

In situ synthesis and immobilization of metallic nanoparticles on a calixarene monolayer

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1 Materials

p-aminophenyltrimethoxysilane (APhS, Gelest), terephthaloyl chloride (TC, Aldrich), silver nitrate (Merck), gold(III) chloride trihydrate (Sigma-Aldrich), palladium (II) acetyl acetonate (99%, Aldrich), platinum acetyl acetonate (98%, Aldrich), copper(II) sulfate pentahydrate (Merck), iodocyclohexane (98%, Aldrich) and thionyl chloride (99%, Merck) were used as received. Triethylamine (GC grade, Fluka), acetone (AR, Merck), ethyl acetate (ACS, Tedia), toluene (HPLC grade, Tedia), tetrahydrofuran (THF, HPLC grade, Tedia), dimethyl acetamide (DMAc, HPLC grade, Tedia), dimethylformamide (DMF, HPLC grade, Fisher), pyridine (ACS grade, Merck), acetonitrile (AR grade, Merck), sulfuric acid (GR grade, Fischer) and hydrogen peroxide (30%, Merck) were used without further purification. Silicon wafers with a layer of native oxide were obtained from Engage Electronics Pte Ltd., and glass beads were obtained from Sigma-Aldrich Pte Ltd..

2 Synthesis of 4-methoxycalix[7]arene

4-methoxycalix[7]arene was newly synthesized through a three-step catalyzed reaction. Diphenylether (40 mL), 4-methoxyphenol (0.622 g), potassium tert-butoxide (0.15 g) and paraformaldehyde (0.51 g) were added to a 100 mL flask. The mixture was sequentially heated for 8 hours at 55 °C, for 2.5 hours at 110 °C and for 3 hours at 170 °C, to yield a yellow slurry. The slurry was cooled to room temperature, and then 20 mL ethyl acetate was added in the slurry. A yellow solid was obtained by filtration of the slurry. Then the solids in powder form were dissolved in pyridine and again filtered to remove the insoluble material. 40 mL of HCl (3 mol/L) was added to the filtrate and the resulting yellow-white precipitate was separated by filtration and then dried in vacuum. 0.2 g of a yellow-white solid was obtained and identified as 4-methoxycalix[7]arene.

3 Deposition of APhS, TC and 4-methoxycalix[7]arene layers

APhS and TC molecules were sequentially deposited on an activated silicon wafer by covalent LbL assembly. The silicon wafer was activated by piranha solution (7:3 v/v (H₂SO₄:H₂O₂)), and then was coated with APhS and TC by successive immersion into 4 mM APhS in toluene and 8 mM TC in THF, respectively. The resulting film would be covalently bound to the silicon surface and the surface populated with acyl chloride groups. The acyl chloride groups on the surface can be easily hydrolyzed by the moisture in the air and thus lose their high activity, so the surface is treated with thionyl chloride in order to convert the hydrolyzed groups back to acyl chloride form prior to the assembly of next layer. The wafer was immersed in a mixture of thionyl chloride and THF (1:4, w/w) for 1 h and then rinsed thrice with acetonitrile. Then, it was immediately immersed into 0.05% (w/w) 4-methoxycalix[7]arene in a mixture of THF and pyridine (10:1, V/V) for 4 h, and several drops of triethylamine was added to the solution as catalyst. The substrate was then rinsed and sonicated in DMAc for 5 min, and rinsed once with acetonitrile. Finally, the sample was dried in vacuum at 60 °C for 1 h.

4 Formation of calix[7]hydroquinone monolayer

Iodocyclohexane (2 mL) and DMF (8 mL) were added to a 100 mL flask. The samples with the 4-methoxycalix[7]arene layer were immersed in the iodocyclohexane solution and then were heated at 150 °C for 4 h in an Argon atmosphere. The flask was then cooled to room temperature and 20 mL of deionised water was added to the flask. After 30 min, the samples were rinsed thrice with deionised water and then were blown dry with nitrogen.

5 In-situ synthesis of monometallic and bimetallic NPs

Prior to incorporation of NPs, the substrate containing the calix[7]hydroquinone layer was immersed in a 5 % aqueous sodium hydrosulfite solution for 3 h to avoid any reverse oxidation of calix[7]hydroquinone by air. The samples were then rinsed thrice in deionized water.

