

Supporting information for:

***In-situ* preparation of network forming gold nanoparticles in agarose hydrogels**

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Experimental

Materials. Hydrogen tetrachloroaurate (HAuCl₄) trihydrate, ruthenium (III) chloride (RuCl₃) hydrate, sodium hexachloropalladate (Na₂PdCl₆) tetrahydrate, sodium hexachloroplatinate (Na₂PtCl₆) hexahydrate were purchased from Sigma Aldrich. Sodium borohydride (NaBH₄) was obtained from BDH, agarose (molecular grade) from Bioline and monohydroxy(1-mercaptoundec-11-yl)tetraethylene glycol from Prochimia. All chemicals were used as received. In all experiments water deionised with a Milli-Q plus 185 system was used.

Preparative Methods. Agarose hydrogels (5.4%w) were prepared by dissolving 285mg of agarose in 5ml of water at 90°C in a glass vial of 20 mm inner diameter followed by sonication until all gas bubbles were removed, and storage for at least one hour at 4°C. The vial was then carefully destroyed with a small metal hammer (caution!) to isolate the resultant hydrogel, which was rinsed with water and cut with a razor blade into discs of ca. 3.2mm thickness. For the preparation of metal nanoparticles a wedge shaped quarter of an agarose hydrogel disc was immersed in 3 ml of a 500 mM feed solution of the respective metal salt for 24 hours. For Au nanoparticles, additional samples were made using 20, 50, 100, 200, 300 and 600 mM HAuCl₄ feed solutions. The hydrogels were then removed from the feed solution, quickly rinsed with water and immediately transferred to 3ml of a freshly prepared 500 mM solution of sodium borohydride to reduce the metal salt. After 24 hours, the particle-loaded gels were removed from the sodium borohydride solution and dialysed in ca. 50 ml of water for 48 hours changing the water every 12 hours. The “wet” gels were stored in closed vials under water. Partially dehydrated (“dry”) gels were formed by storing them in air in an open vial for 60 days at 4°C at 20-30% relative humidity. During this process the gels lose 40% of their original weight as water.

X-ray Powder Diffraction (XRD). Data were collected on a Stoe STADI P diffractometer using Cu K α_1 radiation in transmission foil geometry. Measurements were carried out on ca. 1 mm slices of gel cut with a razor blade. They were held in place between acetate films in order to prevent shrinkage of the sample by the beam due to dehydration.

UV-visible spectroscopy. Solid state spectra were recorded with a Perkin Elmer Lambda 650 S UV/Vis Spectrometer equipped with a Labsphere integrating sphere over the spectral range 190-900nm (6.53-1.38eV) using BaSO₄ reflectance standards. Samples were prepared by compressing a small piece of gel between two glass slides. A sample of unloaded gel was used as a reference.

Electron Microscopy. Three different types of sample preparation have been used, (i) embedding in epoxy resin, (ii) freeze drying and (iii) dissolution of the gel. Before embedding in pure epoxy resin the gels were first dehydrated in a graded series of ethanol solutions (30, 60, 70, 90 and 100%v) for 30 min at each concentration and then infiltrated by a graded series of epoxy resin in absolute ethanol (proportion of resin was $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$ of the total volume) each step for 1 hour. The resin was then polymerised at 60°C for one week. This unusually slow step was necessary in order to avoid irreversible sticking of the sample to the diamond blade during the subsequent cutting process. Ultrathin sections (20-200 nm) were cut using a LKB ultramicrotome. The sections were placed on a carbon-coated copper grid and dried at room temperature. TEM images were obtained using a 120kV FEI technai Spirit TEM and STEM images were obtained using a JEOL 2100F (S)TEM with aberration corrector.

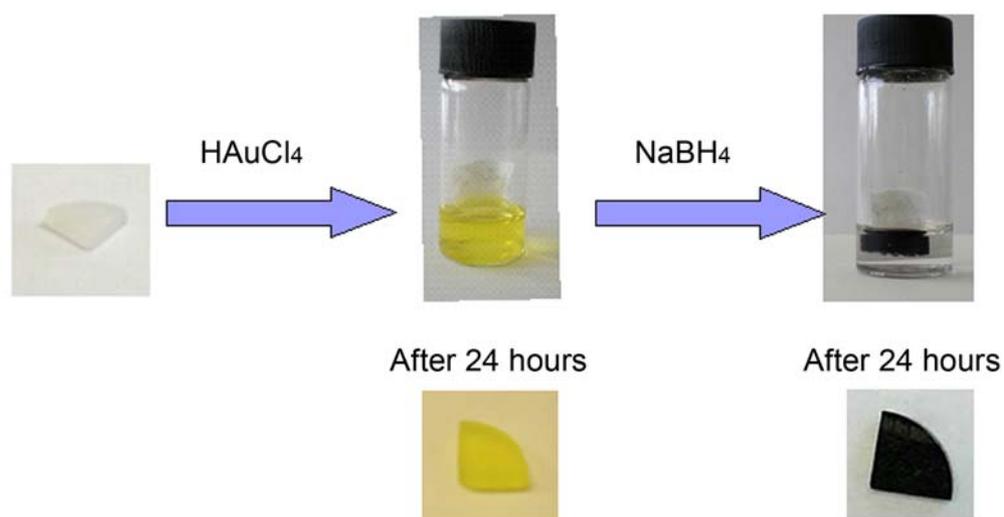
For freeze drying the gels were first frozen for one hours at -20°C, then for 3 hours at -80°C and dried overnight in a Modulyo vaccum dryer. They were then crushed with pestel and mortar and a sample of the resultant dust was carefully picked up with a holey

carbon TEM sample grid. Samples were inspected by HAADF imaging on the Super STEM 1 microscope at Daresbury Laboratories, UK.

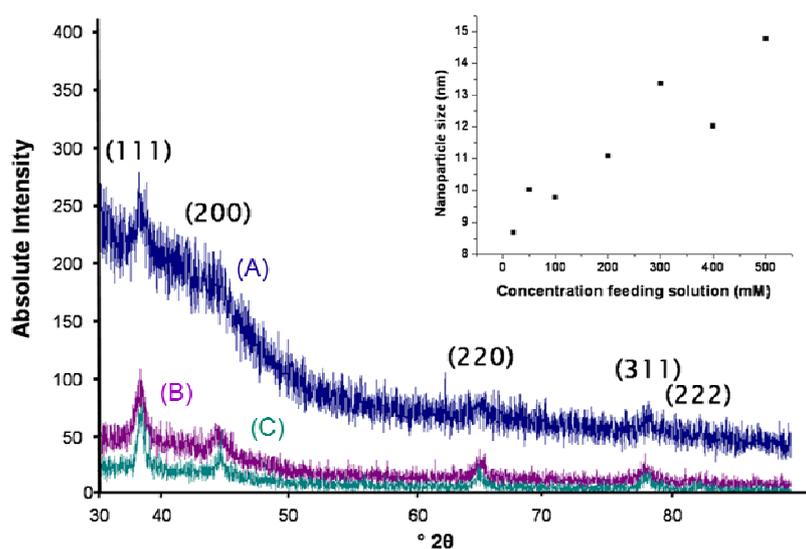
For dissolution, the gels were first exposed to 3 ml of a 7 mM ethanolic solution of monohydroxy(1-mercaptoundec-11-yl)tetraethylene glycol for 24 hours and then dissolved in 2M hydrochloric acid at 70°C. After dissolution this was diluted 10 times with water. For inspection by TEM (120kV FEI technai Spirit TEM) a drop of the diluted solution was allowed to evaporate on a carbon coated copper mesh sample grid.

