COMMUNICATION

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI) FOR:
Gold nanoparticles immobilised in a superabsorbent hydrogel matrix: Facile synthesis and application for the catalytic reduction of toxic compounds

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Supplementary data are provided for:

- Experimental data for Chemicals, Nanoparticle synthesis and UV-Vis analysis.
- Images of various gold nanoparticle synthesised in hydrogels (Fig. S1)
- UV-Vis data for solution synthesised gold nanoparticles (Fig. S2)
- Images of gold nanoparticles formed in the hydrogel with varying volumes of 4 mM Au(III) and the subsequent solid-state UV-Vis data (Fig. S3)
- The catalytic rate of 2-NP reduction as a function of [BtH] concentration (Fig. S4).
- UV-Vis data of AuNP hydrogel catalysis vs. attempted catalysis in the absence of AuNPs. Also shown is the colloidal AuNPs catalysis vs. AuNP hydrogel catalysis in 0.1 M KCl (Fig. S5)
- Visual and UV-Vis demonstration of the recycling of AuNP hydrogels, using methylene blue (Fig. S6 & S7)
- UV-Vis data of colloidal AuNPs of various concentrations. Where AuNP hydrogels soaked in ultrapure water has also been compared to determine any potential leaching of the AuNPs from the hydrogel to the solution (Fig S8)

Experimental data for the chemicals:
All reagent were used without further purification. The chemicals were as follows; Sodium tetrachloroaurate hydrate, (98%, Acros Organics), 4-Nitrophenol (≥99%, Sigma Aldrich), 2-Nitrophenol (98% Sigma Aldrich), methylene blue (for microbiology, Sigma Aldrich), congo red (≥ 35%, Sigma Aldrich), Sodium borohydride solution (12 wt% in 14 M NaOH, Sigma Aldrich), Sodium citrate tribasic dihydrate (ACS ≥99%, Sigma Aldrich), commercial sodium polyacrylate spheres and cubes (Sungpunet, China). Hydrochloric acid (~37%, Fischer Scientific) and nitric acid (70%, Fischer Scientific).

Experimental for AuNP nanoparticle synthesis using citrate: Colloidal gold nanoparticles were synthesized by reduction using citrate: a solution containing both sodium citrate (5 mM) and NaAuCl₄ (1 mM) was either heated to boiling for ~30 minutes, or was allowed to sit at room temperature for 24 hours. No significant difference was observed between performing this in the dark or exposed to light (e.g. on the windowsill). Subsequent nanoparticle formation was confirmed using UV-Vis.

Gold nanoparticle synthesis from citrate in the presence of sodium polyacrylate hydrogels were unsuccessful (i.e. colloid formed outside of hydrogel) unless the volume of aqueous solution added was at or below the saturation limit for the dried hydrogel; this saturation limit was dependent upon the hydrogel used and strongly dependent upon the concentrations employed.

Experimental for AuNP nanoparticle synthesis in the absence of citrate: A typical synthesis of AuNP embedded throughout sodium polyacrylate hydrogels involved soaking dried sodium polyacrylate shapes (either commercially bought or made in-lab) in 4 mM sodium tetrachloroaurate solution for 1 hour. The solution was then heated to boiling for ~30
minutes, until the gel colour changed from yellow to burgundy and the aqueous solution was completely discoloured, indicating formation of gold nanoparticles inside the gel and exhaustion of the available Au.

**Experimental for the catalytic reduction or destruction of organic molecules:**
Reactions were monitored using UV-Vis spectroscopy (PerkinElmer LAMBDA 465 UV-Vis Spectrophotometer with UV Lab software, UK) inside 10 mm pathlength quartz cuvettes, with the sphere sitting below the light path. Spectra were recorded between 200-800 nm; scans were recorded every 1 minute for between 30 to 60 minutes.

A typical procedure involved an AuNP-loaded hydrogel sphere was placed into a cuvette filled with aqueous solutions containing nitrophenol (100 μM), methylene blue (50 μM) or congo red (10 μM). To this NaBH₄ was added in excess, in a 1:1000 ratio for nitrophenol and congo red, and 1:100 for methylene blue.

**Experimental for UV-Vis analysis of AuNP-loaded polyacrylate gels:**
UV-Vis spectroscopy was performed using a home-built microscopy setup incorporating a Princeton Instruments isoflate spectrometer fibre-coupled to the collection optics. The nanoparticle containing spheres were placed in a quartz cuvette and gently manipulated to ensure they were not touching the faces of the cuvette. The samples were then illuminated with plane-polarized white light, with the transmitted light collected using a Mitutoyo 50X MPlan lens. Spectra were taken through the centre of each sphere, with back-reflection alignment used to ensure the beam was normal to all reflective surfaces. In addition, reference spectra through the cuvette alone and background spectra were also taken to allow the calculation of transmittance. Absorbance was calculated by -log₁₀(T).

