Supplementary Information for:

Revitalizing Silver Nanocrystals as a Redox Catalyst by Modifying Their Surface with an Isocyanide-Based Compound

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Experimental Section

Chemicals and Materials. Ethylene glycol (EG) was purchased from J. T. Baker. Poly(vinylpyrrolidone) with an average molecular weight of 55,000 (PVP-55k), sodium hydrosulfide hydrate ($NaHS \cdot xH_2O$), aqueous hydrochloric acid (HCl, 37 wt.%), silver trifluoroacetate (CF_3COOAg, ≥99.99% trace metal basis), ethanol (200 proof), 1,4-phenylene diisocyanide (1,4-PDI, 97%), and sodium borohydride ($NaBH_4$, 99.99% trace metal basis) were all obtained from Sigma-Aldrich. Acetone (HPLC grade, 99.5+%), formic acid (≥88%), triethylamine (≥99%), phosphorous oxychloride (≥99%), chloroform (≥99.5%), and sodium carbonate (≥98%) were received from Alfa Aesar. Ethyl acetate (≥99.5%) was received from VWR Chemicals and 4-nitrothiophenol (4-NTP) was ordered from Oakwood Chemical. All these chemicals were used as received. Dichloromethane (≥99.5%) was obtained from VWR Chemicals and purified using the MB-SPS solvent purification system. Deionized (DI) water with a resistivity of 18.2 MΩ·cm at room temperature was used.

Synthesis of Ag Nanocubes. We synthesized the Ag nanocubes with an average edge length of 37.7 ± 2.6 nm by following a published protocol.[1] The as-obtained Ag nanocubes were washed with acetone and water (once for each solvent) and then re-dispersed in water for future use.

Synthesis of 4,4'-Biphenyldiisocyanide (BPDI). We performed two-step synthesis under nitrogen protection. In the first step, we prepared N,N'-([1,1'-biphenyl]-4,4'-diyl)diformamide by following a published protocol with some revision.[2] Specifically, hydrazobenzene (18.42 g, 0.10 mol) was added into a flask containing 88% formic acid (100 mL) at room temperature under nitrogen. After stirring for 24 h, the mixture was poured into ice-water (500 mL). Next, the yellow solid was collected by filtration and washed with water. After drying, the solid was stirred with chloroform (200 mL) for 10 h before the white solid was collected by filtration and washed with chloroform. After drying under vacuum, the final product was obtained in 16.5 g (69% yield). In the second step, we prepared BPDI by following a published procedure.[3] In a typical process, the N,N'-([1,1'-biphenyl]-4,4'-diyl)diformamide (3.0 g, 12.5 mmol) was added into a mixture solution containing triethylamine (12.8 mL) and dichloromethane (50.0 mL) at 0 ℃ (in an ice-water bath). Next, phosphorous oxychloride (4.9 g, 3.0 mL, 32.2 mmol) was introduced dropwise. Afterwards, the reaction mixture was stirred at 0 ℃ for 1 h and then room temperature for 2 h. The reaction mixture was cooled to 0 ℃ again, followed by the addition of sodium carbonate (6.3 g, 59.4 mmol) in water (25.0 mL) dropwise, and then water (100.0 mL) and dichloromethane (200.0 mL), respectively. This two-phase mixture was stirred for 30 min before the organic phase was separated and the aqueous phase was extracted with dichloromethane (3×50 mL). The combined organic phase was washed with brine (4×50 mL). After the removal of solvent, the brown solid was dissolved in ethyl acetate and solution was filtered through short silica gel column. After removal of ethyl acetate, the product was obtained as 2.3 g (88.5 % yield) of pale yellow solid. The BPDI was purified again by vacuum sublimation at 170 °C and 1.2 x 10^{-5} torr to achieve a sublimation yield of 67.0%. We characterized the product using1H NMR and 13C NMR spectra recorded on Varian Mercury 400 spectrometer, with $CDCl_3$ (99.8%, ordered from Acros Organics) serving as a solvent. Specific details include ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 4 H), 7.48 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 4 H) and 13C-NMR (400 MHz, $CDCl_3$) δ(ppm): 165.39, 140.46, 128.13, 127.05, 126.34.

