueous solution was mixed with 4.96 mL absolute ethanol. And then, the above ethanol solution was injected into 5 mL of truncated octahedral Cu_2O ethanol solution under vigorous stirring. The mixed solution was photo-irradiated by a 300 W Xenon lamp (λ>420 nm) under continuous stirring for 1 h. Finally, the products were purified by centrifugation and washing 2-3 times using distilled water and absolute ethanol and finally dried at 40 °C for 12 h under vacuum. To increase the amount of the added Na_2PdCl_4, 0.06, 0.08, and 0.1 mL were used respectively. NiO/Cu_2O products were synthesized under similar conditions except that the precursor was changed to $NiCl_2$, i.e. 0.1 mL of 2.0 mg/mL $NiCl_2$ aqueous solution and 0.1 mL of 50 mM $NaIO_3$ aqueous solution were added. The facet selectivity analyses were conducted based on manual counting of the number of Cu_2O cubes with predominant (100) facet Pd deposition divided by overall Cu_2O cubes. The manual counting was based on 50 particles.

Deposition of Pd on (111) facet of truncated octahedral Cu_2O under no light irradiation.

In a typical synthesis of Pd/truncated octahedral Cu_2O, 0.03 mL of 2.5 mg/mL H_2PdCl_4 aqueous solution was mixed with 4.96 mL absolute ethanol under vigorous stirring. And then, the above solution was injected into 5 mL of truncated octahedral Cu_2O ethanol solution under vigorous stirring. The mixed solution was reacted for 30 min. A aliquot solution was taken out every 5 min. The final product was purified by centrifugation and washing 2-3 times using distilled water and absolute ethanol and finally dried at 40 °C for 12 h under vacuum.

Characterizations

Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800 field emission scanning electron microscope. Transmission electron microscopy (TEM) were performed on a FEI Tecnai G2 F20 S-TWIN microscope operating at an accelerating voltage of 200 kV. For TEM, samples were sonicated in ethanol and deposited onto a carbon grid. The powder X-ray diffraction (XRD) data were collected using a Bruker D8 Advance X-ray Powder diffractometer with Cu Kα radiation. UV–vis diffuse reflection absorption spectra were recorded using a PE Lambda 650s UV-vis spectrometer.

Photocatalytic Activity Measurements

20 mg of the as-obtained photocatalysts was added to 50 mL of 1×10^{-4} M MO aqueous solution in 100 mL reactor. Methyl orange (MO) was used as a probe to assay photocatalytic activity of the as-obtained samples. The suspended solution was stirred for 90 min. to reach an adsorption/desorption equilibrium in the darkness. And then, the mixed solution was under photo-

irradiation from a distance of ca. 15 cm using hand-held UV lamps, i.e. λ=365 nm and λ=254 nm lamps respectively. 1 mL aliquot of the reaction suspension was taken out at a given time interval and centrifuged. Photocatalytic activity was evaluated according to absorption spectra of MO dyes recorded on a PE Lambda 650s UV-vis spectrophotometer. As for visible light test, a 300 W Xe lamp (PLS-SXE300, 150 mw/cm^2) equipped with a 420 nm cut-off filter was used. As for N_2 purge, the MO aqueous solution of the tested samples was purged for 1 h under N_2 with a purity of 99.99% and the reaction vessel was kept closed during the reaction.

Supplementary Figures:

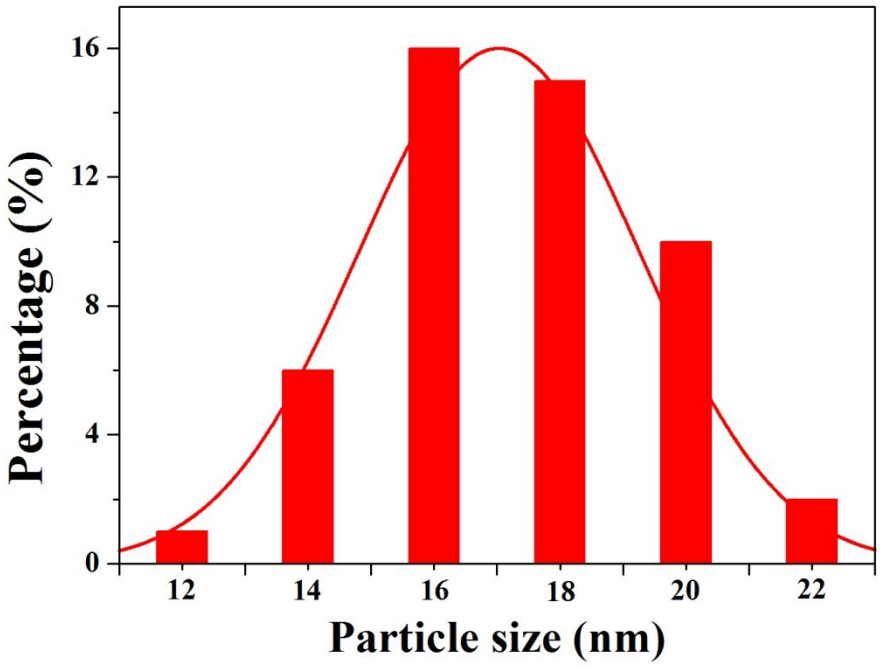

Figure S1. Size distribution histogram of Pd NCs on (100) facets of truncated octahedral Cu_2O.