**Experimental data for cryoTEM analysis:**
Cryo-Transmission Electron Microscopy (cryoTEM) of AuNP-loaded hydrogels were achieved by thinning, adhering to lacy carbon grids (Ted Pella) and plunge-frozen into liquid ethane with a Leica GP (Leica Microsystems). Thin, peripheral areas of the hydrogels were imaged on a Talos Arctica (ThermoFisher) fitted with a 4k x 4K Falcon 3EC camera with a binning of 1 in linear mode under the control of Talos Imaging and Analysis software (ThermoFisher). Gold nanoparticle size distribution was analysed in ImageJ. A total number of 568 gold nanoparticles were imaged. An average diameter of 18.0 nm was observed with a standard deviation of 8.6 and a median diameter of 15.7 nm.

**Sample preparation for ICP-AES analysis:**
Several AuNP hydrogels were synthesised from the procedure stated above, using 3.33 mL of 4 mM NaAuCl₄ per hydrogel. The AuNP-loaded hydrogel was then washed briefly with ultrapure water, and left in 10 mL of ultrapure water for ca. 72 hours. From this solution, 0.5 mL was taken, placed in a narrow sample vial and dried in an oven at 80°C overnight; to this sample vial was then added 0.75 mL of freshly prepared *aqua regia* (4:1 v/v basis using concentrated (37%) HCl and concentrated (70%) HNO₃, respectively). This was left loosely sealed overnight to fully digest any Au(0) present, and then diluted with 15 mL of ultrapure water in order to yield an aqueous sample suitable for ICP-AES analysis.

From this study, ICP-AES confirmed that 3% of the added Au(III) leached out from the AuNP-loaded hydrogel upon extended soaking in ultrapure water. However, AuNP are characterised by a strong and distinctive Plasmon resonance band. UV-Vis analysis of colloidal AuNP (as shown by Fig. S7) vs the leachate solution after 10 days soaking demonstrated that if any AuNP did leach then their level was below the limit of detection (AuNP equivalent to 10 μM Au(III)). Therefore the Au(III) quantified is attributed to un-reduced starting material.

The same experiment was attempted with AuNP-loaded hydrogels, where they were prepared, dried, and then soaked in various volumes of *aqua regia*; all samples were successfully able to decolourise the hydrogels while leaving the actual spherical hydrogel intact, demonstrating AuNP oxidation. However, severe matrix effects were also observed for these samples when subjected to ICP-AES analysis, such that recovered values of Au(III) were between 50% and 150% of the expected values.

It is notable that in the presence of [BH₄]⁻, the leached Au(III) could form AuNP in solution *in situ*; however, these would be uncapped and unstable. Furthermore, the use of citrate-capped AuNP displayed the expected homogeneous catalysis results (N.B. hydrogel samples didn’t). Additionally, even citrate-capped demonstrated zero homogeneous activity in the high ionic strength KCl solutions investigated, whereas the hydrogel samples retained apparent heterogeneous activity in these high ionic strength systems, further reinforcing the observed results that the AuNP are completely immobilised inside the hydrogel, but still accessible from solution, whereas any leached Au(III) were unable to form a stable and catalytically active colloid, given the absence of capping agents.

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Fig. S1 displays;
(a) An aqueous colloid of AuNP formed by mixing 0.5 mM NaAuCl₄ and 5 mM NaCit and leaving to react at room temperature for 24 hours. After, dried commercial cubes of sodium polyacrylate hydrogel were added; these swelled significantly, absorbing water from the AuNP colloid, but zero penetration of the AuNP into the hydrogel was observed
(b) A cube of sodium polyacrylate hydrogel, after being loaded with AuNP by adding 0.5 mM NaAuCl₄ and 5 mM NaCit such that all of the solution was adsorbed by the dry hydrogel, such that no distinct aqueous phase was left. This was left at 24 hours at room temperature, to leave the swollen hydrogel with AuNP distributed throughout.
(c) Cubes of sodium polyacrylate hydrogel, after being loaded with AuNP as described above, and then transferred to pure water; the AuNP were not observed to leach out of the hydrogel, despite the hydrogel swelling significantly in the pure water. The pink tinge to the water is due to the light diffracting through the water and cubes.
(d) Photos of sample vials after being placed in an oven at 70°C for 24 hours, into which has been added a ca. ~16 mg dry commercial sodium polyacrylate hydrogel sphere and an aqueous solution of 4 mM NaAuCl₄ (NB: no NaCit employed here). In the foreground, 2 mL of solution was added; the sphere swelled extensively, all Au(III) partitioned into the hydrogel, and was reduced at the elevated temperatures to form AuNP throughout the hydrogel. In the background, 15 mL of solution was added; extensive quantities of Au(III) partitioned in the sphere, although not to saturation. Elevated temperatures (ca. 100°C) were required to initiate nucleation in these more concentrated systems. In general, volumes of 10 mL per sphere or less were employed (for 4 mM solutions), as above this volume Au(III) extraction was not quantitative, and the structure of the gel began to be compromised, with cracks appearing
(e) Comparison of the AuNP formed inside a commercial sodium polyacrylate hydrogel sphere (right) and a cylinder of in-lab produced sodium polyacrylate hydrogel (left); this also demonstrates the range of sizes, shapes and scalability available using this method.