Raman Measurements. We fabricated the sample cell by punching a hole capable of holding about 25 μL of liquid in the surface of a polydimethylsiloxane (PDMS) block and then having it mounted on a piece of glass slide. We placed a glass coverslip on the cell to avoid solvent evaporation. We recorded the Raman spectra using a Renishaw inVia Raman Spectrometer integrated with a Leica microscope using a 100× objective lens with the excitation of a 532-nm laser at a power of 5 mW (10%). The scattered light was dispersed using a holographic notch filter with a grating of 2400 lines/mm. We collected all time-dependent Raman spectra using the *extended* mode, during which the spectrometer scanned across the spectral region from 2500 cm^{-1} to 500 cm^{-1} with an acquisition time of 10 s. We also collected some Raman spectra using *static* mode. In this case, we recorded a Raman spectrum from 1663.74 to 2679.38 cm^{-1} by setting the center position at 2200 cm^{-1} with an acquisition time of 1 s for each spectrum, accumulating 300 spectra to improve signal-to-noise ratio.

In Situ SERS Monitoring of the Reduction of 4-NTP Adsorbed on the Surface of Ag Nanocubes Pre-functionalized with 1,4-PDI. In the first step, we collected a Raman spectrum from a 10^{-4} M solution of 1,4-PDI in ethanol. We then prepared an ethanol suspension by adding

8 µL of Ag nanocubes into 300 µL of 10^{-4} M 1,4-PDI solution. Upon sonication, we withdrew an aliquot of 25 µL from the as-obtained suspension at t = 5 min to collect one SERS spectrum and then repeated the same procedure at t = 60 min to collect another SERS spectrum. Afterwards, we mixed 200 µL of the suspension with 200 µL of 10^{-5} M 4-NTP ethanol solution in a centrifuge tube. Upon mixing using vortex, we withdrew an aliquot of 25 µL from the mixture at t = 5 min to record the first spectrum. We then withdrew another sample of 25 µL from the mixture at t =15 min to record the second spectrum. For a set of controlled experiments, we followed the same procedure except that we changed the concentrations of the 1,4-PDI and/or 4-NTP solutions, altered the sequence by adding Ag nanocubes into 4-NTP solution and then 1,4-PDI solution, and replaced 1,4-PDI with BPDI.

In Situ SERS Monitoring of the Reduction of 4-NTP on the Pristine Ag Nanocubes. In the first step, we recorded a Raman spectrum from the 10^{-5} M 4-NTP solution in ethanol. We then prepared an ethanol suspension by mixing 8 µL of the as-prepared Ag nanocubes with 300 µL of the 4-NTP solution. After sonication, we withdrew an aliquot of 25 µL at t = 15 min to collect one spectrum and then repeated the same procedure at t = 30 min to collect another spectrum. In the third step, we mixed 200 µL of the as-obtained suspension with 200 µL freshly prepared ice-cold $NaBH_4$ aqueous solution (0.1 mg/mL) and then withdrew an aliquot of 25 µL at t = 5 min to collect one spectrum and repeated the same procedure at t = 30 min to record another spectrum.

Instrumentation and Characterization. An Eppendorf 5430 centrifuge was used for collecting and washing Ag nanocubes. The transmission electron microscopy (TEM) image of Ag nanocubes was captured using a Hitachi HT7700 microscope (Hitachi, Japan) operated at 120 kV. All Raman and SERS spectra were collected using a Renishaw inVia Raman spectrometer (Wotton-under-Edge, U.K.) coupled with a Leica microscope (Wetzlar, Germany).

