

## Catalytic Reduction of Nitro-Group Terminated Monolayers by Ag Nanoparticles; A Novel Strategy for Site-Selective Patterning of Organic Monolayers

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### Electronic Supplementary Information

#### Experimental Procedures

Silver nitrate (reagent grade), 4-aminobenzenethiol (4-ABT, reagent grade), and silver powders (99.9+%) with nominal particle size of 2-3.5  $\mu\text{m}$  were purchased from Aldrich. Before use, the silver powders were washed consecutively with ethanol (Hayman, >99.9%), acetone (Merck, >99.5%), *n*-hexane (Junsei, extra pure), and tetrachloromethane (J. T. Baker, HPLC grade). This process was performed to clean the silver powders and to remove any carbon impurities on the powdered silver. Sodium borohydride (analytical grade) and 4-nitrobenzenethiol (4-NBT, reagent grade) were purchased from Lancaster and TCI, respectively. Unless otherwise specified, other chemicals were reagent grade, and triply distilled water (resistivity greater than 18  $\text{M}\Omega\text{-cm}$ ) was used throughout.

The stock solution of 1 mM 4-NBT in ethanol was bubbled with nitrogen before use. For the self-assembly of 4-NBT on powdered silver, 0.50 g of 2-3.5  $\mu\text{m}$ -sized silver powder was placed in a small vial into which 5.0 mL of ethanol and 5.0 mL of 4-NBT stock solution were subsequently added. The remaining solid powders were washed with excess ethanol and left to dry in ambient conditions for 2 h. Thereafter, 100 mg of the dried samples were placed in small vials into which 3.0 mL of 1, 10, 50, 100, or 200 mM  $\text{NaBH}_4$  aqueous solutions were added; freshly prepared  $\text{NaBH}_4$  solutions were used throughout. After 10 min, the aqueous phase was decanted, and the remaining solid particles were washed with excess water and left to dry under  $\text{N}_2$  atmosphere. In another experiment, aqueous  $\text{AgNO}_3$  solutions were added into the vials containing 4-NBT anchored silver powders and  $\text{NaBH}_4$  solutions by up to 10  $\mu\text{M}$ . Post-treatments were the same as before, and all the dried samples were finally subjected to DRIFT analyses. For a comparative study, 4-ABT anchored Ag powders were prepared. In addition, 4-NBT SAMs were also fabricated on thick, flat Ag substrates and treated with  $\text{NaBH}_4$  solutions, as for the SAMs fabricated on powdered silver. These samples were analyzed by reflection-absorption infrared (RAIR) spectroscopy.

The thick, flat Ag substrates were prepared by resistive evaporation of titanium (Aldrich, >99.99%) and silver at  $1 \times 10^{-6}$  Torr on batches of glass slides, cleaned previously by sequentially sonicating in isopropyl alcohol, hot 1:3  $\text{H}_2\text{O}_2(30\%)/\text{H}_2\text{SO}_4$ , and triply distilled  $\text{H}_2\text{O}$ . Titanium was deposited prior to silver to enhance adhesion of silver to the substrates. After a deposition of approximately 200 nm of silver, the evaporator was back-filled with nitrogen.

