A versatile approach for decorating 2D nanomaterials with Pd or Pt nanoparticles

Xianjue Chen, a Wenzhe Zang, b Kasturi Vimalanathan, a K. Swaminathan Iyer a and Colin L. Raston a,*

aCentre for Strategic Nano-Fabrication, School of Chemistry and Biochemistry, The University of Western Australia, Crawley, WA 6009, Australia Fax: 61 8 6488 8683; Tel: 61 8 6488 3045; E-mail: colin.raston@uwa.edu.au

bState Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing, 210093, P. R. China.

S1 Method summary

Graphite flakes were used as received from Alfa Aesar with averagely 7-10 µm in diameter. Hexagonal boron nitride flakes 2-3 µm in diameter were used as received from Sigma Aldrich. Aqueous suspensions of graphene and h-BN were prepared using our recently reported procedure.1 The as-synthesized graphene and h-BN dispersions were washed 4 times using high-speed centrifugation (Centrifuge 5418, Eppendorf). For each centrifugation, 1 mL of Milli-Q water was added to a 1.5 mL vial and centrifuged for 30 min at ~16800 × g. The supernatants of the resulting products were removed and then Milli-Q water was added for the next round of processing. Gentle bath sonication (Ultrasonic cleaner, Unisonics) was applied to re-disperse the slurry. Aqueous solutions of H2PdCl4 and H2PtCl6 with concentrations of 0.5 mM were used directly. The mixture was centrifuged twice at high-speed (30 min, ~16800 × g) to remove free standing Pd(II) and Pt(IV) species in solution. The slurry was re-dispersed in 1 mL of water and used for hydrogen gas reduction. After 20 minutes bubbling, the solution was collected and the product washed twice with water, coupled with centrifugation (30 min, ~16800 × g). The final product was used directly for characterization. The samples were dropped onto 200 mesh holey carbon copper grids for TEM characterizations. A JEOL 2100 LaB6 TEM equipped with a Gatan Orius charged-coupled device camera operating at 120 kV was used for TEM (Figure S2, S3 and S4 in ESI), SAED and EFTEM data acquisition. JEOL 3000F FEGTEM was used for obtaining TEM (Figure 2 and 3) and HRTEM data. Image J software was used for processing all the TEM images.
S2 Selected area electron diffraction (SAED) pattern of Pd decorated graphene

Figure S2 shows the SAED pattern from a selected area of the Pd decorated graphene sheet. Figure S2a gives an individual graphene sheet with a uniform decoration of Pd nanoparticles. The area for obtaining the SAED pattern is shown in Figure S2b with a selected aperture. Figure S2c gives a typical SAED pattern for multi-layer graphene sheets with expected six-fold symmetry. The intensity of the \{1100\} peaks is lower than that of the \{2110\} peaks, which indicates that this sheet is few-layer.

Figure S2. (a) TEM image of a Pd nanoparticles decorated graphene sheet. (b) The selected area for obtaining electron diffraction pattern. (c) SAED pattern from the indicated area.
S3 Energy-filtered transmission electron microscopy (EFTEM) analysis of the Pd decorated BN sheets

In order to identify the presence of $h$-BN, EFTEM analysis was carried out on the Pd decorated $h$-BN sheets, as shown in Figure S3a. A well decoration of Pd nanoparticles can be observed on the $h$-BN surfaces. Elemental mappings of boron and nitrogen from the area indicated in Figure S3a reveal the presence of both of the elements (Figure S3b and S3c), which confirm the 2D materials are $h$-BN sheets.

Figure S3. (a) TEM image of a Pd nanoparticles decorated BN sheet. (b) Boron and (c) Nitrogen maps obtained from the same area.
Pt decorations with higher concentrations

As a set of control experiments, higher starting concentrations (10mM, 50mM) of Pt(IV) were used for the decoration of Pt on h-BN sheets. The results (Figure S4) show a different morphology of the formed Pd particles. Instead of growing on the surfaces of h-BN sheets as individual small nanoparticles when the starting concentration was relatively low (< 0.5 mM), the Pt metal nanoparticles tend to agglomerate, as shown in Figure S4b. Most of the Pt clusters are not longer attached to the surface of h-BN sheets.

Figure S4. TEM images of Pt nanoparticles decoration on BN sheets with the starting concentrations of (a, b) 10 mM and (c, d) 50 mM.