# Organic-Inorganic Hybrid Materials: Nanoparticle Containing Organogels with Myriad Applications †Electronic Supplementary Information

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### **1** Synthetic procedures

Reagents were used as supplied, without further purification. UV-Visible spectroscopy was performed with a Perkin-Elmer Lamda-25 instrument. Emission spectra were collected on a Varian Carey Eclipse Fluorescence Spectrophotometer. <sup>1</sup>H NMR spectra were collected at 600 MHz on a Brucker AV600 Avance III spectrometer, fitted with cryoprobe.

TEM samples were prepared by dropping a small amount of gel cut with a scalpel onto carbon-coated copper or gold grids (Agar Scientific) and drying in air. TEM micrographs were collected using a Jeol 2100 microscope, fitted with a Gatan Orius digital camera at a beam acceleration of 200 kV. EDX was collected with Oxford Instruments UTW EDX running Aztec software. Energy filtered TEM measurements were collected using a Philips CM200 FEG TEM with an ISIS EDX system and Gatan Imaging filter for EELS. Images processing was performed with Gatan DigitalMicrograph.

SEM micrographs were collected on a field emission Jeol 6700F FEG SEM operating at 5 kV and environmental Hitatchi S-3400N SEM operating at 10 kV.

SQUID measurements were performed by pipetting a fixed amount  $(5 \ \mu L)$  of the molten gel into a measurement tube. Magnetisation data was taken using a Quantum Design MPMS superconducting quantum interference device VSM Magnetometer (San Diego, USA) at 300 K using a field range of  $\pm 7$  T.

#### 1.1 Synthesis of 1

LMWO **1** was synthesised using the procedure described in<sup>1</sup>, however the product was used crude, without further purification. Yield was 81.7% <sup>1</sup>H NMR (600 MHz CDCl<sub>3</sub>)  $\delta_H$  4.19 (dd, 2H, J = 6.4, 14.0 Hz), 4.11 (m, 2H), 3.96 (dd, 2H, J = 5.6, 8.6 Hz), 3.74 (d, 2H, J = 6.8 Hz), 1.65-1.50 (m, 20H).

#### **1.2** Synthesis of Nanoparticles

Au nanoparticles were synthesised via a Brüst chemical reduction in toluene in the presence of NaBH<sub>4</sub> and TOAB. Fe<sub>3</sub>O<sub>4</sub> and CoO nanoparticles were synthesised by decomposition of the metal oleate in oleic acid and 1-octadecene (ODE). Ni nanoparticles were synthesised from decomposition of Ni(II)acac in oleylamine and trioctyl phosphine (TOP). All procedures are as described in Crick *et al.*<sup>2</sup>. DDT was added to the surface of the gold colloid by stirring the TOAB stabilised particles with excess DDT at room temperature for 24 hours and then washing via precipitation. TOP/TOPO capped CdSe/ZnS Quantum Dots were synthesised from a modified procedure of Bear *et al.*<sup>3</sup> using a longer reaction time to produce red/orange QDs with an emission of  $\lambda = 605$  nm.

Pyrene modified MWCNTs were produced as described, by mixing MWC-NTs with a oleyl-functionalised pyrene.<sup>4</sup>.

### 1.3 Standard procedure for gelling nanoparticles

All nanoparticles were precipitated as part of the normal washing procedure and then suspended in 1-octadecene (ODE) at various strengths, ranging from highly dilute to neat strength concentrations. To produce a 3 wt% nanoparticle gel, a solution of the nanoparticles in ODE (1 ml) was added to gelator **1** (30 mg) and warmed to 65 °C with a heat gun, or heater plate, until solution was complete. The heat was removed and the solution was allowed to cool to room temperature naturally, forming a gel that was tested by inversion.

### 1.4 Production of NPs *in-situ* with sputter coating

A portion of 4 wt% gel containing no nanoparticles, approximately 5 mm thick was placed on a metal stub in the chamber of a Quorum Q150R ES sputter coater with gold target. A 20 mA current was set, and the sample was sputtered under Argon atmosphere for 60 s. Initially the colouration of the sample was highly localised in three areas, but after 24 hours had diffused throughout the material. The process was repeated with a silver target.

## 2 Electron microscopy and analysis

## 2.1 SEM

SEM micrographs were obtained at reduced pressure with a Hitatchi Environmental SEM system, and under ultra-high vacuum with a Jeol Field Emission system. Both sets of images show a pore-like microstructure, which becomes more obvious on drying the sample in the high-vacuum.



Figure 1: SEM images of a 4 wt% gel (a) as synthesised *via* environmental SEM and (b) after solvent removal under vacuum, by field emission SEM.

### 2.2 Additional TEM

Fig. 2a-c show energy filtered TEM of the Ni NPs in a gel matrix showing that the processing into the gel incorporated no oxygen into the particles. Fig. 2d shows the irregular growth of TOAB stabilised AuNPs in the gel, leading to the changes in the absorption spectrum documented in the main paper. It is hypothesised that during gelling the particles are brought into close proximity and the charge stabilisation afforded by the TOAB is not enough to prevent them from coagulating. Whereas the DDT stabilised particles are better passivated.



Figure 2: (a) EFTEM of Ni NPs in gel matrix with zero loss (b) Ni Map TEM (c) O map TEM (d) TOAB-stabilised AuNPs in gel matrix (e) Ag NPs created by sputtering (f) Ni NP gel in glass vial.

## 2.3 EDX

EDX spectra were taken to verify the presence of nanoparticles in the gel. Most samples were on gold grids (containing a certain amount of copper), however all gold samples were analysed on copper grids.



Figure 3: EDX of DDT stabilised AuNP gel



Figure 4: EDX of CdSe/ZnS QD gel



Figure 5: EDX of  $\mathrm{Fe_2O_3}$  NP gel



Figure 6: EDX of Ni NP gel



Figure 7: EDX of CoO NP gel



Figure 8: EDX of AuNP gel from sputtering



Figure 9: EDX of AgNP gel from sputtering

## 3 Moulding

The gel could be moulded into a range of shapes via hot pouring after nanoparticle incorporation. These large objects maintained their shape for several weeks, and in the case of the MWCNT based gel (Fig. 10b), seemingly indefinitely, hinting that the CNTs may impart favourable mechanical properties to the material.



Figure 10: Selection of moulded gel shapes: (a) containing quantum dots under room lighting, (b) containing MWCNTs after 4 months of standing in room conditions and (c) a larger structure with no nanoparticles.

## 4 Nanoparticle Recovery

The recovery of nanoparticles from the gel was facile and an example is shown in Fig. 11. The gel-nanoparticle composite was placed in a centrifuge tube with a small amount of ethanol and a drop of chloroform and vortexed to cause complete decomposition of the gel and emulsification of the ODE into the ethanol. This mixture was then centrifuged at 4000 rpm for 5 minutes to precipitate the nanoparticles. The supernatant containing the ODE and **1** in ethanol was decanted, and the ethanol removed leaving pristine ODE gel. The residual nanoparticles could be taken up in more ODE or other non-polar solvents.



Figure 11: Recovery of nanoparticles from the gel: (a) The Ni NPs in a gel matrix were freed by adding (b) a mixture of ethanol and chloroform to decompose the gel. After centrifugation (c) the supernatant was decanted to leave solid NPs in the tube and an ethanolic solution of the gel. (d) On removal of the ethanol the pristine gel was reformed and the NPs could be taken up in hexane.

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