

Effective gel for gold nanoparticle formation, support and metal oxide templating

1. Experimental Section

1.1 Material preparation

Preparation of agarose and Au/agarose gel: Agarose powder (2 g, molecular biology grade from Scientifix) was added slowly to a beaker containing water (100 mL) at room temperature, with vigorous stirring to create a cloudy suspension. The solution was heated until boiling for 5-10 minutes and became clear. It was immediately poured gently, to avoid creating too many bubbles, into moulds (24x150 mm Pyrex test tubes). The moulds, sealed with Parafilm, were left to sit at room temperature overnight to allow for complete gelation. The gelled product was easily removed by inserting a tiny spatula down the side of the tube to create an air bubble, and then sliding the gelled agarose out.

Three methods were studied for the incorporation of the gold nanoparticles into the agarose gel structures. For method A, the aqueous agarose solutions were heated as above until the solutions became clear and then hydrogen tetrachloroauric acid (1-10 mL of 1 wt. % HAuCl_4 aqueous solution, Sigma-Aldrich) was added, and after brief further stirring the samples were gelled according to the procedure above. In method B the aqueous agarose solutions were heated and the hydrogen tetrachloroauric acid (1-10 mL of 1 wt. % HAuCl_4 aqueous solution) was added followed immediately by a warmed sodium citrate solution (2.5-10 mL of 1 wt. % sodium citrate aqueous solution, Sigma-Aldrich). After brief further stirring the samples were gelled following the procedure above. For method C, where preformed gold nanoparticles were used, the Turkevich citrate reduction was followed to prepare the gold sol.¹¹ Typically, 100 mL of water was heated to boiling in a 250 mL Erlenmeyer flask. 1-10 mL of 1 wt. % HAuCl_4 stock solution was added with stirring, followed by 2.5-10 mL of hot (100 °C) sodium citrate stock solution. The solution was boiled for 10 minutes with stirring, during which time the solution colour changed from the pale yellow of the gold salt, to clear after citrate addition, followed by grey blue, pale purple, dark purple, magenta, then finally bright wine red. The solution was cooled to room temperature and made up to 100 mL with water in a volumetric flask. This solution was then used as the aqueous solution to which the agarose powder was added then heated to boiling and cooled, as above, to produce the gold/agarose gel.

Preparation of gold nanoparticle/ TiO_2 nanocomposites: To prepare the agarose gels for templating with an alkoxide precursor that reacts immediately on contact with water, the water within the gel had to be exchange to a solvent compatible with the precursor. Firstly, the as-synthesised gels were cut into smaller pieces ($0.5 \times 0.5 \times 1.0 \text{ cm}^3$) and transferred from water into ethanol in 3 steps (water to ethanol ratio 2:1, 1:2 then 0:1, soaking 6 h in each solution), and likewise from ethanol to 2-propanol. Subsequently, the gel pieces were soaked in 70 wt. % titanium (IV) isopropoxide in isopropanol solution for 18 h, before being transferred into a water/isopropanol (1:1 by

volume) solution for hydrolysis and condensation reactions (6 h). The samples were then dried at room temperature for 2 days followed by 6 h at 60 °C. To remove the agarose template and crystallise the inorganic oxide the samples were heated at 450 °C (ramp 3.54 °C min⁻¹) under flowing air (10 h).

1.2 Material preparation:

Scanning electron microscopy (SEM) (Philips XL30 or FEI QUANTA 200F, operated at 20 kV) was used to examine the morphology of the samples. To prepare the agarose gel or Au/agarose gel samples for SEM, they were solvent exchanged from water into ethanol and then into acetone before being dried using a carbon dioxide critical point drying technique (Baltec CPD 030 critical point dryer). The calcined samples were broken into several pieces so that fresh surfaces could be viewed. All samples were mounted onto carbon-coated SEM stubs, and then sputter coated with gold using an Edwards S150B sputter coater.

Transmission electron microscope (TEM) images were taken using either a Philips CM120 BioTWIN TEM operating at 120 kV or a JEOL 2010F TEM operating at 200kV, fitted with a Gatan Imaging Filter (GIF) and an Oxford Instruments ISIS energy dispersive x-ray spectroscopy (EDS) system, for qualitative analysis. The samples were embedded in an LR-white resin and ultramicrotomed to a thickness of 90 nm prior to TEM analysis.