Table S1 Size of Pd NCs on Cu_2O with the increase of added Na_2PdCl_4 amount

Added Na_2PdCl_4 Amount (mL)	Size of Pd NCs (nm)
0.04	15.2
0.06	16.8
0.08	18.4
0.10	22.4

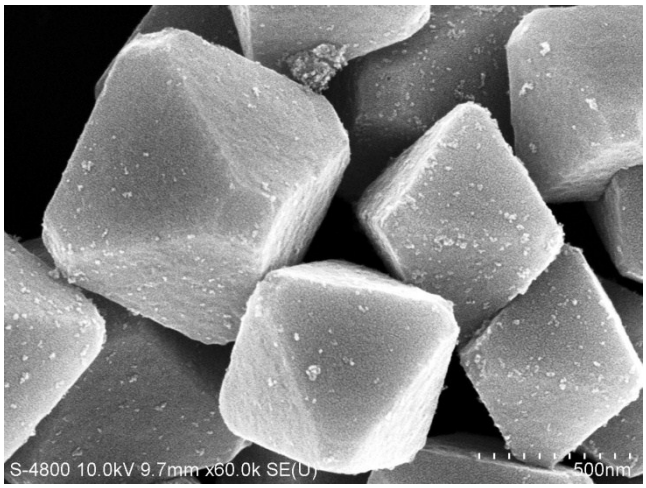

Figure S2. SEM image of Pd/truncated octahedral Cu_2O prepared under no visible light irradiation, showing Pd NCs were preferentially grown on (111) facets.

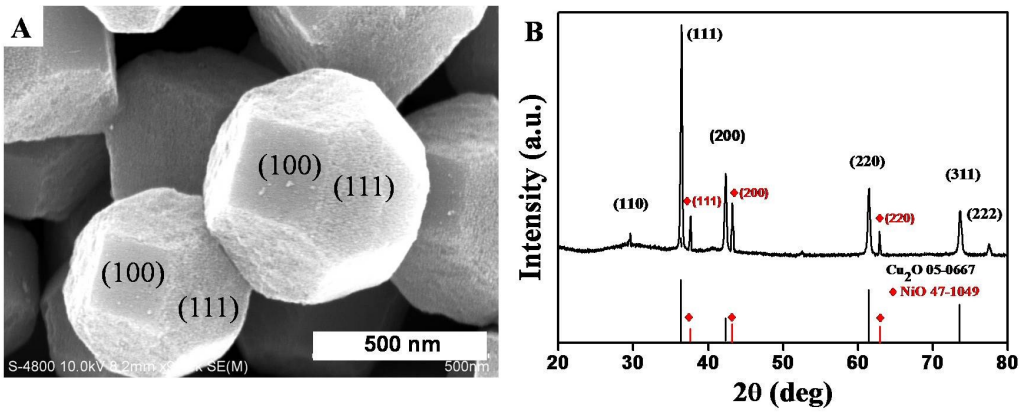

Figure S3. SEM image (A), XRD (B) of NiO/truncated octahedral Cu_2O, proving NiO NCs were selectively grown on (111) facets of truncated octahedral Cu_2O.