Supplementary Figures and Tables

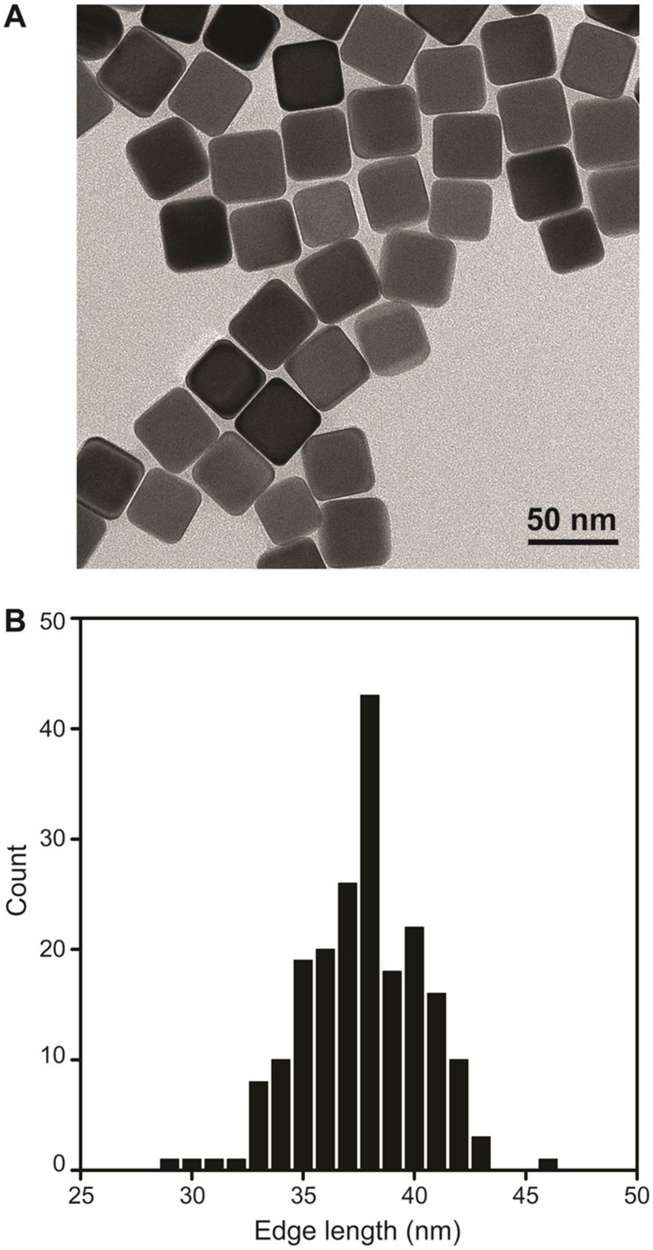

Figure S1. (A) a TEM image of Ag nanocubes. (B) The particle size distribution histogram of the Ag nanocubes, which gives the average edge length of 37.7 ± 2.6 nm.

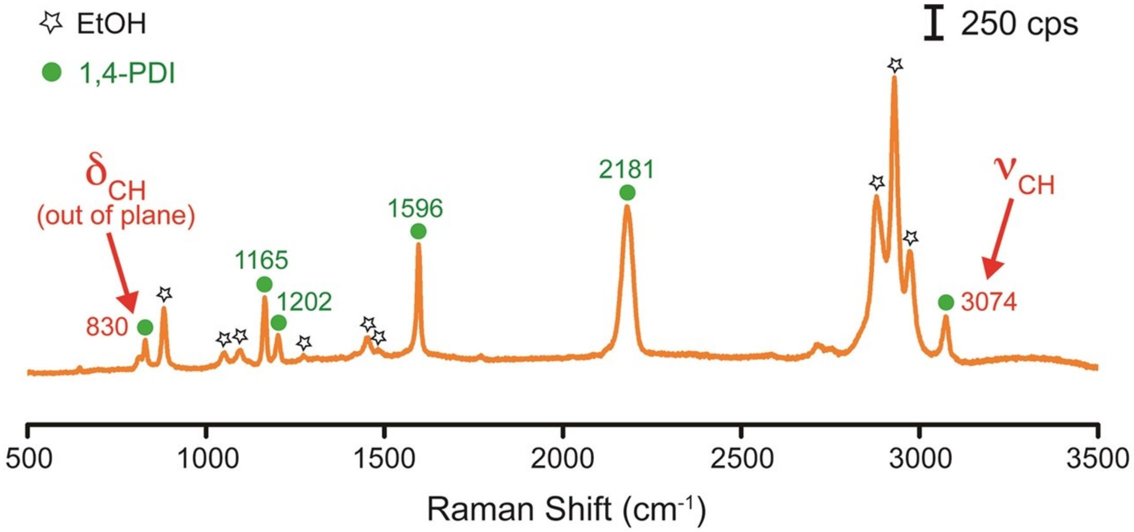

Figure S2. SERS spectrum collected from an ethanolic suspension of Ag nanocubes and 1,4-PDI at 10^{-4} M at *t* = 60 min.

