

Synthesis of hierarchically porous inorganic–metal site-isolated nanocomposites

Haifei Zhang^{*}, Irshad Hussain, Mathias Brust, and Andrew I Cooper

Donnan and Robert Robinson Laboratories, Department of Chemistry, University of
Liverpool, Crown Street, Liverpool L69 3BX, UK.

* To whom correspondence should be addressed. E-mail: zhanghf@liv.ac.uk
Tel: 0044 151 7943484. Fax: 0044 151 7943588

Supplementary Information

To the Editor of *Chemical Communications*,

19 April 2006

Materials Preparation:

General Method: The crosslinked polyacrylamide (PAM) beads were prepared using oil-in-water-in-oil (O/W/O) sedimentation polymerization (ref. 10). These PAM were then soaked in concentrated gold nanoparticle solutions for one week (sodium acrylate stabilized (ref. 5); average particle diameter 15 nm). The excess (substantially decolourised) aqueous phase was then decanted from the beads. The red composite beads were then soaked in a pre-prepared silica sol or alumina sol overnight to produce PAM/GNPs/inorganic composite beads. The individual preparations are detailed below.

GNP–PAM–silica beads: (1) **Preparation of silica sol:** Tetraethyl orthosilicate (98%, 33.75 cm³), distilled water (10.50 cm³) and 0.9 N HCl solution (0.15 cm³) were mixed and sonicated in an ice-water bath to form a homogeneous solution and then stored at –20 °C for at least two weeks before use. (2) **Preparation of the composite beads:** The GNP–PAM beads were immersed in the silica sol and then stored overnight at –20 °C because the silica sol was found to gel rapidly at room temperature. The soaked beads were filtered using a funnel (no filter paper was required since the beads are large, ~2 mm). The beads were then placed on tissue paper and dried in air at room temperature overnight, after which the sample was transferred into an oven at 70 °C (24 h) and 120 °C (24 h).. Any residual solvent was then removed under vacuum at the same temperature (12 h).

GNP/PAM/alumina beads: (1) **Preparation of aluminium sol:** Acetone (6.0 cm³) was added into a 50 ml flask and then aluminium tri-*sec*-butoxide (15 cm³, 97%) was added while stirring. Stirring was continued for 30 minutes with the flask sealed from the air. (2) **Preparation of the composite beads:** The wet GNP–PAM beads were washed using isopropanol and allowed to dry in air. These composite beads were then immersed in the aluminum sol which was kept in a fume cupboard at room temperature overnight. The soaked beads were filtered using a funnel and washed with acetone six times. The beads were then placed on tissue paper and dried in air at room temperature overnight, after which the sample was transferred into an oven at 70 °C (24 h) and 120 °C (24 h).. Any residual solvent was then removed under vacuum at the same temperature (12 h).

Calcination process: The composite beads were calcined in air using a Carbolite ashing furnace. The temperature was ramped from room temperature to 520 °C at 0.5 °C/min, held at this temperature for 4 h, and then cooled to room temperature at 1 °C/min.

Characterization: (1) Nitrogen sorption isotherms were measured using the volumetric method with a Micromeritics ASAP 2010 analyser at –196 °C. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. Pore size distributions were calculated from the adsorption branch of the isotherm using the Barrett, Joyner, and Halenda (BJH) method. (2) GNP–silica bead morphology was characterized using a Hitachi S-2460N SEM (low magnification) and a Zeiss Gemini Supra 55VP (high magnification). For GNP/silica beads, the morphology and elemental analysis were carried out using a Hitach S4800 Field Emission SEM with an Oxford Inca EDX analyzer.

