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Self-Assembled Envirogel – Selective extraction and *in-situ* Reduction of Precious Metal Salts from Waste gives Hybrid Gels with Embedded Electrocatalytic Nanoparticles**

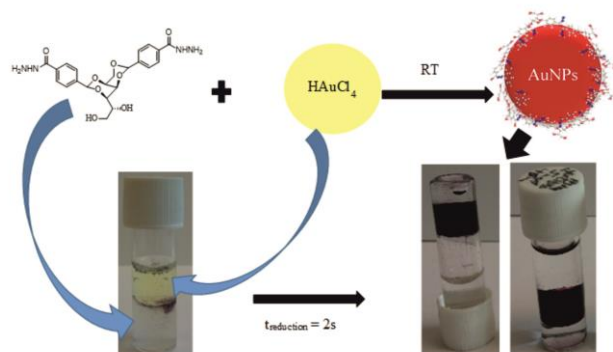
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Abstract: This paper reports a hydrogel based on 1,3:2,4-dibenzylidenesorbitol (DBS), modified with acyl hydrazides which extracts gold/silver salts from model industrial waste, with preferential uptake of precious heavy metals over other common metals. Reduction of gold/silver salts occurs spontaneously in the gel to yield metal nanoparticles located on the gel nanofibres. High nanoparticle loadings can be achieved, endowing an additional function – electrochemical activity. These hybrid gels exhibit higher conductances than gels doped with carbon nanotubes and can be used to modify electrode surfaces, enhancing electrocatalysis. Conductive soft materials have the potential to bridge the soft world of biology and the hard world of electronics. We reason this simple industrially and environmentally relevant approach to conducting materials – from waste to wealth – is of considerable significance.

Hydrogels are increasingly attracting attention for a wide range of high-value applications.^[1] In particular, low-molecular-weight hydrogels allow molecular-scale information to be programmed-in via simple organic synthesis and then amplified into nanofibres through self-assembly.^[2] Self-assembled gels combine a solid-like nanofibre matrix (typically <1%) with a solvent-like gel phase typically >99%). The high compatibility with water means these gels have great potential as environmental remediation agents, and a number of papers have reported their use as filtration media for water purification, with interest in systems in which ligands displayed on the gel nanofibres form specific interactions with the pollutants, enabling selective removal.^[3] We refer to such gels as ‘envirogels’ based on their application.

The combined hard/soft properties of hydrogels mean they have potential as interfacial materials between the soft world of biology

and the hard world of electronics and interest has been developing in using polymer hydrogels to achieve this.^[4] Supramolecular gels have been much less explored.^[5] Conductive gels can be approached in a number of different ways – including using a conductive liquid-like phase. Of strategies in which the solid-like network becomes conducting, the simplest approach is to mix known conductive materials into a gel, for example, single walled carbon nanotubes, graphene or conjugated polymers.^[6] In this approach, the gel only acts as a matrix in which conducting units are suspended – there is limited ability to organise them. A second approach is to assemble gels from conductive organic components which then provide conducting pathways.^[7] The final approach is to template the formation of conducting systems using the self-assembled nanofibres.^[8] This has the potential advantage of organising highly conducting materials on the nanoscale. Metal nanoparticles have been organised within gels^[9] and have the potential to conduct.^[8a,b] Of particular interest are systems which



work in water, and enable spontaneous *in situ* nanoparticle formation.^[10] We reasoned that an envirogel could selectively remove precious heavy metals from waste water, followed by *in situ* nanoparticle formation, and that this could be combined with the use of the resulting materials in electronics. Our success in fusing these concepts – from waste to wealth – is reported in this paper.

Fig. 1. Structure of DBS-CONHNH₂ and schematic of gold salt adsorption and *in-situ* reduction, along with representative photographs of the gels.

We selected our recently reported hydrogelator, DBS-CONHNH₂, for this application as it is based on the industrially-relevant 1,3:2,4-dibenzylidenesorbitol framework^[11] and forms pH-stable hydrogels via a simple heat-cool cycle (Fig. 1). We have already demonstrated the ability of this gel to bind dyes^[12] and pharmaceuticals.^[13] The sequestration of precious metal ions from

