

## **Magnetoswitchable Single-Electron Charging of Au-Nanoparticles Using Hydrophobic Magnetic Nanoparticles**

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### **Supplementary information**

Monoamino-functionalized Au nanoparticles (NPs) (1.4 nm) containing a single triphenylphosphine ligand functionalized with 1,3-propane diamine were purchased from Nanoprobes (U.S.A.). Magnetic nanoparticles, Fe<sub>3</sub>O<sub>4</sub>, coated with undecanoic acid shell were synthesized according to the published procedure (Shen, L.; Laibinis, P. E.; Hatton, T. A. *Langmuir* **1999**, *15*, 447-453) with the difference that only a single capping layer was generated on the surface of the nanoparticles. A Au-coated (50-nm gold layer) glass plate (Analytical  $\mu$ -Systems, Germany) was used as a working electrode. 11-Mercaptoundecanoic acid (1 mM ethanolic solution) was self-assembled on the Au electrode overnight to yield the amino-functionalized Au surface. The resulting amino-functionalized Au electrode was then reacted overnight with the amino-functionalized Au NPs (1  $\mu\text{g mL}^{-1}$ ) in 0.1 M HEPES-buffer, pH = 7.2, in the presence of EDC, 10 mM.

Linear potential sweep voltammetry measurements were performed using an electrochemical analyzer (model 6310, EG&G) connected to a personal computer with EG&G 270/250 software. The measurements were carried out at ambient temperature (25 $\pm$ 2  $^{\circ}\text{C}$ ) in a conventional electrochemical cell consisting of a modified Au working electrode (0.78 cm<sup>2</sup> geometrical area, ca. 1.2 roughness factor, exposed to the solution) assembled at the bottom of the electrochemical cell, a glassy carbon auxiliary electrode, and a saturated calomel electrode (SCE) connected to the working volume with a Luggin capillary. All potentials are reported with respect to this reference electrode. Phosphate buffer (0.1 M, pH 7.0) was used as a background electrolyte. The undecanoic acid-functionalized magnetic nanoparticles were added to the cell in a toluene solution (0.5 mL, 1 mg mL<sup>-1</sup>), yielding an upper organic solution layer immiscible with the aqueous

electrolyte solution. The undecanoic acid-functionalized magnetic nanoparticles were attracted to the Au electrode surface from the upper organic layer by positioning a 12-mm diameter magnet (NdFeB/Zn-coated magnet with the remanent magnetization of 10.8 kG) below the bottom electrode. The magnetic nanoparticles were removed from the electrode surface and re-transported to the organic phase by positioning the external magnet on the top of the electrochemical cell. Argon bubbling was used to remove oxygen from the solutions in the electrochemical cell. The cell was placed in a grounded Faraday cage.

A QCM analyzer (Fluke 164T multifunction counter, 1.3 GHz, TCXO) and quartz crystals (AT-cut, 9 MHz, Seiko) sandwiched between two Au electrodes (area 0.196 cm<sup>2</sup>, roughness factor ca. 3.2) were employed for the microgravimetric analyses in air.