Electrical measurements. For the characterisation of charge transport across the gels cylindrical samples of 8.5 mm diameter were cut out from the original 3.2 mm thick wedges using a circular blade. The samples were sandwiched between two independently contacted Au foil electrodes inside a PTFE housing. To ensure good contact and reproducibility of results, a slight mechanical pressure of ca. 1.7 kPa was applied with a PTFE cylinder and a 10g weight. The current-voltage response was measured using an Autolab PGSTAT 10 potentiostat (Windsor Scientific, UK) in two electrode configuration.

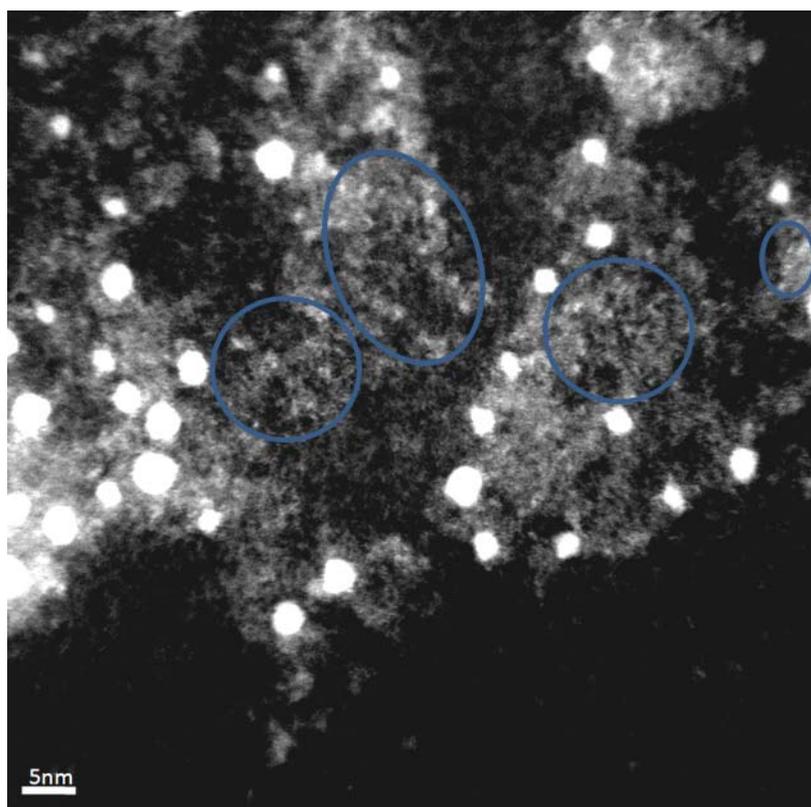
S1. Scheme of the synthesis of gold nanoparticles in agarose gel. The Hydrogel is soaked in Au salt solution for 24hrs followed by immersion in a solution of sodium borohydride for 24hrs. The gel was rinsed with milli-Q water between the two steps.



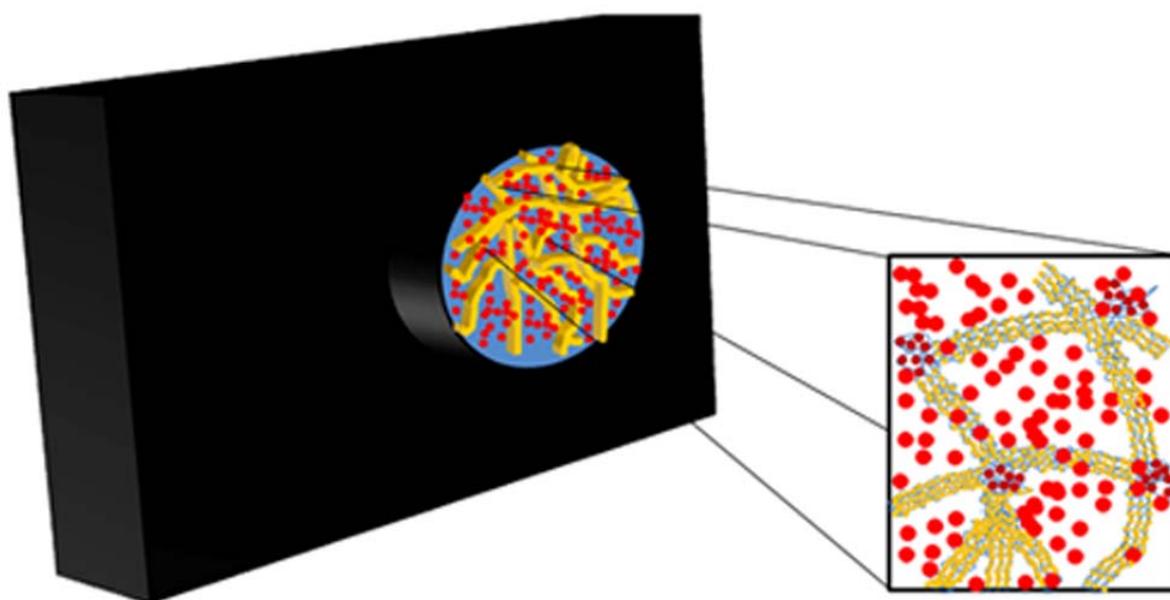
S2. X-ray diffraction pattern of Au nanoparticle-loaded agarose gel obtained with feed solutions of HAuCl_4 at different concentrations and evolution of nanoparticles size estimated by line broadening analysis using the Scherrer equation



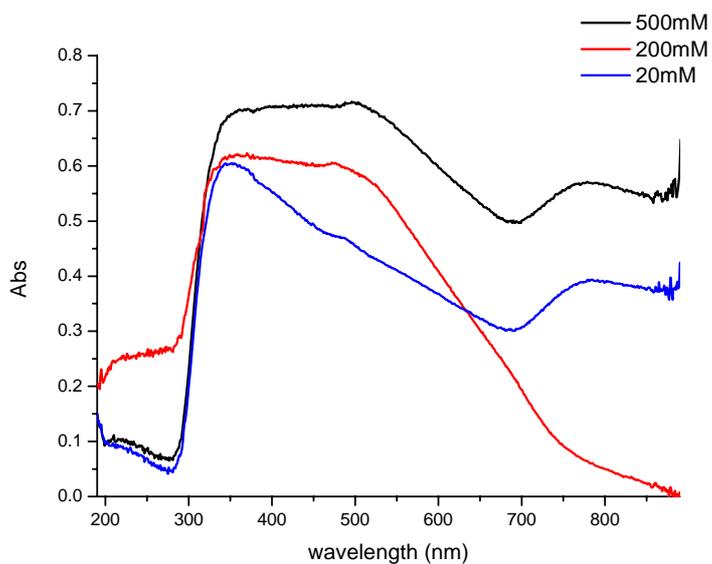
S3. Enlarged image of Figure 2c. Au clusters of 0.8 nm and below are distinguishable in the areas circled in blue. These correspond to nucleation numbers of 13 or less atoms.