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water was initially demonstrated by testing uptake from aqueous solutions (10 mM, 2.0 mL) of gold (Au^{3+}) or silver (Ag^+) salts added on top of the gel (0.4% wt/vol) and allowed to diffuse in for 48 h under ambient conditions. Analysis of the supernatant by ICP-MS and/or UV spectroscopy was used monitor the loss of metal ions. The maximum uptake capacity of the envirogel was estimated to be as high as 2000 mg g^{-1} (metal/gelator) for Au and 900 mg g^{-1} for Ag – higher than many adsorbents reported in the literature and competitive with some of the best.^[14] The envirogel began to collapse at its maximum loading capacity ($>2000 \text{ mg g}^{-1}$) and this could be attributed to disruption of fibre-fibre interactions caused by the build-up of nanoparticles (NPs) on the nanofibre networks (see below). The gel changed colour to ruby red or yellow as Au^{3+} or Ag^+ diffused into it (Fig. 1) – characteristic of the nanoparticle forms of these metals capped with hydrazides,^[15] suggesting that the gel fibres can reduce and cap metal NPs *in situ* within the network. It is known that hydrazides can mediate metal-ion reduction,^[15] and as such this is a rare example of a gel in which metal NP formation occurs spontaneously, without any external reductant, simply nucleated by the nanofibres. The Au^{3+} ions changed colour within 2 s while Au^+ required about 30 min. This could be attributed to their reduction potentials – for Au^{3+} ($\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}^0$, 1.50 V vs SHE) and Ag^+ ($\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0$, 0.80 V vs SHE). Furthermore, the gel even responded to an ultra-trace ($< 5 \text{ nM}$) presence of Au^{3+} and Ag^+ in water, giving these gels potential as colorimetric sensors for Au^{3+} and Ag^+ ions in aqueous waste.

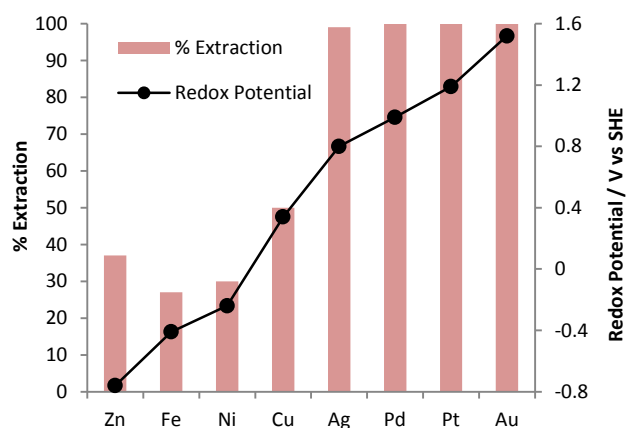


Fig. 2. Percentage metal ion recovery from mixed aqueous solutions by DBS-CONHNH₂ hydrogel (left axis) and redox potentials of the metals (right axis).

A key review explores green approaches for recovery and re-use of precious metals,^[16] and highlights the extraction of such metals from waste electronic and electrical equipment (WEEE) – in mobile phones, as much as 30% of total metal content is Au/Ag (other metals include Fe, Cu, Ni, Zn and Pb).^[17] There is also increasing interest in mining small-scale precious metal deposits using leaching rather than more traditional approaches,^[18] and extracting precious metals from non-traditional sources such as sewage sludge.^[19] We therefore decided to test the feasibility of using our gel as a low-energy, high selectivity leaching extraction method from mixtures containing Ni and Cu, metals which occur in nature alongside the platinum group elements and Zn and Fe, to test selectivity in recovery of critical metals over earth abundant elements. An aqueous solution containing Ni^{2+} , Cu^{2+} , Zn^{2+} , Fe^{2+} , Pt^{2+} , Pd^{2+} , Au^{3+} and Ag^+ (all chlorides, except AgNO_3 , all 100 mg l^{-1} , 5 mL, 1.64–3.94 μmol) as a model leaching solution was allowed to diffuse into

the envirogel (mass of gelator, 4 mg, 8.4 μmol) for about 48 h under ambient conditions (Fig. 2). Dilute HNO_3 (0.1 M) was added to the mixture of metal ions to ensure solubility of all the metals in water. The supernatant was analysed by ICP-MS for residual metals. The gel exhibited higher affinity towards precious metals, of value in environmental remediation. The metal ions best extracted were those with the highest reduction potentials (Fig. 2) – suggesting selectivity is a consequence of the ability of the hydrazide groups to reduce precious metals *in situ* (see further discussion below). Clearly Pd and Pt within gels could be of use in chemical catalysis, but this paper focusses on the precious metals Au and Ag. Obviously, it is important to test such systems on real waste, rather than model waste,^[16] but this was beyond the scope of our preliminary studies here and will be the focus of future work.