Nitrogen adsorption-desorption measurements for surface area and porosity were conducted on a Micromeritics 3000 Tristar surface area and porosity analyzer at 77 K. The samples were evacuated at either room temperature (organic containing samples) or 150 °C (inorganic samples) overnight before analysis. The surface areas were calculated by using the Brunauer-Emmett-Teller (BET) method.

X-ray diffraction (XRD) was performed using a Philips PW1800 diffractometer (Cu K α radiation wavelength of 1.54045 Å) to characterise the phase and crystallinity of the final products.

UV-vis absorbance spectra of the gold sols were obtained using a CARY50 Bio UV-visible spectrophotometer between 400-700 nm. UV-vis diffuse reflecting spectra of Au/TiO₂ composites were recorded on a Cary 5G UV-Vis-NIR spectrophotometer.

The gold content of the composites was measured by inductively coupled plasma mass spectrometry (Varian ICP-MS). The calcined samples (5 mg) were dissolved in a HF + HNO₃ (1:1 by volume) solution in Teflon beakers at 110 °C for 2 h, and then the acid was evaporated at 130 °C before redissolving the solid overnight in aqua regia. The samples were diluted by factors of 6 x 10⁵ - 6 x 10⁶ with 5 % HCl spiked with cobalt and rhenium as internal standards. The instrument was calibrated with a series of mixed gold (1.9 - 24 ng/g) and titanium (310 - 390 ng/g) standard solutions permitting gold and titanium concentrations of the acidified solution to be determined. The gold content was measured as (Au×100%)/(Au+Ti).

The gold distribution in porous titania was investigated using a Camera IMS 5f dynamic secondary ion mass spectrometer (SIMS). The samples were mounted into EPO-THIN epoxy resin (Selby-Biolab), and polished carefully to achieve a smooth surface. The samples surfaces were sputter coated with carbon to minimise charging

during SIMS analysis. A 10 keV Cs^+ primary ion source was used to generate negative secondary ions (^{18}O , ^{49}Ti , $^{49}\text{Ti}^{18}\text{O}$, $^{49}\text{Ti}^{16}\text{O}_2$, $^{49}\text{Ti}^{18}\text{O}_2$, ^{197}Au) which were counted for 1 second each per cycle on an ETP electron multiplier. A 30 nA primary ion beam, with an approximate diameter of $\sim 50\text{ }\mu\text{m}$, was rastered over the surface of each sample creating a crater with approximate dimensions of $250\times 250\text{ }\mu\text{m}$. An aperture in the secondary column was used to provide an analytical area of $60\text{ }\mu\text{m}$ diameter in all measurements (thereby minimising any crater edge effects in the analysis). Each sample surface was sputtered for around 500 seconds prior to analysis to enable equilibrium sputtering conditions to be achieved. Further Cs^+ bombardment for 1500 to 6000 seconds allowed stable counts for each mass of interest to be collected. The resulting craters were around $3\text{ }\mu\text{m}$ deep. Crater depth was determined using a KLA Tencor Alpha-step IQ stylus profilometer.

2. Results:

Using the citrate reduction of the tetrachloroauric acid in either method B or C resulted in absorbance spectra that did not vary with time (up to 16 days, see Fig. 1s below). Method A where the gold ions were reduced by the agarose, did show substantial variation in the absorbance spectra with time. The citrate reduction is substantially faster than the agarose reduction of the gold ions, therefore, within 10 minutes of removing the gold/agarose gel samples from methods B and C from the heating plate, no further changes to the gold colloid formed was observed.