S4. Enlarged image of Figure 2d.

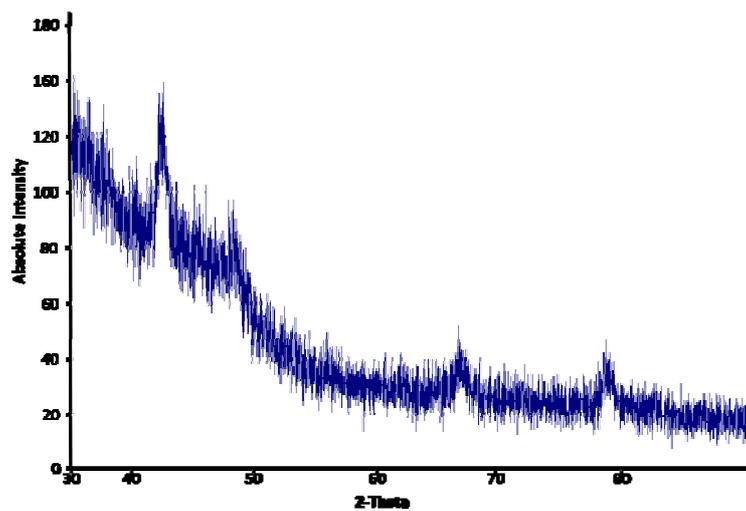


S5. UV-vis spectra of gels containing Au nanoparticles obtained with different concentration of feed solution. Note the appearance of a plasmon band above 500 nm indicating the presence of particles larger than about 3 nm.

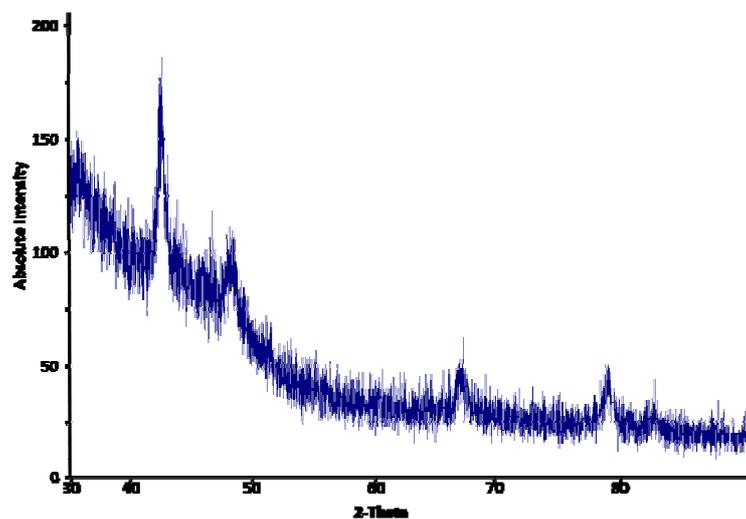


S6. X-ray diffraction pattern of Au nanoparticle-loaded agarose gel obtained with feed solutions of HAuCl₄ at different concentrations