To gain insight into the NPs in the gel, we used UV-Vis, infrared (FT-IR) and X-ray photoelectron (XPS) spectroscopies. The composite hydrogel-AuNP or AgNP systems display strong absorption bands in the visible region at about $\lambda_{\text{max}} = \text{ca. } 525 \text{ nm}$ (AuNPs) or $\lambda_{\text{max}} = \text{ca. } 420 \text{ nm}$ (AgNPs), corresponding to the SPR bands of the metal nanoparticles. FT-IR spectroscopy indicated that the characteristic bands for C-N, C=O, N-H (bends), N-H and OH (stretches) at 1333, 1600, 1644, 3178 and 3315 cm^{-1} shifted by 9, 15, 46, 48 and 90 cm^{-1} respectively when Au^{3+} or Ag^+ ions were adsorbed. It can therefore be inferred that the metals interact directly with the envirogel nanofibres. In XPS experiments, in the presence of Au, the C1s and O1s peaks were shifted. Most significantly, however, the N1s peak was broadened – potentially indicative of strong interactions between N and Au, yielding a variety of environments. The Au4f peaks at binding energies (BEs) were 84 and 88 eV, corresponding to $4f_{7/2}$ and $4f_{5/2}$ of Au in the Au^0 oxidation state with a spin-orbit splitting (SOS) of 4 eV – no peaks corresponding to Au^{3+} were observed, supporting complete Au^0 nanoparticle formation. In the presence of Ag, there were also changes to C1s and O1s, in particular the O1s peak corresponding to C=O. There was a very significant change to N1s (but no broadening), supporting N-Ag interactions. The Ag3d peaks at BEs of 368.2 and 374.4 eV correspond to Ag^0 , suggesting reduction of Ag^+ to Ag^0 – no Ag^+ was observed.

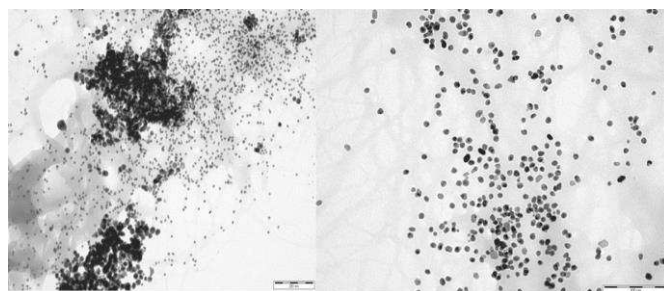


Fig. 3. Transmission electron microscopy (TEM) images of gold (left) and silver (right) nanoparticles as formed *in situ* within the DBS-CONHNH₂ hydrogel.

Transmission electron microscopy (TEM) was used to investigate the self-assembled fibrillar xerogel and hybrids in the presence of Au and Ag (Fig. 3). NP diameters were estimated as ca 5.0 and 10.0 nm for AuNPs and AgNPs respectively (see ESI). For Au, the nanoparticles were found mainly ($>90\%$) on the gel fibres rather than in solvent pockets within the gel-network. The imaging was done both on unstained and stained xerogels, to improve the contrast on the nanofibres, but some nanoparticles appeared to be washed-off after staining. For AgNPs, almost all ($>99\%$) were imaged on the nanofibrillar network. Nanoparticle organisation has been previously reported as a consequence of ligand-metal

interactions.^[9,20] We propose that localisation of NPs on nanofibres is a result of direct interactions between the hydrazide functionalized gel fibres and metal ions, leading to their reduction on the periphery of the nanofibres.

We determined the impact of NPs on gel thermal stability (T_{gel}) using simple reproducible tube-inversion methodology. An aqueous solution (50 μL) of Au^{3+} at a range of concentrations was added to a hot hydrosol of a fixed concentration (10 mM) of the gelator and cooled to room temperature – then the thermal stability was studied. There was no obvious change in the colour of the NPs on heating the gel-NP hybrid. Moreover, the T_{gel} increased from ca 65°C to 87°C on increasing the concentration of Au^{3+} (see ESI). Such an improvement has previously been reported by Bhattacharya and co-workers,^[21] and it was suggested that AuNPs may help crosslink the gel fibres. Clearly the nanofibres prevent uncontrolled aggregation of $\text{Au}(0)$ or $\text{Ag}(0)$ during spontaneous *in situ* reduction. We therefore further probed the stability of these hybrid materials to external influences using UV-Vis spectroscopy to monitor the NP SPR band. The ambient pH was adjusted between pH 2 and 12 with 0.1 M HCl and 0.1 M NaOH, but the SPR bands of the NPs in the hydrogel remained constant – suggesting a high degree of pH-tolerance of both parts of these hybrid material (gel fibres and metal NPs). The AuNPs and AgNPs also remained stable under ambient conditions over a period of 90 days.