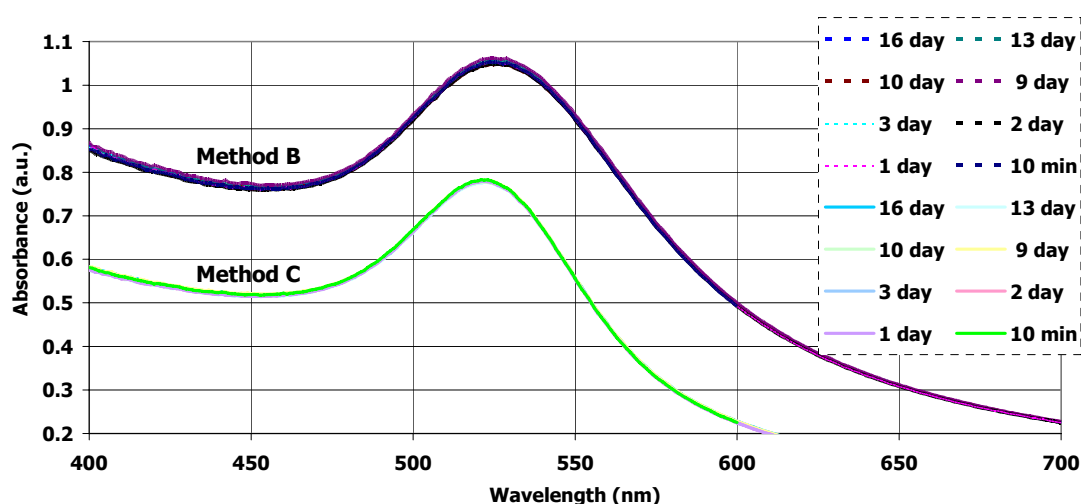


Fig. 1s UV-vis spectra of method B and method C of 0.25 mM initial Au concentration as a function of time (10 minutes through to 16 days).

The presence of gold in the final TiO_2 structure was confirmed by UV-vis diffuse reflectance spectroscopy, see Figure 2s for method C sample.

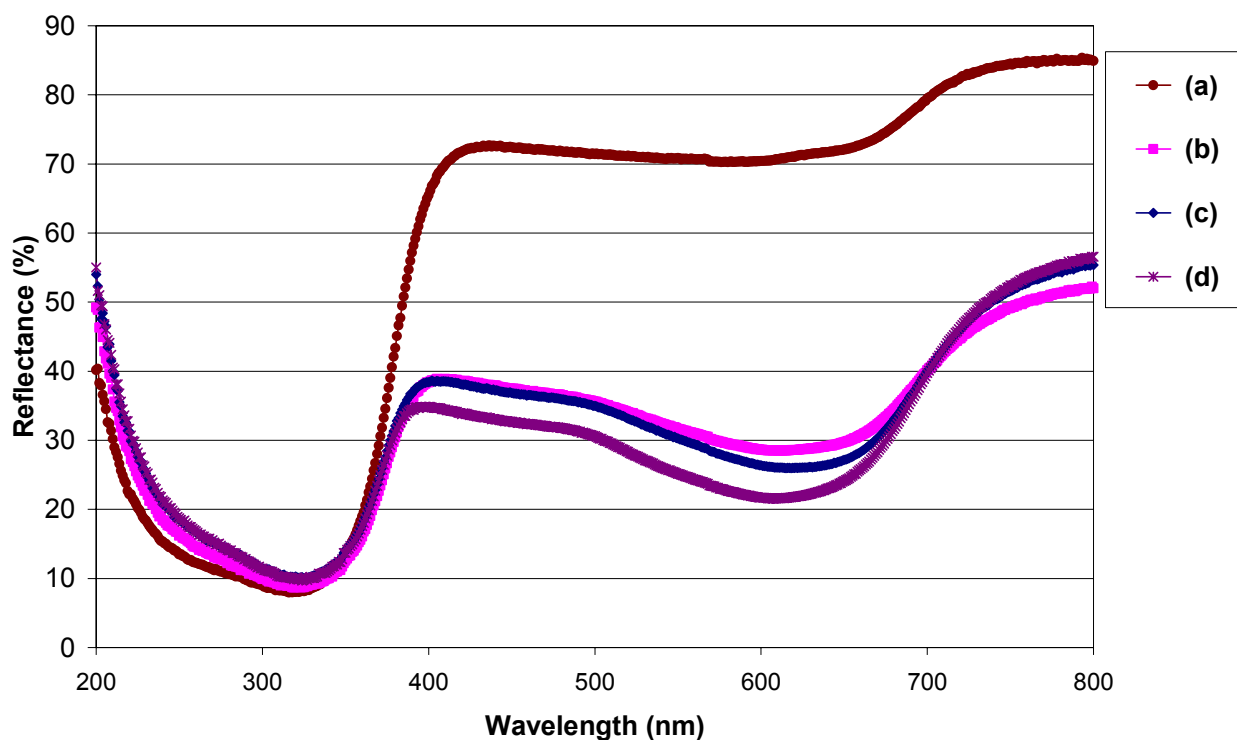


Fig. 2s UV-vis diffuse reflectance spectra of Au/TiO₂ composites with an initial gold concentration of (a) 0 mM, (b) 0.25 mM Au, (c) 0.50 mM and (d) 1.25 mM Au prepared by method C.