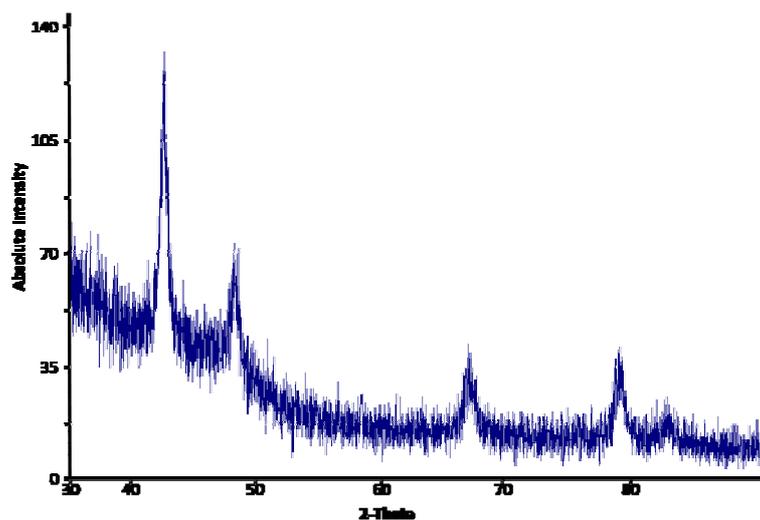
S6.1. feed solution 50 mM H_{AuCl}₄



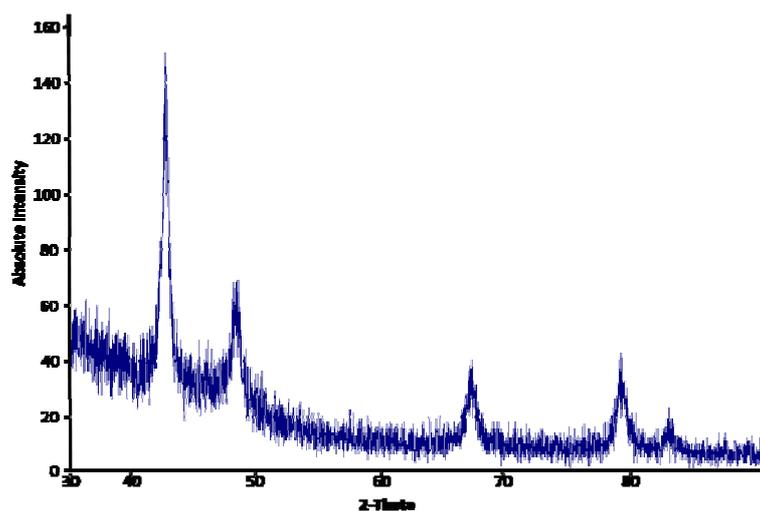
S6.2. feed solution 100 mM H_{AuCl}₄



S6.3. feed solution 300 mM H_{AuCl}₄

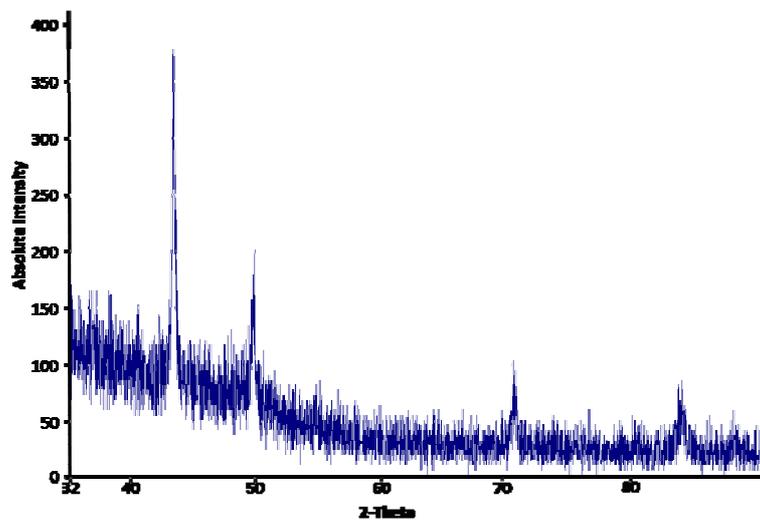


S6.4. feed solution 400mM H_{AuCl}₄

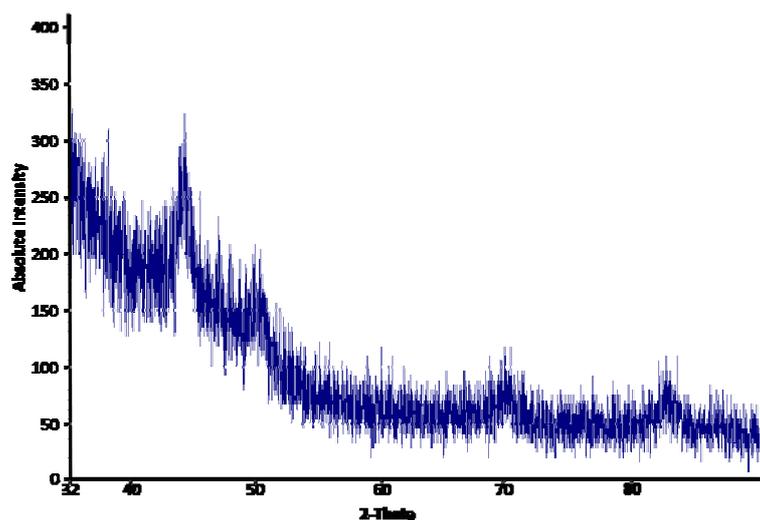


S7. X-ray diffraction pattern of the agarose gels reduced with sodium borohydride after immersion in feed solutions of Na₂PdCl₆, Na₂PtCl₆ and RuCl₃

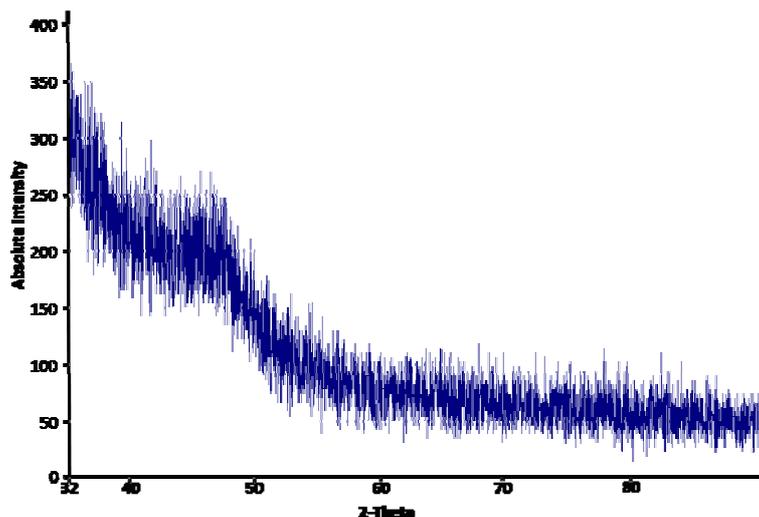
S7.1. 500 mM Na_2PdCl_6



S7.2. 500 mM Na_2PtCl_6

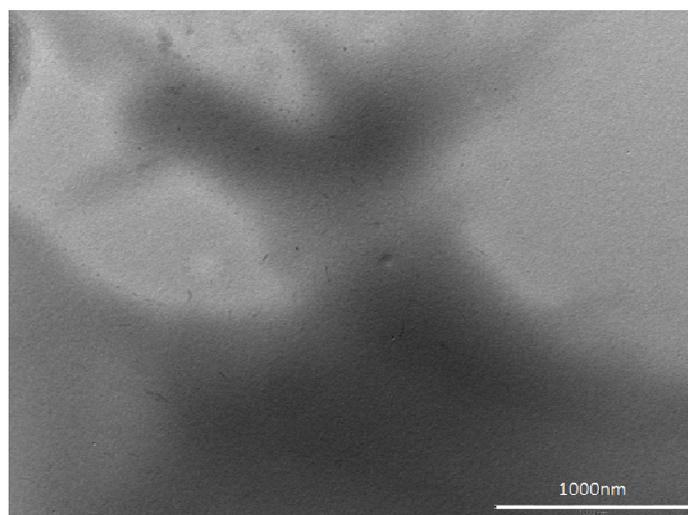


S7.3. 500 mM RuCl₃

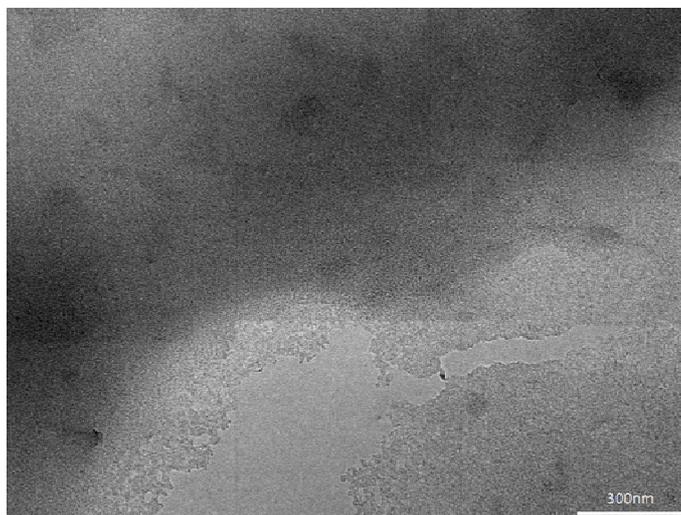


S8. Transmission Electron Microscopy of metal nanoparticle-loaded agarose gels. Note the decoration of the gel framework by small clusters visible in each case as grey cloud structure.