Ag NPs were synthesized in-situ in the calix[7]hydroquinone layer by immersing the samples in 10 mL silver nitrate aqueous solution (0.2 %, w/w) for 3 h. Afterwards, the samples were rinsed thrice in deionized water and dried in vacuum.

Pd, Pt, Au and Cu NPs were synthesized in-situ in the calix[7]hydroquinone layer using appropriate precursors. Pd NPs were synthesized by immersing the calix[7]hydroquinone-laden substrate into palladium(II) acetyl acetonate in THF solution (0.2 %, w/w) for 3 h. Immersion in platinum acetyl acetonate in THF solution (0.2%, w/w) for 3 h was used to form Pt NPs. Au NPs and Cu NPs were synthesized by immersing the substrate in gold(III) chloride trihydrate (0.2 %, w/w) and copper(II) sulfate aqueous solutions (0.2 %, w/w) for 3 h, respectively.

The oxidized calix[7]hydroquinone (viz., the quinone form) can be reduced to the hydroquinone form by immersing the substrate into 5% (w/w) sodium hydrosulfite aqueous solution for 3 h. Therefore, the above in-situ synthesis process and cyclical redox reactions can be repeated multiple times to obtain nanoparticles with different components. Pd-Ag bimetallic NPs were synthesized by deposition of Pd and Ag on the calix[7]hydroquinone layer sequentially, which is shown as Schematic 1b.

The synthesis process on the surfaces of silicon wafer and glass beads is similar. During the fabrication of the multilayer film and NPs on surfaces of glass beads, the reaction solutions were shaken on a shaker in order that all the surfaces of glass beads could sufficiently contact the reactant in solution.

6 Characterization

Ellipsometry (WVASE 32, J.A. Woollam Co. Inc.) was used to characterize the thickness of the multilayer films. Scanning spectra were acquired over the wave length range of 250-600 nm at 70°. A CAUCHY model was used to fit the layer thickness, in which the refraction index was fixed at 1.47. The thickness for each sample was measured at three different locations.

A Kratos Analytical AXIS HSi spectrometer with a monochromatized Al K α X-ray source (1486.71-eV photons) at a constant dwell time of 100ms and pass energy of 40 eV was used in the X-ray photoelectron spectroscopy (XPS) characterization. The C1s hydrocarbon peak at 284.6 eV was adopted as reference for all binding energies.

Surface roughness and morphologies were investigated by a Nanoscope III atomic force microscope (AFM). All tests were conducted under the tapping mode, and a monolithic silicon tip was used. The drive frequency was 330 \pm 50 Hz, and the scan rate was 1.0-1.2 Hz.

The NPs were imaged by *field emission* transmission electron microscope (FETEM) (JEM 2010F, JEOL, Japan). A very thin slice of the silicon wafer with NPs was prepared by a precision ion polishing system (GATAN 691). The sample was milled from the backside at an angle of 8° until a hole appeared in the center of the sample, and then it was milled further at 3° for another 10 min. NPs on surfaces of glass beads were imaged directly by FETEM.