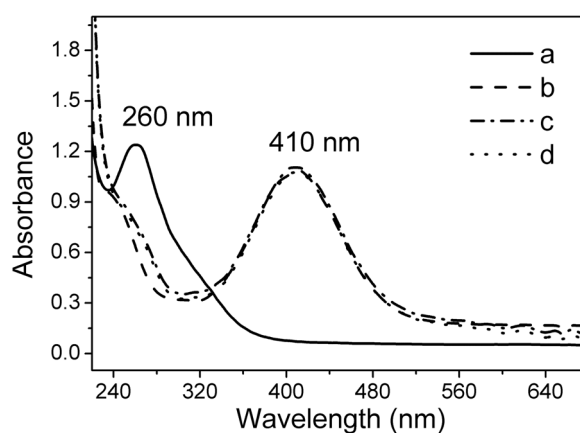
Infrared spectra were obtained using a Bruker IFS 113v Fourier transform IR spectrometer equipped with a global light source and a liquid  $\text{N}_2$ -cooled wide-band mercury cadmium telluride detector. To record the DRIFT spectra, a Harrick Model DRA 3CI diffuse reflectance accessory was employed. Each powdered sample was transferred to a 4-mm diameter cup (Harrick microsampling cup) without compression, and leveled by a gentle tap. A total of 256 scans were measured in the range 4000-600  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$  using the previously scanned pure Ag powder as the background. On the other hand, each RAIR spectrum was obtained by averaging 1024 interferograms at 4  $\text{cm}^{-1}$  resolution, with p-polarized light incident at  $80^\circ$  with respect to the vacuum-evaporated silver substrate, as reported previously.<sup>S1</sup> To reduce the effect of water vapor rotational lines, the sample and reference interferograms were recorded alternately after every 32 scans. The Happ-Genzel apodization function was used in Fourier transforming all the interferograms. The RAIR spectrum is reported as  $-\log(R/R_0)$ , where  $R$  and  $R_0$  are the reflectivities of the sample and the bare clean metal substrates, respectively. Considering that infrared radiation will not penetrate into the metal particles, and that the usual Kubelka-Munk equation is not applicable to the present system, the DRIFT spectrum is also reported in  $-\log(R/R_0)$ .

Raman spectra were obtained using a Renishaw Raman system model 2000 spectrometer equipped with an integral microscope (Olympus BH2-UMA). The 514.5-nm radiation from a 20 mW air-cooled  $\text{Ar}^+$  laser (Melles-Groit Model 351MA520) or the 632.8-nm radiation from a 17 mW air-cooled He/Ne laser (Spectra Physics Model 127) was used as the excitation source. Raman scattering was detected with  $180^\circ$  geometry using a peltier-cooled ( $-70^\circ\text{C}$ ) CCD camera (400 $\times$ 600 pixels). The data acquisition time was usually 90 s. The holographic grating (1800 grooves/mm) and the slit

permitted a spectral resolution of  $1\text{ cm}^{-1}$ . The Raman band of a silicon wafer at  $520\text{ cm}^{-1}$  was used to calibrate the spectrometer, and the accuracy of the spectral measurement was estimated to be better than  $1\text{ cm}^{-1}$ . The Raman spectrometer was interfaced to an IBM-compatible PC, and the spectral data were analyzed using Renishaw WiRE software, version 1.2, based on the GRAMS/32C suite program (Galactic Industries).

UV/Vis spectra were recorded, using a SCINCO S-2130 spectrophotometer, for 4-NBT dissolved in water before and after the addition of borohydride.

Patterning was accomplished by micro-molding in the capillary method<sup>S2</sup> using a polydimethylsiloxane (PDMS) stamp with a strip pattern (width:  $2\text{ }\mu\text{m}$  and interdistance:  $5\text{ }\mu\text{m}$ ). A mixed solution of  $1\text{ mM NaBH}_4$  and  $10\text{ }\mu\text{M AgNO}_3$  was used as ink. When the added ink was dried off, the Ag substrate was washed with ethanol and then dipped into Au sol solution for 1 h; gold sol solution, prepared by the citrate reduction of  $\text{KAuCl}_4$  solution,<sup>S3</sup> was composed of gold nanoparticles with an average diameter of  $17\pm 1\text{ nm}$ .



**Figure S1.** UV/Vis absorption spectra of  $50\text{ }\mu\text{M}$  aqueous solutions of (a) 4-ABT and (b) 4-NBT, and similar UV/Vis spectra taken for  $50\text{ }\mu\text{M}$  4-NBT solutions 30 min after the addition of sodium borohydride to a final concentration of (c)  $10\text{ mM}$  and (d)  $200\text{ mM}$ ; pH was adjusted to be at 10.0 using NaOH solution.

## References

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