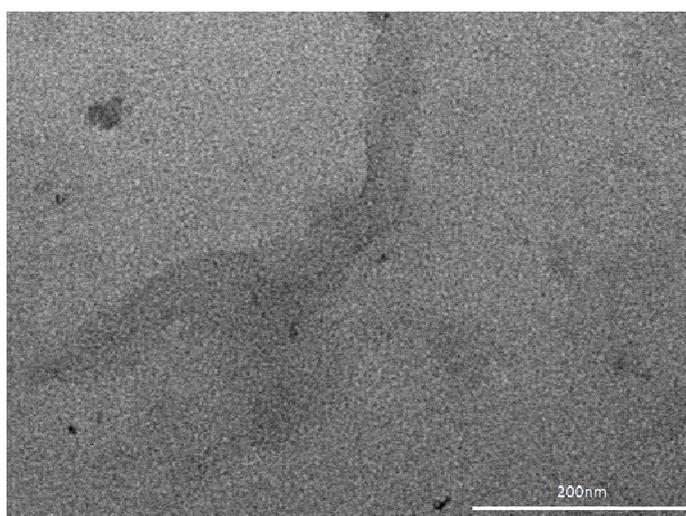
S8.1. 20 mM feed solution of HAuCl₄



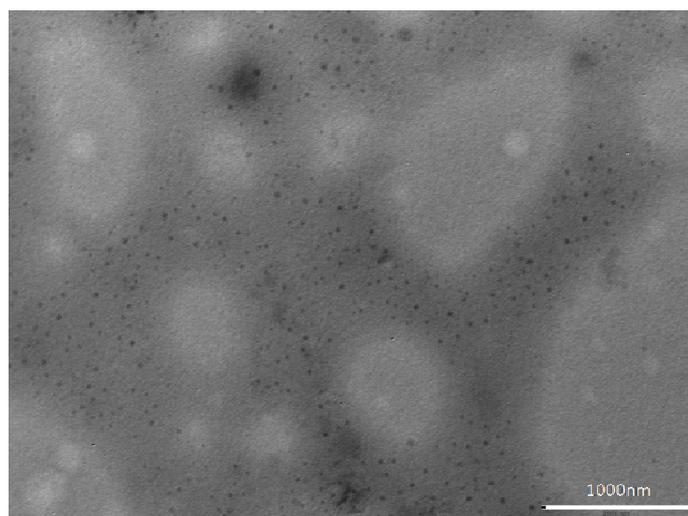
S8.2. 500 mM feed solution of HAuCl_4



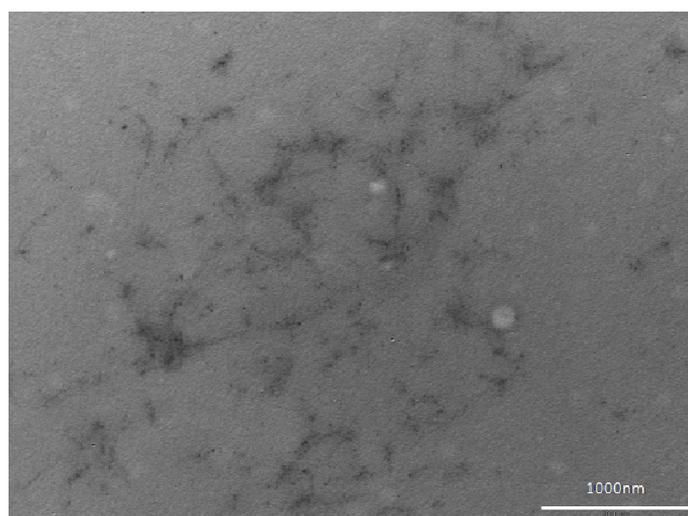
S8.3. feed solution 500 mM Na_2PdCl_6



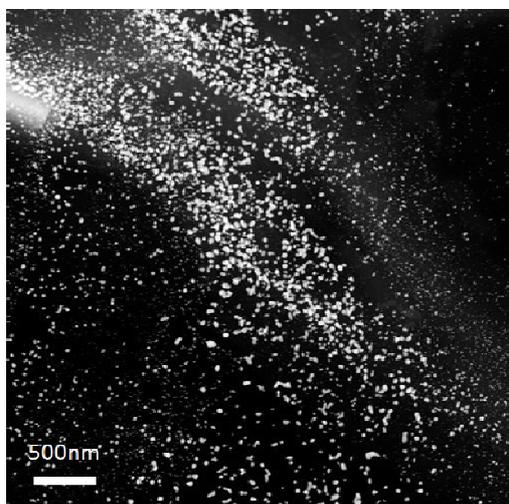
S8.4. feed solution 500 mM Na_2PtCl_6



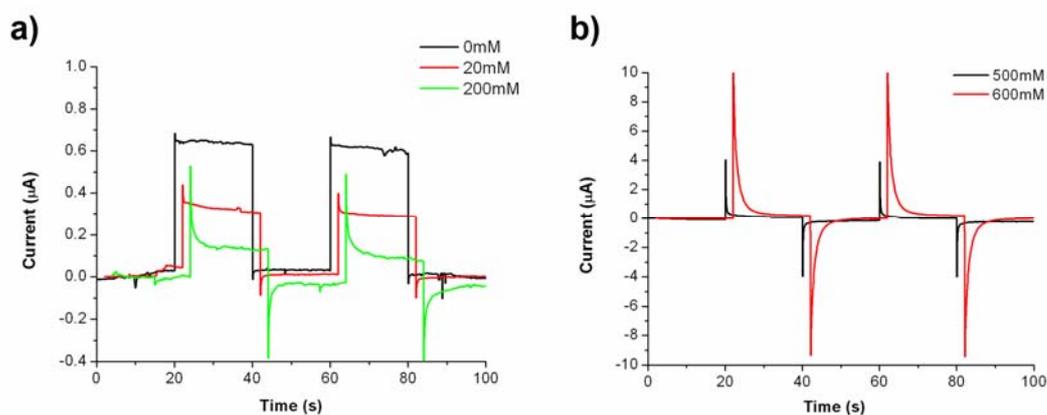
S8.5. feed solution 500 mM RuCl₃



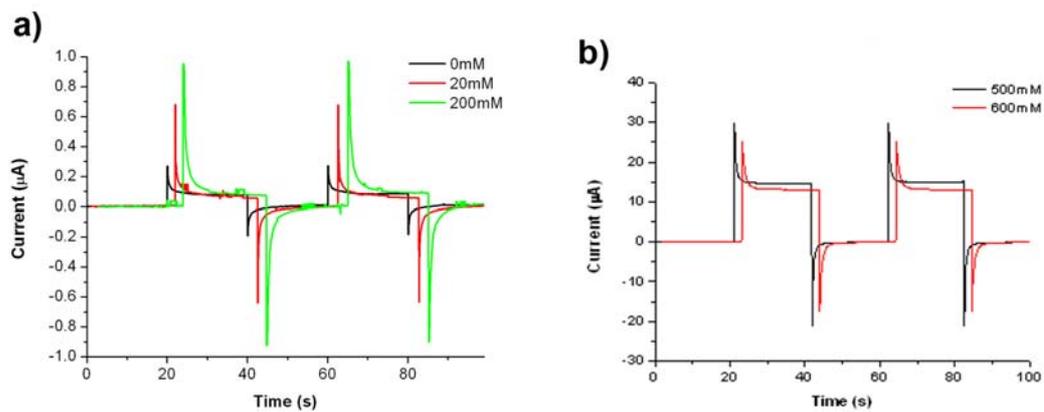
S9. Scanning Transmission Electron microscopy of Au nanoparticle-loaded agarose gel obtained with a 500 mM feed solution of HAuCl_4 . Note the increased number of large nanoparticles (bright specks) in the water phase of the gel in comparison with Figure 3a in the paper.