We then wanted to study the electronic properties of these gels, reasoning that since the AuNPs form along the DBS gel fibres, our material would maintain NP stability and integrity during electrochemical applications. In their own right, supramolecular gels are relatively weak and difficult to handle/manipulate. To create a gel which could be incorporated into devices, we therefore mixed self-assembling DBS-CONHNH₂ with agarose polymer hydrogel to create a hybrid hydrogel (dual-network gel) – an effective strategy for making self-assembled gels more robust.^[22] A simple heat-cool cycle led to the formation of the hybrid hydrogel material – NP formation was wholly analogous to that observed in DBS-CONHNH₂ alone.

To probe the electronic performance of these hybrid materials, we initially measured their conductances. The hydrogels were made in a mould and extruded, providing hydrogels with reproducible dimensions. These gel blocks were suspended in solutions of Au^{3+} or Ag^+ and the process of metal ion incorporation and *in-situ* reduction into NPs occurred. We constructed graphite block electrodes glued to a glass slab and separated by a fixed distances, such that they could accommodate various gel block sizes ($\varnothing = 0.5$ cm - 1.0 cm). After careful calibration, a block of the gel was inserted into the space between the two graphite rods, and we hence determined the conductance of nanogel-AuNP, nanogel-AgNP, nanogel alone (negative control) and nanogel doped with single walled carbon nanotubes (SWNTs) (positive control). It is clear from Figure 4 that both nanoparticles and SWNTs enhance conductance. Given that TEM showed the Ag and AuNPs within DBS-CONHNH₂ gels to be 5-10 nm and located on gel fibres rather than in solvent pockets, we assume that they will not diffuse through the gel. Rather, we interpret the enhanced conductivity of gel-AuNPs as arising from a conductance mechanism similar to that in metalloproteins which contain electron-transfer chains of redox active iron-sulfur, heme or Cu centres between which electrons are envisaged to tunnel through the protein polymer matrix.^[23] As shown in Figure 4, the blocks of nanogel-nanoparticle composites were also air-dried for about 3 h until 30% of the water was lost via evaporation. Conductance increased significantly – more so for the systems incorporating nanoparticles than those with SWNTs.

Although there are many nanofibres in the wet hydrogel, they are highly solvated and therefore have relatively few contacts with one another, limiting conductivity. We propose that drying increases network connectivity, decreasing the distance between NPs and hence increasing conductance. This effect will be less important for SWNTs than for nanoparticles because SWNTs already have extended conduction pathways, whereas electron “hopping” mechanisms between metal sites are known to be highly dependent on separation distances.^[23]

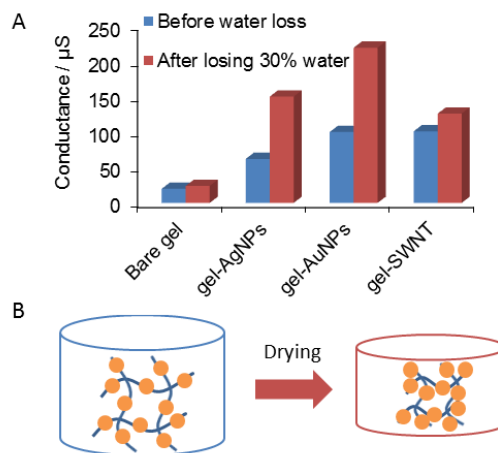


Fig. 4. A: Conductances of hybrid hydrogels incorporating AuNPs and AgNPs compared against native hybrid hydrogel and hybrid hydrogel incorporating SWNT – gel blocks were 0.80 cm in diameter. Data are illustrated for solvated hydrogels and hydrogels after removal of 30% of water by drying (diameter = 0.68 cm). B: Cartoon of effect of gel drying on close packing of gel morphology and embedded nanoparticles.