The gold nanoparticles obtained using method A in the agarose gel can be seen in the TEM image in Fig. 3s (a). On inclusion of the TiO₂ and removal of the agarose template, the porous Au/metal oxide structure could be viewed, Fig. 3s (b). The presence of the gold nanoparticles (as highlighted in Fig. 3s (c and d) for method A) was confirmed by energy dispersive X-ray spectroscopy for each method, see Fig. 4s.

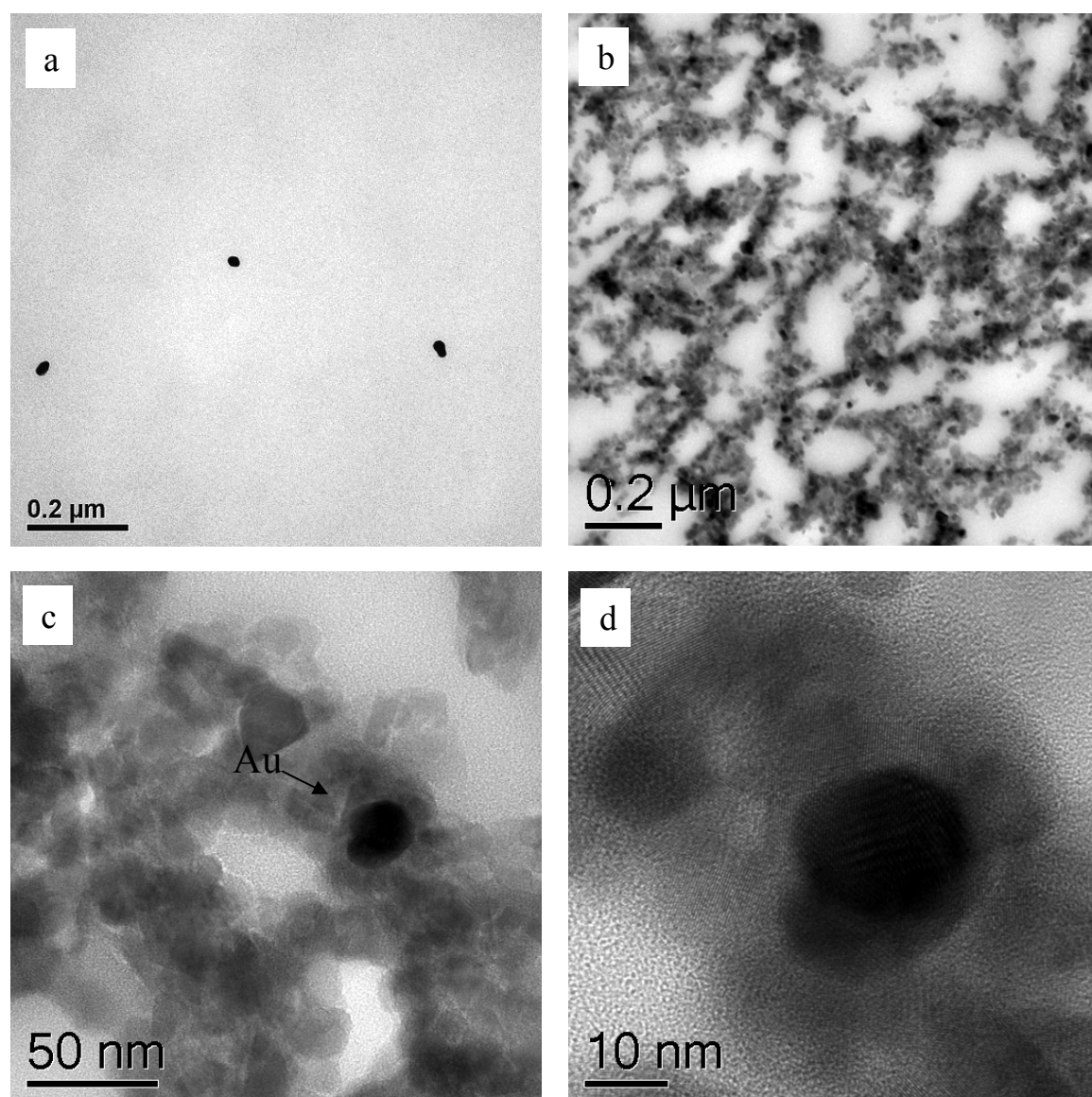


Fig. 3s TEM images of (a) the Au/agarose hybrid, and (b-d) the Au/TiO₂ composites from method A sample (0.50 mM initial Au concentration) with increasing magnification.