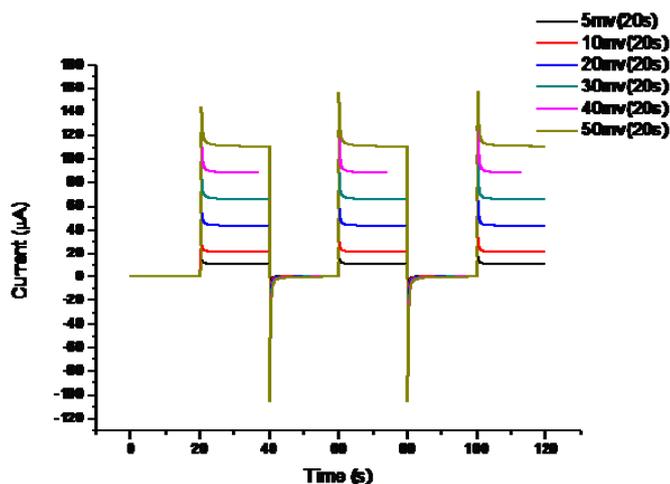
S10. Current-time response of “wet” gels prepared with hydrogen tetrachloroaurate feed solutions at concentrations from 0 to 200 mM (a) and at 500 and 600 mM (b).



S11. Current-time response of “dry” gels prepared with hydrogen tetrachloroaurate feed solutions at concentrations from 0 to 200 mM (a) and at 500 and 600 mM (b).

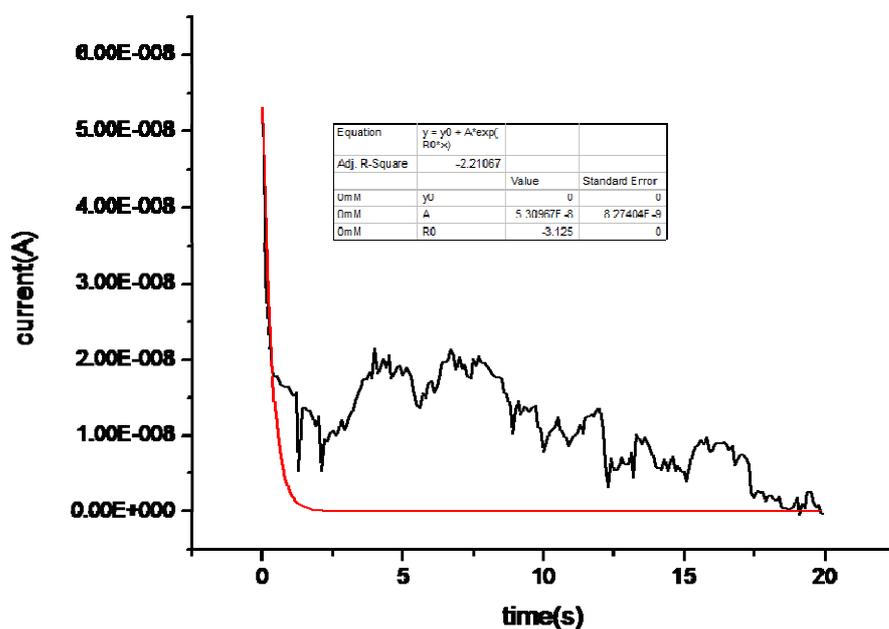


S12. Current-voltage responses of the “dry” Au nanoparticle-loaded agarose gel obtained with a 500 mM feed solution of HAuCl_4 . Note the perfect Ohmic response of the system. The current is proportional to the voltage.

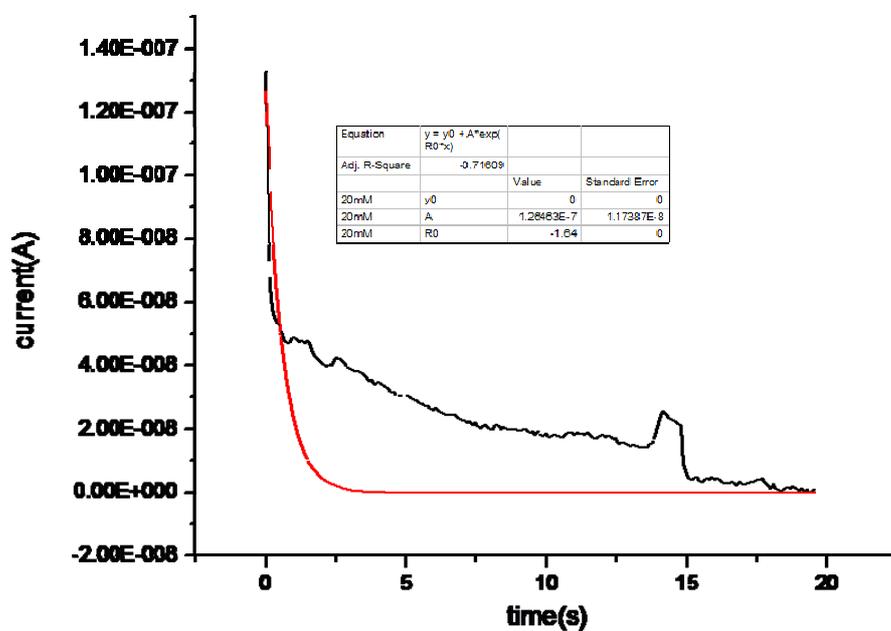


S13. Current-voltage response and Fitting of the transient current part of the signal obtained with “wet” Au nanoparticle-loaded gels. Red curves are fits and black curves are measurements. Note that the fitting was obtained by the determination of τ from the graphs. An exponential fitting has been used by setting the y_0 as 0 and including τ in the exponential coefficient in the following equation: $y=y_0+Ae^{(-t/\tau)}$

