Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Self-assembled calixarene aligned patterning of noble metal nanoparticles on graphene

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Methods Summary

Materials

Pristine graphite flakes (043480, 7-10 μm, 99%) from Alfa Aesar was used as received. *p*-Phosphonic acid calix[8]arene was synthesized following the literature method.[1] Aqueous suspensions of graphene were prepared using our reported procedure.[2] The as-synthesized graphene dispersion was washed 5 times using high-speed centrifugation (Centrifuge 5418, Eppendorf). For each washing, 1 mL Milli-Q water was made up in the 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 washing. Gentle bath sonication (Ultrasonic cleaner, Unisonics) was applied to re-disperse the slurry. Noble metal precursors of hydrated ruthenium(III) chloride ($RuCl_3$) and chloroplatinic acid (H_2PtCl_6) at 0.5 mM were used directly. The mixture was centrifuged twice (30 min, ~16800 × *g*) to remove freestanding solvates Ru(III) and Pt(IV) species in solutions. The slurry was re-dispersed in 1 mL of Milli-Q water and used for reduction using hydrogen gas. After 20 minutes bubbling, the products were washed twice with water, coupled with centrifugation (30 min, ~16800 × *g*). The final products were used directly for characterizations. For dispersing *p*-phosphonic acid calix[8]arene in chloroform, a 500 mL stock solution with a concentration of 2×10^{-3} mg/mL was prepared, followed by serial dilution to targeted concentrations.

Characterizations

The aqueous suspension of NMNPs/graphene nano-hybrids were dropped cast onto 200 mesh holey carbon copper grids followed by evaporation in air for TEM characterization. JEOL 3000F FEGTEM was used for obtaining TEM and HRTEM data. Image J was used for processing all the TEM images.

AFM images were acquired in air using a Bruker Dimension FastScan AFM with Nanoscope V controller, operating in PeakForce Tapping mode. *p*-Phosphonic acid calix[8]arene in chloroform at 2×10^{-3} mg/mL, 2×10^{-4} mg/mL, and 2×10^{-4} mg/mL were drop-cast onto freshly cleaved HOPG and dried in air prior to AFM analysis. Bruker ScanAsyst Air probes with a nominal tip radius of 2 nm and nominal spring constant of 0.4 N/m were used. Imaging parameters including set-point, scan rate (1-2 Hz) and feedback gains were adjusted to optimize image quality and minimize imaging force. Images were analysed using the Bruker Nanoscope Analysis software (version 1.4). The AFM scanner was calibrated in the x, y and z directions using silicon calibration grids (Bruker model numbers PG: 1 µm pitch, 110 nm depth and VGRP: 10 µm pitch, 180 nm depth).

p-Phosphonic acid calix[8]arene nanofiber on HOPG

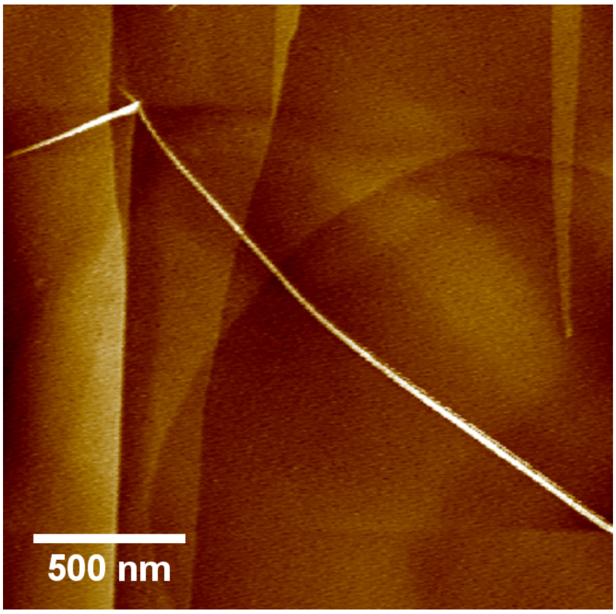

Figure S1. AFM image of self-assembled *p*-phosphonic acid calix[8]arene nanofiber on HOPG at a higher concentration of 2×10^{-3} mg/mL in chloroform.

Reference

(1) T. E. Clark, M. Makha, A. N. Sobolev, D. Su, H. Rohrs, M. L. Gross, J. L. Atwood and C. L. Raston, *New J. Chem.*, 2008, **32**, 1478-1483.

(2) X. Chen, R. A. Boulos, P. K. Eggers and C. L. Raston, *Chem. Commun.*, 2012, **48**, 11407-11409.