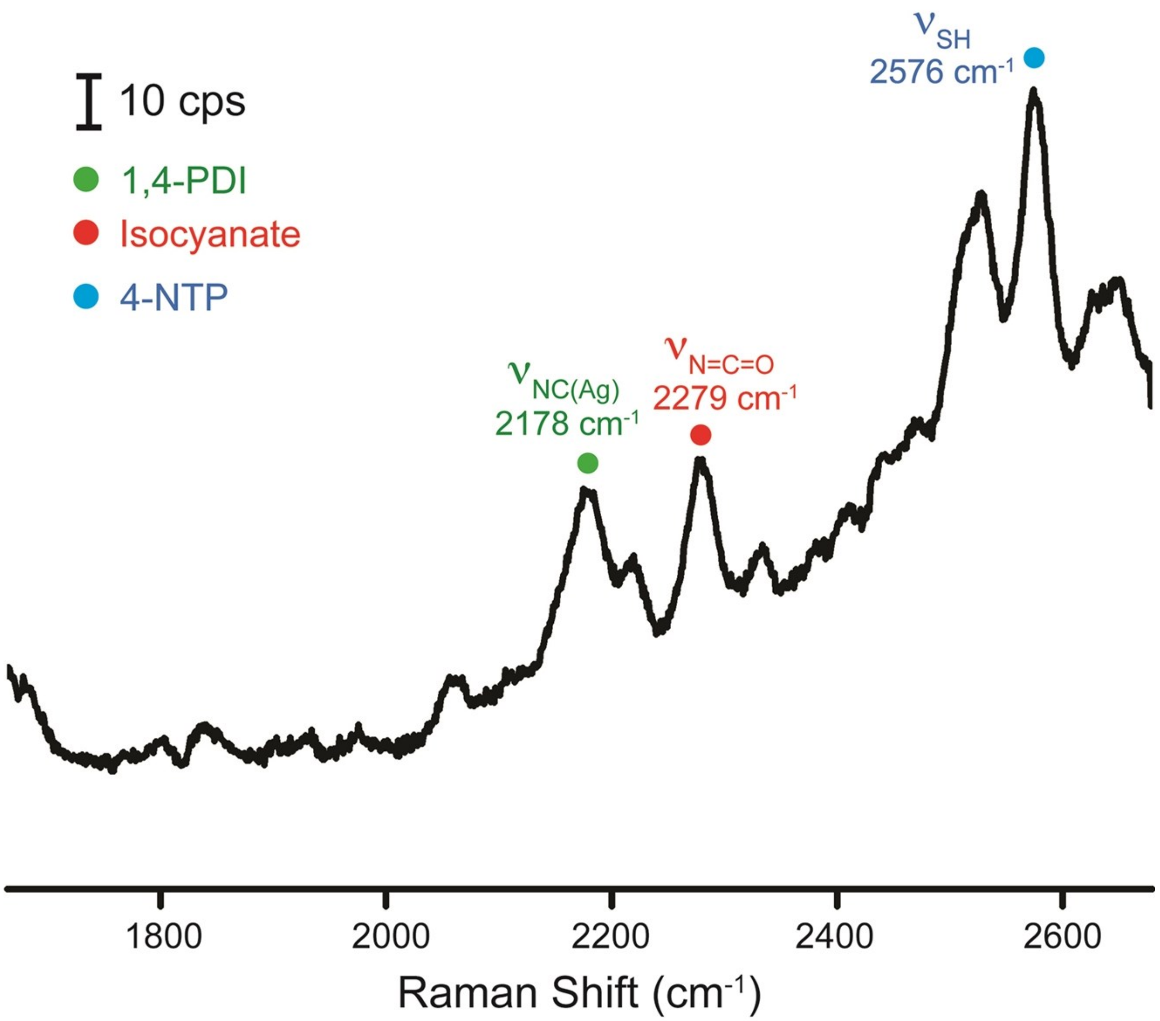

Figure S3. SERS spectrum collected from the suspension after mixing Ag nanocubes with a 1,4-PDI solution in ethanol (10^{-4} M) for 60 min, followed by the addition of a 4-NTP solution in ethanol (10^{-5} M) and waiting for 5 min.