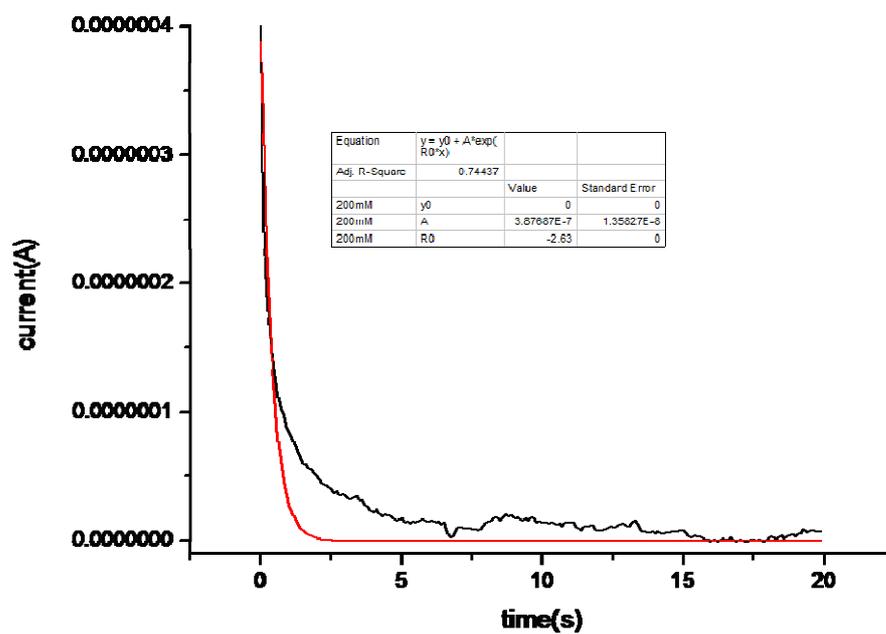
S13.1. Current-voltage response and Fitting of the transient current part of the signal on the pure “wet” gel (absence of nanoparticles).



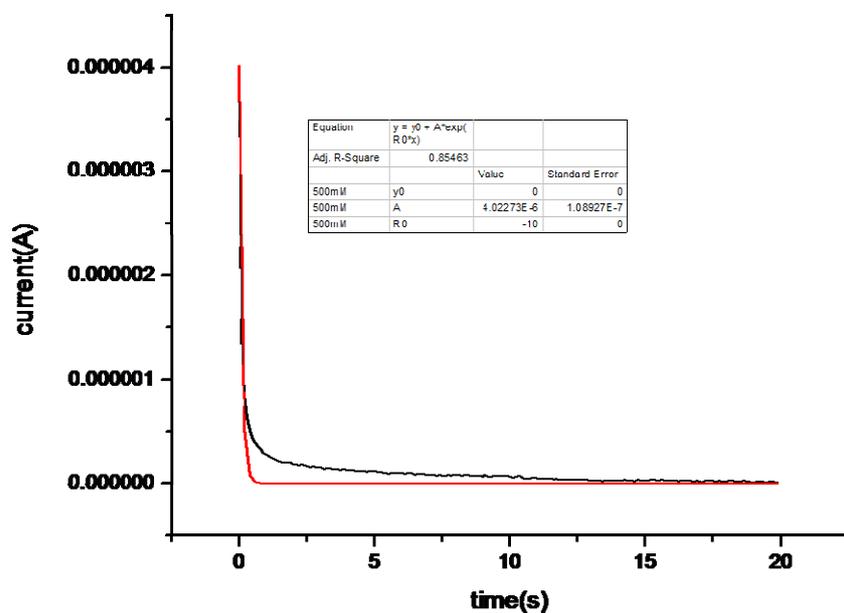
S13.2. Current-voltage response and Fitting of the transient current part of the signal on the “wet” gel (20mM HAuCl₄ feed solution)



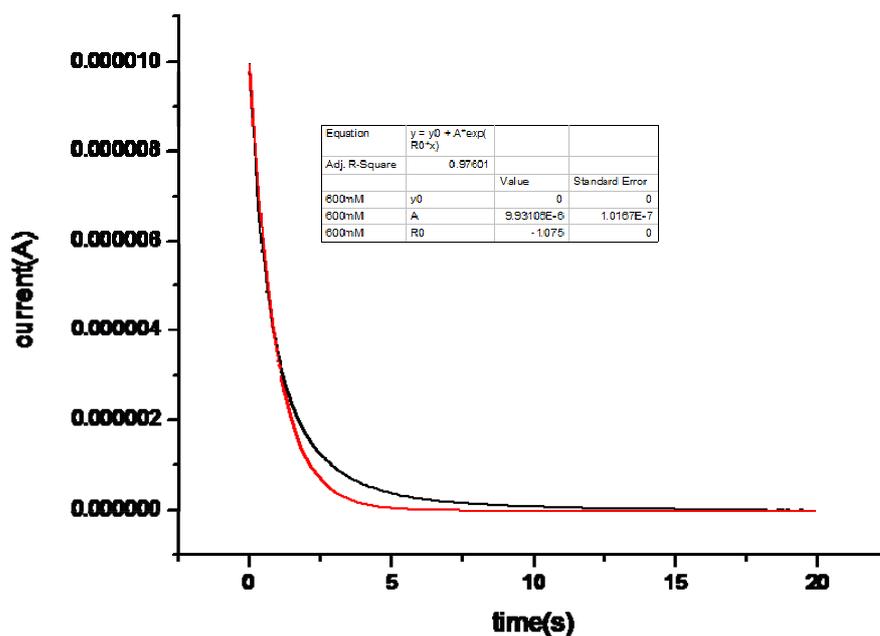
S13.3. Current-voltage response and Fitting of the transient current part of the signal on the “wet” gel (200mM HAuCl₄ feed solution)



S13.4. Current-voltage response and Fitting of the transient current part of the signal on the “wet” gel (500mM H_{AuCl}₄ feed solution).

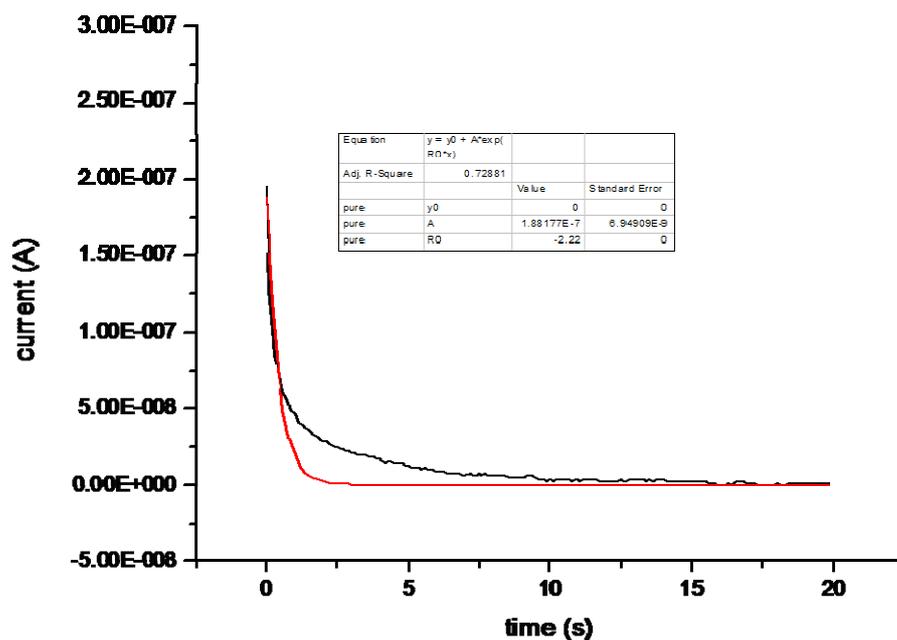


S13.5. Current-voltage response and Fitting of the transient current part of the signal on the “wet” gel (600mM H_{AuCl}₄ feed solution).

