Electronic Supplementary Information (ESI)

Extremely low catalyst loading for electroless deposition on non-conductive surface by a treatment for reduced graphene oxide

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EXPERIMENT

Apparatus:

The microstructures of reduced graphene oxide (rGO) and Pd nanoparticles were observed using transmission electron microscopy (TEM) operated at 200 kV. The graphitic structures of GO and rGO were characterised by an X-ray diffractometer (PANalytical Empyrean) and Raman spectroscope (stellar-Pro ML150 laser, Renishaw 633 nm HeNe laser and Leica DM 2500M microscope). The amount of deposited Pd nanoparticles (Pd loading) was determined using an inductively coupled plasma mass spectrometer (ICP-MS). Ni deposition was monitored by a quartz crystal microbalance (QCM, Seiko Eg&G QCM922A) with a SiO_2-coated Au resonator at a basic frequency of 8.9 MHz (Seiko Eg&G QA-A9M SIO2-S). The sheet resistances of polyimide substrate with/without rGO coating is measured by four-point probe tester.

Chemicals:

Graphene oxide (GO) solution (dispersion in water, 2 mg/ml), sodium hypophosphite monohydrate ($NaH_2PO_2{\cdot}H_2O$), palladium(II) chloride ($PdCl_2$), sodium citrate dehydrate ($HOC(COONa)(CH_2COONa)_2 \cdot 2H_2O$), boric acid ($H_3BO_3$) nickel(II) sulphate hexahydrate ($NiSO4_2 \cdot 6H_2O$) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich. The GO solution was diluted to 0.2 mg/ml with deionised (DI) water.

Reduced graphene oxide (rGO) pre-treatment:

A SiO_2-coated AT-cut quartz crystal substrate was washed with ethanol and left to dry in air. The washed and dried substrate was dipped into the diluted GO solution (0.2 mg/ml) for 1 min. The substrate was then air-blown and dried to remove the excess solution adhered to it. It was then dipped into a NaH_2PO_2 solution (0.2 M) for 1 min, resulting in the reduction of GO to rGO. The above-mentioned sequence was repeated five times.

Pd catalyst loading on a QCM substrate:

The rGO-coated substrate was dipped into $PdCl_2$ (1.5 mM or 30 μM with 1% HCl) for 10 s followed by dipping into NaH_2PO_2 (0.2 M), in sequence, for 10 s. The substrate was air-blown after every step. The stepwise Pd catalyst loading process was repeated twice; then the substrate was washed with DI water and dried by air blow.

In situ measurement of Ni deposition by QCM:

The rGO-coated and Pd-nanoparticle-deposited QCM substrate was assembled with Dip Cell (Seiko Eg&G QA-CL3) before electroless Ni deposition. The assembled unit was immersed in NaH_2PO_2 for 7 mins to maintain the activity of the Pd nanoparticles under aqueous conditions before testing. The Ni bath solution for electroless Ni deposition contained 0.2 M sodium citrate, 0.5 M boric acid, 15 g/L Nickel (II) sulphate hexahydrate and 25 g/L sodium hypophosphite monohydrate. The pH of the Ni bath solution was adjusted to 9.0 by NaOH. During the QCM measurement, the assembled Dip Cell with quartz substrate was immersed in the Ni bath solution to detect the frequency change during electroless deposition, and the temperature of the Ni bath solution was maintained at 60 °C. In addition, as blank sample, a quartz substrate was treated by 2 cycles of Pd (in 30 μM $PdCl_2$ solution) then dipped into the bath solution whose composition, pH and temperature were the same as those of the Ni bath solution except that Nickel (II) sulphate hexahydrate was not contained.

We used QCM to measure the amount of Ni deposited during the Ni electroless deposition [1-3]. The deposition of Ni changes the mass of the substrate, which is detected by calculating the decrease in the frequency of the quartz by the QCM using the Sauerbrey equation [4].The mass activity is expressed as the mass of Ni deposited, m_{Ni}, normalised by the loading of Pd nanoparticles, m_{Pd} [5], using the following equation:

$$Mass\ Activity = \frac{m_{Ni}}{m_{Pd}}.$$

The Pd loading, or m_{Pd}, was measured by ICP-MS.