7 Figure S1

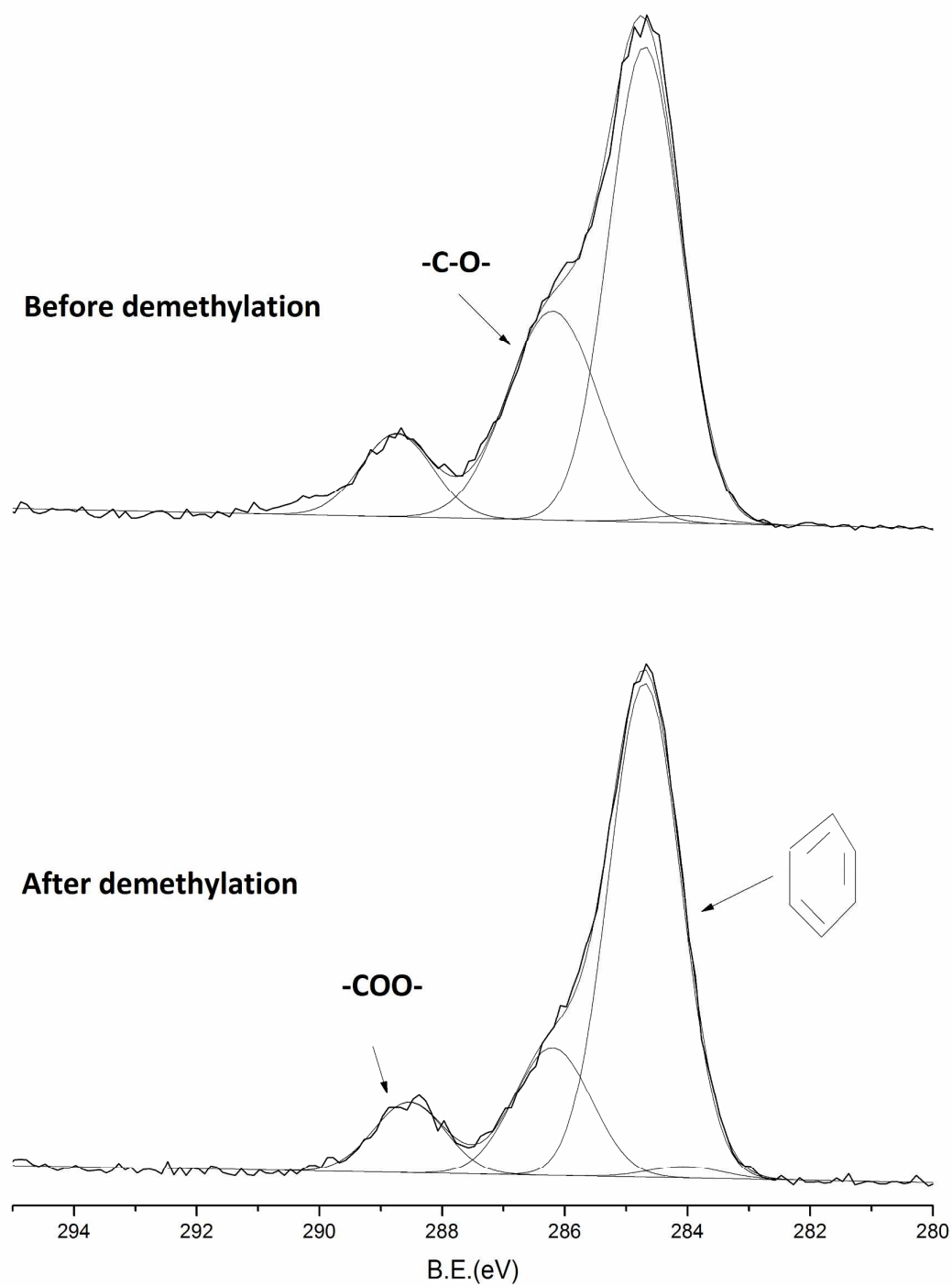


Fig. S1 C1s XPS spectra of the calix[7]arene layer before and after demethylation

