#### Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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

Hassan A.H. Alzahrani,<sup>a†</sup> Mark A. Buckingham, <sup>a†</sup> William Wardley,<sup>b</sup> Richard D. Tilley,<sup>c</sup> N. Ariotti,<sup>d</sup> and Leigh Aldous<sup>a\*</sup>

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 [BH<sub>4</sub>]<sup>-</sup> 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**)

<sup>a.</sup> Department of Chemistry, Britannia House, King's College London, London, SE1 1DB, UK.

\* Corresponding author: <a href="mailto:ligh.aldous@kcl.ac.uk">ligh.aldous@kcl.ac.uk</a>

### Experimental data for the chemicals:

All reagents were used without further purification. The chemicals were as follows; Sodium tetrachloroaurate hydrate, (98%, Acros Organics), 4-Nitrophenol ( $\geq$ 99%, Sigma Aldrich), 2-Nitrophenol (98% Sigma Aldrch), methylene blue (for microbiology, Sigma Aldrich), congo red ( $\geq$  35%, Sigma Aldrich), Sodium borohydride solution (12 wt% in 14 M NaOH, Sigma Aldrich), Sodium citrate tribasic dihydrate (ACS  $\geq$ 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 NaAu(Cl)<sub>4</sub> (1 mM) was either heated to boiling for  $\sim$  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 windowseal). 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  $\sim$  30 minutes, until the gel colour changed from yellow to burgundy and the aqueous solution was completely discoloured,

<sup>&</sup>lt;sup>b.</sup> Department of Physics, King's College London, London, UK.

<sup>&</sup>lt;sup>c-</sup> School of Chemistry, Australian Centre for NanoMedicine and Electron Microscope Unit, Mark Wainwright Analytical Centre, MWAC - University of New South Wales, Sydney, NSW 2052, Australia

 <sup>&</sup>lt;sup>d</sup> School of Medical Sciences and Electron Microscope Unit Mark Wainwright Analytical Centre, The University of New South Wales, NSW 2052, Australia.
<sup>†</sup> The authors contributed equally to this work.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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  $\mu$ M), methylene blue (50  $\mu$ M) or congo red (10  $\mu$ M). To this NaBH<sub>4</sub> 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 isoplane 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 AuNPloaded 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 NaAuCl<sub>4</sub> 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%) HNO<sub>3</sub>, 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  $\mu$ M 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]<sup>-</sup>, 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 homogenous 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.

#### Journal Name

#### Fig. S1 displays;

(a) An aqueous colloid of AuNP formed by mixing 0.5 mM NaAuCl<sub>4</sub> 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 NaAuCl<sub>4</sub> 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.



Fig. S1 – (a) Colloidal AuNPs synthesised *via* the Turkevisch method, to which dry cubes of sodium polyacrylate hydrogel were added, to which no penetration of AuNPs is observed. (b) A cube of sodium polyacrylate hydrogel loaded with AuNP by using *in situ* citrate reduction. (c) Citrate capped AuNPs synthesised inside sodium polyacrylate cubes, then added to ultrapure water where no leaching of AuNPs is observed. (d) Image of sodium polyacrylate hydrogel immersed in 2 mL of 4 mM NaAuCl<sub>4</sub>, using 2 ml (closest vial) and 15 ml (rear vial), highlighting how partition and spontaneous AuNP has occurred for 2 ml at 70°C, and for 15 mL it is now saturated with Au(III). And (e) Image of both synthesised (left) and commercial (right) polyacrylate hydrogels with embedded AuNPs.

**Fig. S2** shows UV-Vis data for solution synthesised gold nanoparticles by citrate reduction (0.5 mM NaAuCl<sub>4</sub> and 5 mM NaCit), either by boiling the aqueous solution (solid line) or leaving the solution for 24 hours at room temperature (dashed).



Fig. S2 - UV-Vis spectra of gold nanoparticles formed in solution by citrate oxidation, under heated, (solid) ambient temperature with light (dashed) and ambient temperature in the dark (dotted). The vertical dotted lines represent the two  $\lambda_{max}$  at: 522 nm (heated) and 529 nm (ambient).

**Fig. S3** displays the solid-state UV-Vis spectra of AuNPs synthesised within the polyacrylate hydrogel when the hydrogels were swollen in volumes of 10, 8, 6, 4 and 2 mL of 4 mM Au(III) solution.



Fig. S3 – UV-Vis spectra of AuNPs synthesised in a polyacrylate gel soaked in different volumes, (1) 2 (2) 4 (3) 6 (4) 8 and (5) 10 mL of 4 mM concentration of Au(III), the dotted line indicates the  $\lambda_{max}$  at 550 nm.

**Fig. S4** shows the catalytic rate of reduction of 2-nitrophenol in the presence of an AuNP hydrogel sphere, as a function of  $[BH_4]^-$  concentration. This demonstrates that as the concentration of  $[BH_4]^-$  increases, the rate constant increases until it reaches a plateau. This is expected based upon the Langmuir-Hinshelwood model mechanism (*cf.* [1]) where the rate-determining step is the surface adsorption of the two reactants (2-nitrophenol and  $[BH_4]^-$ , the latter likely as a surface-hydrogen species). At higher concentrations of one or the other, saturation of the surface results in no observed correlation between rate and concentration. However, all reactions followed zero-order processes in this study, and it is not yet clear if the limiting step is partition into the hydrogel from bulk solution, or surface adsorption.