Characterisation of the rGO reduced by NaH_2PO_2:

Since rGO deposited on quartz substrate is not thick enough for XRD and Raman spectroscopy, the reduction of GO by NaH_2PO_2, GO (2 mg/ml) and NaH_2PO_2(0.2 M) was tested after mixing with a ratio 1:9 to obtain a sufficient amount of rGO mixture in solution. The mixture gel was separated from water by centrifugation and fillteration. Subsequently, the mixtrue was dried in a drybox for XRD and Raman spectroscopy in order to characterise the graphitic structure. The same amount of GO (2 mg/mL) was also dipped on glass slices and put in a drybox to obtain GO powder.

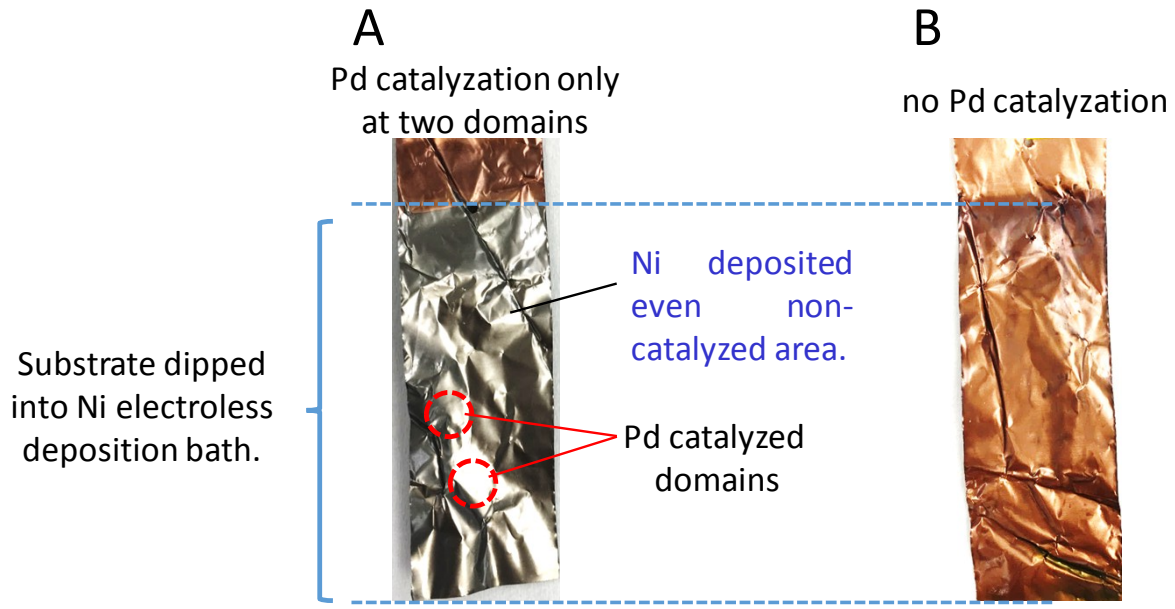

Figure S1: On conductive substrate, electroless deposition takes place widely everywhere, regardless of the Pd-catalysed position. For (A), only two domains (indicated by red dot circles) on copper foil were Pd-catalysed. Then, the copper foil was dipped into the electroless deposition bath (see the experimental section). Since the copper foil is conductive, electroless deposition occurred not only at the Pd-catalysed domains but everywhere on the foil (see Figure 1A as well). Note that the electroless deposition did not occur blank substrate without Pd catalyzation as in (B). Since the Ni redox potential is lower than Cu, Ni does not deposit on Cu substrate via galvanic displacement deposition. In addition, as is well-known, since Cu does not catalyse the oxidation of NaH_2PO_2, the reducing agent used in the deposition bath, Ni electroless deposition does not occur on Cu substrate by NaH_2PO_2 [6].

Movie S1: rGO treatment enables sufficient Ni electroless deposition on a polyimide substrate, even with extremely low Pd loading. The right sample, 3.2ppm Pd with rGO (see Table 1), was well coated with Ni while much less Ni deposited on the left sample, 3.2ppm Pd (no rGO). The playback speed is x128.

References

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