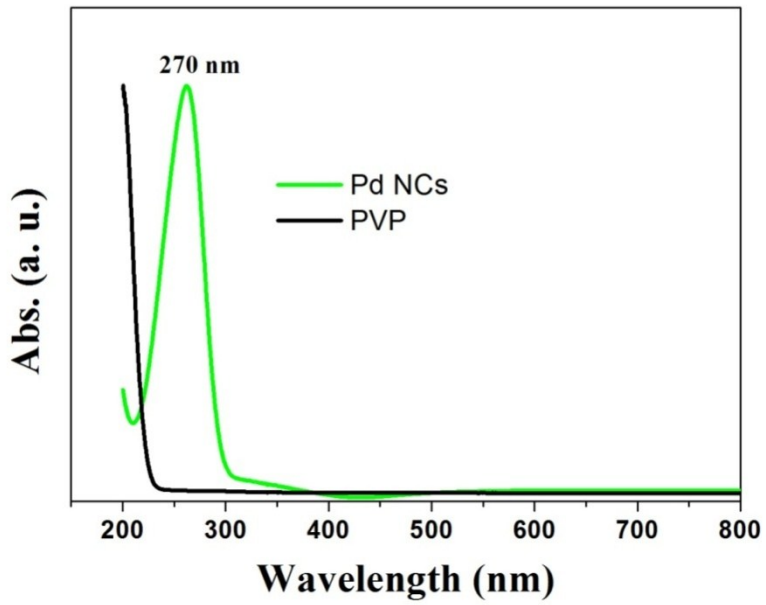

Figure S4. UV-vis absorption spectra of pristine Pd NCs and PVP. Pd NCs had a plasmon peak at ca. λ=270 nm. Note PVP was used as ligand.

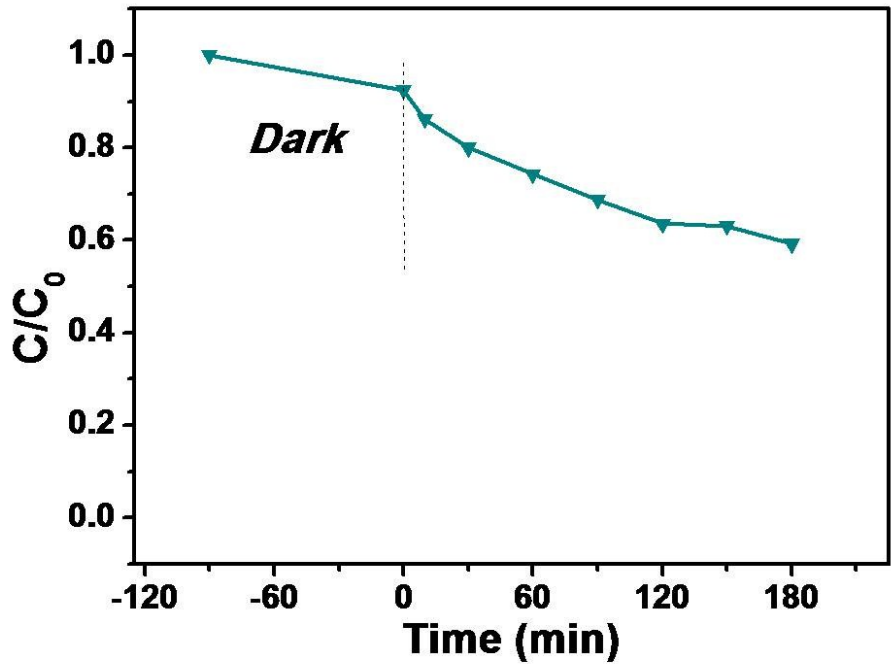

Figure S5. Photocatalytic activity at λ=254 nm of Pd/(111) Cu_2O prepared under no light irradiation

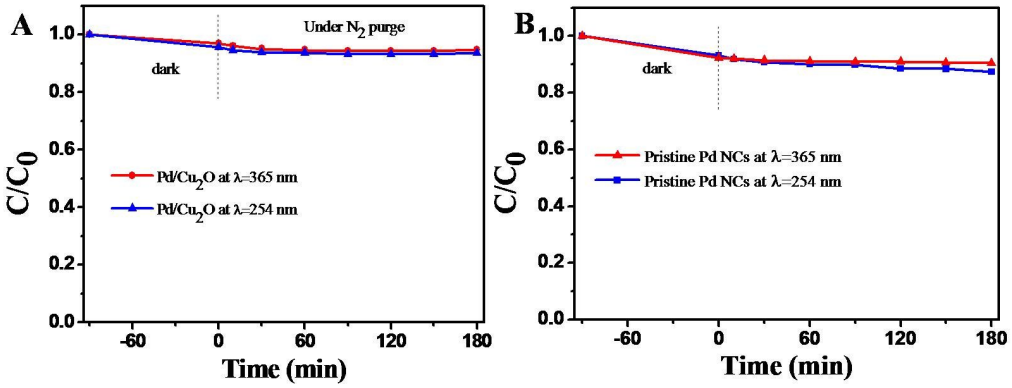

Figure S6. Two control experiments. (A) is, after using N_2 purge, photocatalytic activities of Pd/truncated octahedral Cu_2O under single wavelength UV light irradiation. (B) is photocatalytic activities of pristine Pd NCs under single wavelength UV light irradiation.

References

[1] Y. Xiong, J. Chen, B. Wiley, Y. Xia, Y. Yin, and Z.-Y. Li, *Nano Lett.*, 2005, **5,** 1237.