In addition to determining bulk conductance, we made a preliminary exploration of the potential of these materials for electrode modification. In fuel cell applications, carbon electrodes have been used as cathodes for O₂ reduction.^[24] However, such electrodes are poor O₂ reduction electrocatalysts, hence, deposition of nanoparticles has been used to activate the carbon.^[25] Even though electrochemical deposition and adsorption are commonly employed for depositing gold nanoparticles onto electrodes, limitations such as (i) formation of bulk gold and (ii) leaching of nanoparticles into electrolyte remain. We reasoned that our hybrid gels could effectively ‘wire’ NPs onto the electrode via their inherent nanofibrillar networks, whilst maintaining NP stability and integrity during use. Our gel networks transform planar carbon supports into porous, solvated 3D-structures of electrochemically-active surfaces, overcoming traditional issues with solvent access to nanostructured carbon. Reports of this approach to new technology are scarce except for some examples using polymer gels.^[26]

We generated our AuNPs hybrid nanogel as described above. To remove any traces of unreacted Au^{3+} , it was submerged into deionized water (200 ml) for 2 h and the water renewed until leaching was no longer observed. It is essential that free Au^{3+} ions are completely removed prior to electrocatalytic investigations, or they will diffuse into the electrolyte or become electroplated onto the electrode surface. No leaching of AuNPs was observed, which confirmed their trapping within the gel. The gel-catalysed O₂ reduction was investigated using cyclic voltammetry, scanning in air between -0.25 V and 0.15 V at 20 mV/s for 5 cycles. The bare carbon rod showed a typical non-Faradaic, capacitive current response (Fig. 5, red line). The electrode modified with just hybrid

hydrogel produced a differently shaped CV (Fig. 5, green line), with clear oxidative (positive) current at potentials more positive than +0.2 V vs SCE (equivalent to +0.42 V vs SHE). We attribute this oxidation to the hydrazide functionality since the observed CV is similar to that of native DBS gel.^[27] This helps explain the correlation between % metal uptake and redox potential (Fig. 2) – the gel can only reduce metal ions with a midpoint potential > +0.42 V vs SHE. When the hybrid hydrogel loaded with AuNPs was used on the electrode (Fig. 5, blue line) a large reductive current was observed at potentials more negative than -0.2 V vs SCE – this was attributed to Au-catalysed O₂ reduction. Therefore, the nanogel demonstrates that metal nanoparticles embedded in this gel can enable communication with a carbon electrode.

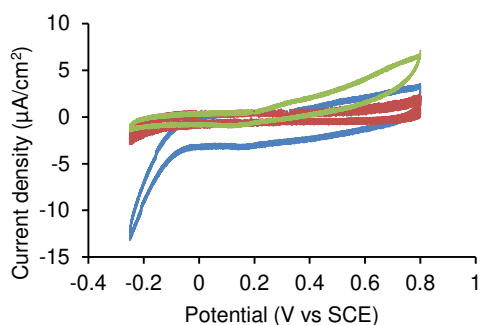


Fig. 5. Cyclic voltammetry of bare carbon rod electrode (red) and carbon rod electrodes modified with hybrid hydrogel both in the absence (green) and presence (blue) of AuNPs illustrating the relative currents associated with oxygen reduction.

We report a simple, pH stable hydrogel which can extract precious metal ions with a degree of selectivity from metal ion mixtures typical of leaching solutions. These ions can then be reduced *in situ* to form Au or Ag nanoparticles with a degree of organisation on the gel nanofibres. These hybrid materials are conductive as a result of the embedded nanoparticles, and can operate as modified electrodes – they hence have potential high value applications in nanoelectronics. Conductive nanostructured nanocomposites may be useful to bridge the soft matter world of biology and the hard matter world of electronics. In summary, we propose this system as a model envirogel demonstrating how we can simply, in one step, convert ‘waste to wealth’.

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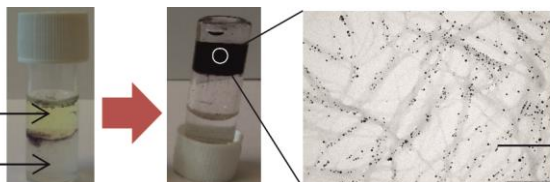
Entry for the Table of Contents

COMMUNICATION

Envirogel:

Au(III) or Ag(I)
+ Other Metals

Gel



Conductive
Gels

From Waste to Wealth – hydrazide-functionalised hydrogels are able to extract and reduce precious metal waste into nanoparticles, and hence generate conductive gel-phase materials with potential electronic applications

Babatunde O. Okesola, Sindhu K. Suravaram, Alison Parkin, David K. Smith*

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Self-Assembled Envirogel – Selective Extraction and *in-situ* Reduction of Precious Metal Salts from Waste gives Hybrid Soft Materials with Embedded Electrocatalytic Nanoparticles