Fig. S4 – Figure demonstrating the catalytic rate for the catalytic reduction of 0.1 mM 2-NP in the presence of an AuNP hydrogel, where the concentration of excess  $[BH_4]$  has been varied.

### Journal Name

**Fig. S5** shows the UV-Vis absorbance values with time for (a) (blue) 4-nitrophenol (399 nm) and (purple) 2-nitrophenol (418 nm) and (b) (blue) methylene blue (665 nm) and (red) Congo Red (486 nm), where circles represent the catalytic system in the absence of the AuNP-loaded hydrogels and squares represent the same systems in the presence of the AuNP-loaded hydrogels. Figure (c) also shows a comparison of the absorbance recorded for the reduction of 4-nitrophenol (399 nm) in the presence of 0.1 M KCl with either an AuNP-loaded hydrogel sphere (squares) or the same quantity of gold injected as a citrate-capped AuNP colloid, prepared using the Turkevich route (diamonds) clearly showing the lack of catalytic activity of the solution-based AuNP colloid.



**Fig. S5** – a) UV-Vis absorbance data showing the absorbance with time of a) 4nitrophenol (blue) and 2-nitrophenol (purple) in the presence of  $[BH_4]^-$  both in the presence (square) and absence (circle) of a AuNP hydrogel. b) methylene blue (blue) and congo red (red) in the presence of  $[BH_4]^-$  in the presence (square) and absence (circle) of a AuNP hydrogel. And c) 4-nitrophenol reduction by  $[BH_4]^-$  where the absence of catalytic ability of citrate-capped colloidal AuNP is shown in the presence of 0.1 M KCl (black), and 4-nitrophenol catalysis with AuNP hydrogel under the same conditions (blue).

**Fig. S6** demonstrates the recyclability of the AuNP hydrogel for the catalysed [BH4]-reduction of methylene blue. As discussed in the paper, the decolouration of methylene blue is too fast to measure *via* UV-Vis, therefore a pictorial representation is presented. The film of blue colour at the air/liquid interface is due to re-oxidation of methylene blue by oxygen. The recycling was demonstrated qualitatively by achieving more than 25 recycles of the AuNP hydrogel.

**Fig. S7** demonstrates the recyclability of the AuNP hydrogel for the catalysed [BH<sub>4</sub>]-reduction of Congo Red dye. The absorbance recorded during the reduction of three samples of Congo Red, using the same AuNP hydrogel sphere, are shown; linear components are shown in green, blue and purple for the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> cycle, respectively. The rate of reaction, as expressed by the gradient of these plots, was unchanged (within error). Please note that a lower AuNP loading was used compared to that shown in Fig. 3 (half the quantity of AuNP), hence the slightly longer reaction times compared to Fig. 3.



Fig. S6 a) Two identical methylene blue solutions in the absence of AuNP hydrogel, b) After  $[BH_4]$  addition to the two solutions, c) Addition of a AuNP hydrogel to one of the two solutions, d) After catalytic reduction of methylene blue, e) Addition of more methylene blue to the solution, f) After catalytic reduction of second methylene blue solution.



**Fig. S7** – UV-Vis spectra demonstrating the recyclability of the AuNP hydrogel with Congo Red dye, through three successive catalysed reductions using the same AuNP hydrogel sphere.

### Journal Name

**Fig. S8** (a) shows the UV-Vis spectra for citrate-capped AuNP formed from an initial solution of 1 mM Au(III), and then diluted to be AuNP colloids with equivalent Au(III) concentrations of 100  $\mu$ M, 80  $\mu$ M, 60  $\mu$ M, 40  $\mu$ M, 20  $\mu$ M and 10  $\mu$ M; (b) shows the relationship between this equivalent Au(III) concentration at absorbance at 530 nm.

An AuNP hydrogel was soaked in an ultrapure water solution for 10 days; if all AuNP was released the solution would contain AuNP equivalent to *ca.* 2.7 mM Au(III). However, no plasmon resonance band could be observed, and the baseline had an absorbance of  $0.01 \pm 0.005$ , confirming that if any AuNP did leach the quantity was below detectable levels (less than 10  $\mu$ M Au(III)).



**Fig. S8** – a) The UV-Vis spectra of colloidal AuNPs with an equivalent Au(III) concentration of 1 mM (blue), 100  $\mu$ M (teal), 80  $\mu$ M (dark green), 60  $\mu$ M (green), 40  $\mu$ M (orange), 20  $\mu$ M (red) and 10  $\mu$ M (beige). b) Plot of equivalent Au(III) concentration vs. absorbance at 530 nm for colloidal AuNPs in aqueous solution.

#### References

[1] Kinetic Analysis of Catalytic Reduction of 4-Nitrophenol by Metallic Nanoparticles Immobilized in Spherical Polyelectrolyte Brushes, Stefanie Wunder, Frank Polzer, Yan Lu, Yu Mei, Matthias Ballauff, *J. Phys. Chem. C* **2010**, *114*, 19, 8814-8820