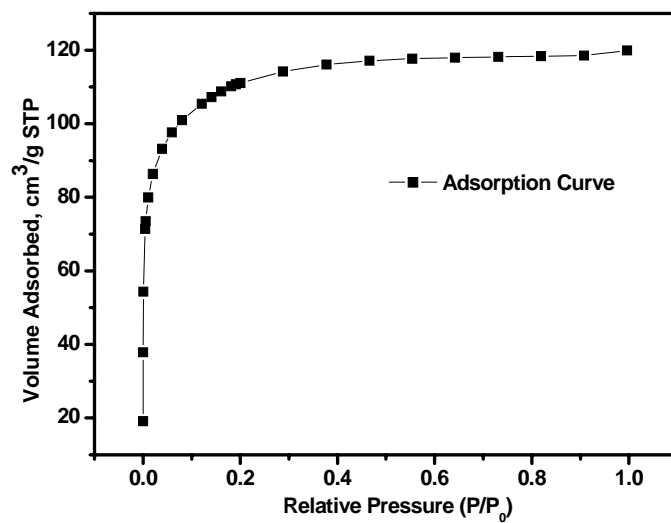


Figure S1. N₂ adsorption isotherm at 77 K for the hierarchically-porous GNP-silica beads.

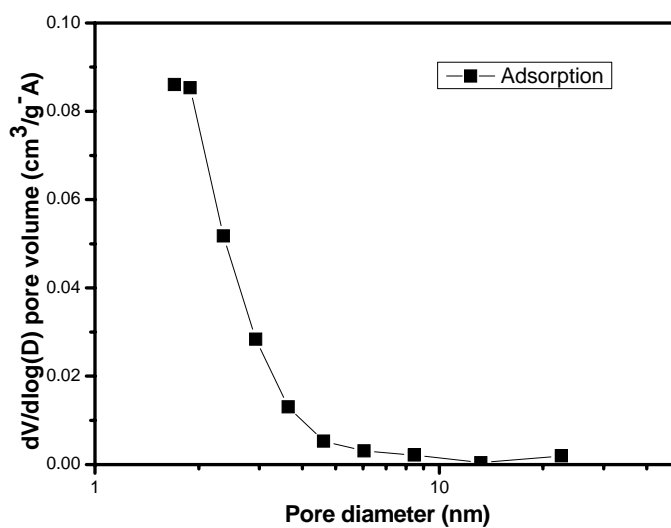


Figure S2. Pore size distribution for GNP-silica beads, as calculated from the N₂ adsorption data using the Barrett, Joyner, and Halenda (BJH) method.

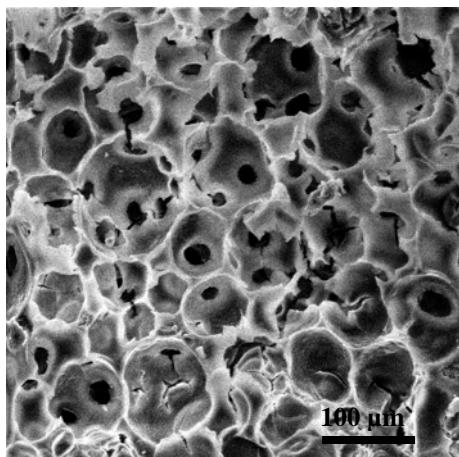


Figure S3. SEM image shows the interconnected macropore structure of the GNP–alumina beads (scale bar = 100 μm).

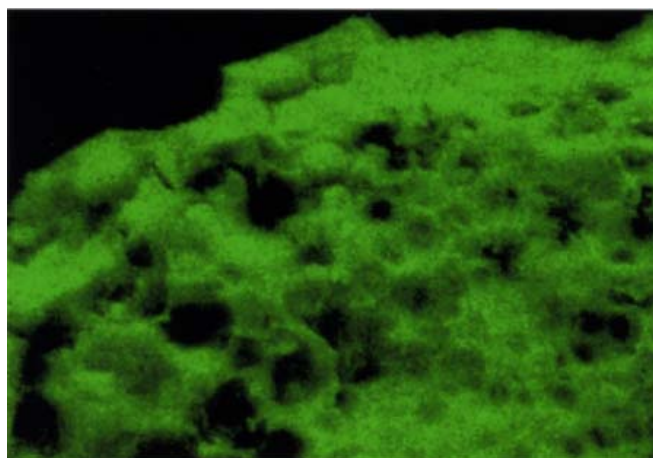


Figure S4. Aluminium mapping for one quarter of the GNP-alumina bead shown in Figure 3a, recorded using an Oxford Inca EDX analyzer.