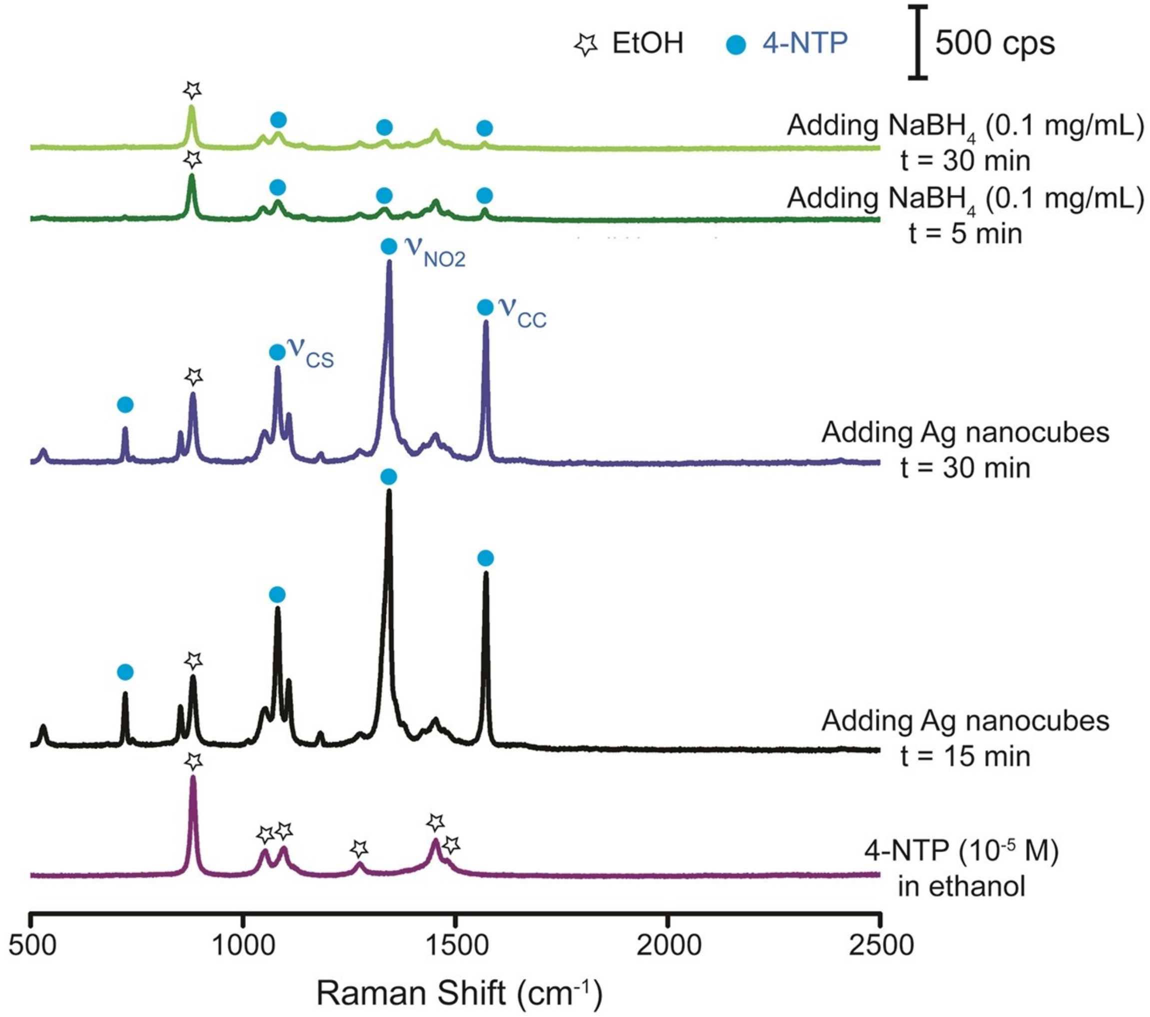

Figure S4. Raman spectrum recorded from the 4-NTP solution (10^{-5} M) in ethanol and time-elapsed SERS spectra collected from an ethanolic suspension of Ag nanocubes and 4-NTP before and after the addition of aqueous $NaBH_4$ (0.1 mg/mL).

Table S1. The SERS and ordinary Raman shifts of 1,4-PDI and their assignments.

SERS (cm^{-1})	Ordinary (cm^{-1})	Assignments[4]
	645	C-C-C in-plane bending
	707	C-C-C puckering
812	806	ring breathing
830	823	C-H out-of-plane bending
1166	1170	C-H in-plane bending
1203	1193	C-NC stretching
1596	1602	C-C stretching
2180 (Ag-atop)	2126	C-N stretching

References for the Supporting Information

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4 S. M. Gruenbaum, M. H. Henney, S. Kumar, S. Zou, *J. Phys. Chem. B* **2006**, *110*, 4782−4792.