8 Figure S2

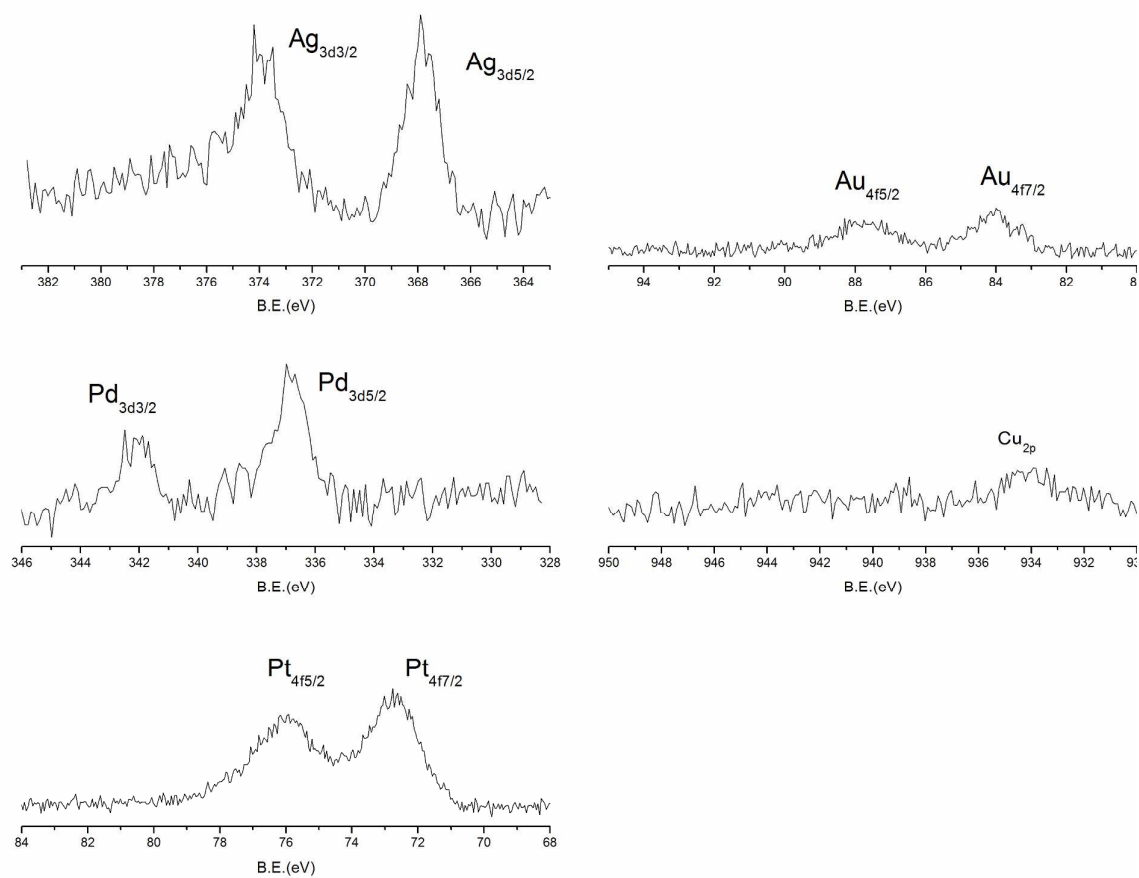


Fig. S2 XPS spectra of the Ag, Pd, Pt, Au, Cu on the calix[7]hydroquinone monolayer

9 Figure S3

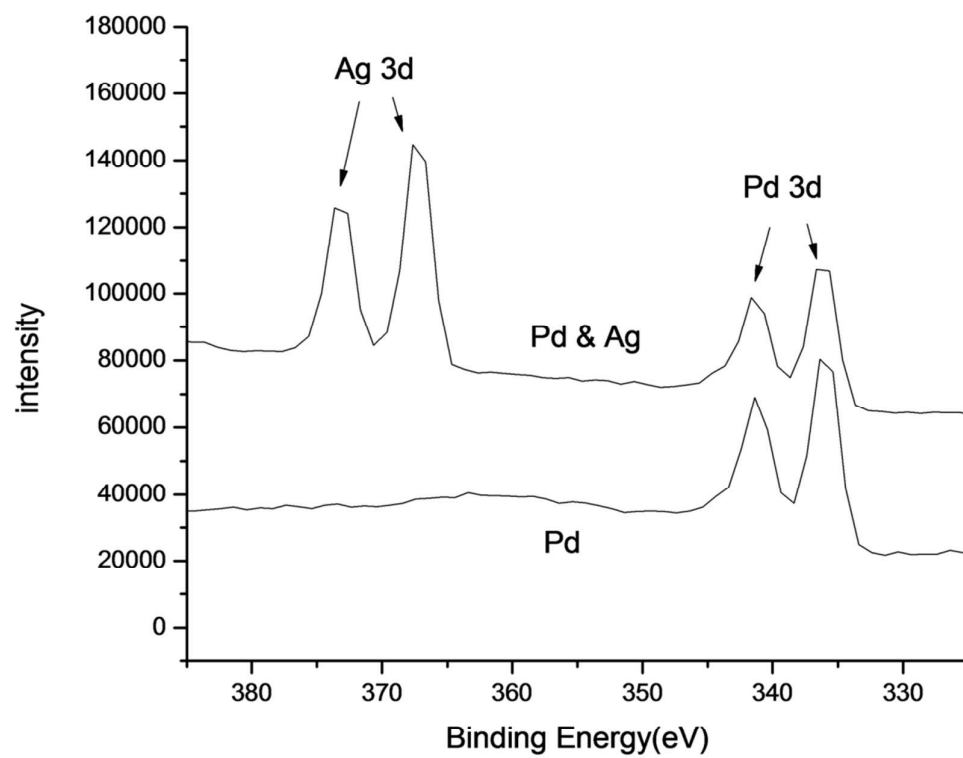


Fig. S3 XPS spectra of the Pd and Pd-Ag NPs