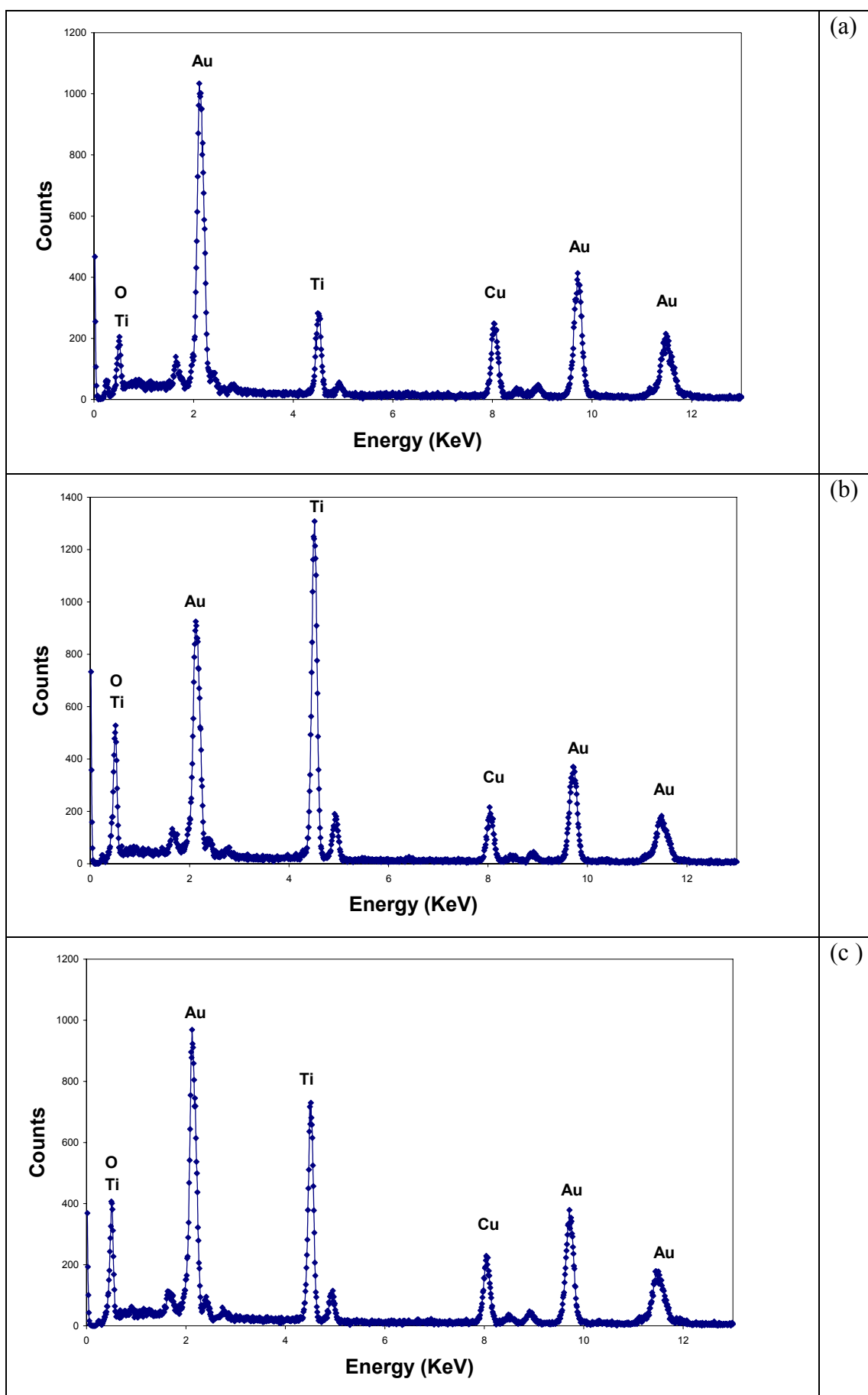


Fig. 4s EDX of the Au/TiO₂ samples synthesized by methods (a) A, (b) B and (c) C with an initial Au concentration of 0.50 mM.