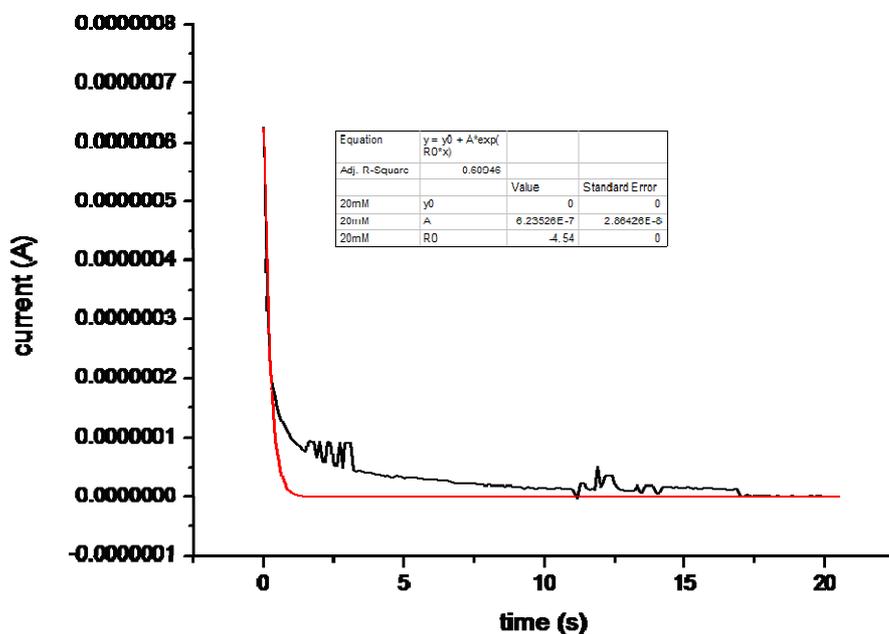


S14. Current-voltage response and Fitting of the transient current part of the signal on “dry” gels immersed in feed solutions of H₂AuCl₄. Note that the fitting of the “dry” gels is better than that of the “wet” ones, except for higher metal loadings. We attribute this to the Ohmic behaviour that is only fully justified in “dry” gels and highly loaded wet ones. The simplified model of a leaking capacitor is not adequate to describe the behaviour of the wet gels with low metal loading, where conduction occurs only by ionic migration. While the transient part can still be described well, the fits fail to describe the non-Ohmic currents.

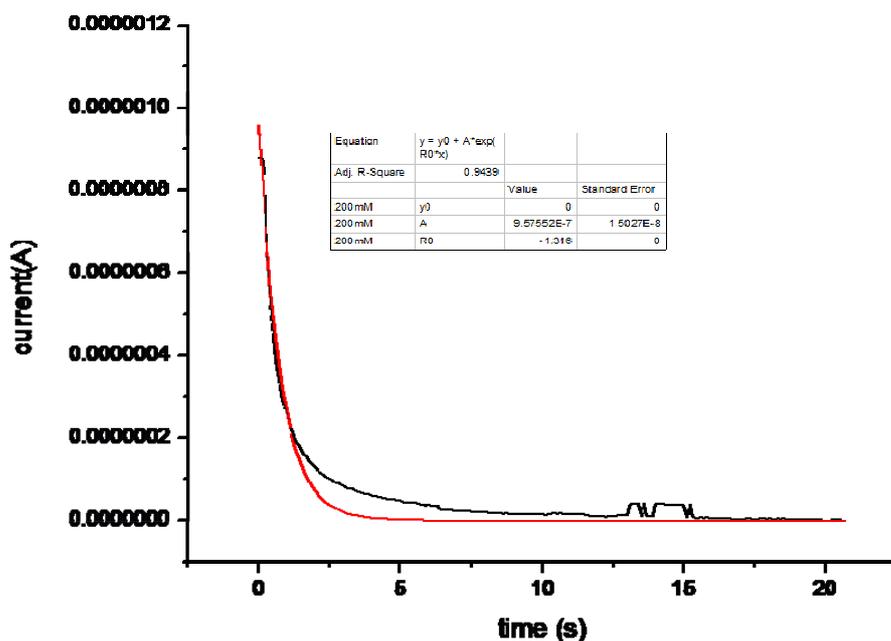
S14.1. Current-voltage response and Fitting of the transient current part of the signal on the pure “dry” gel (absence of nanoparticles).



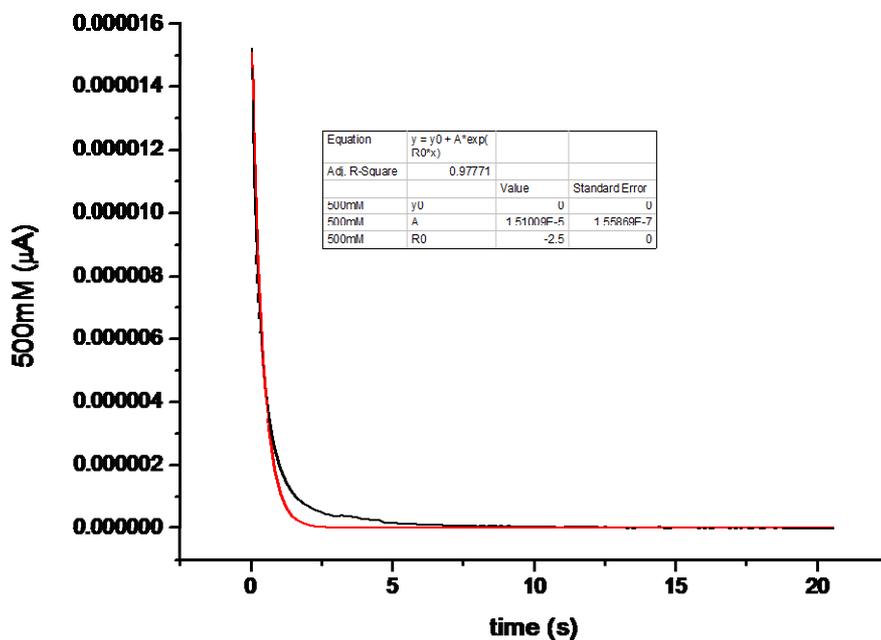
S14.2. Current-voltage response and Fitting of the transient current part of the signal on the “dry” gel (20mM H_{Au}Cl₄ feed solution).



S14.3. Current-voltage response and Fitting of the transient current part of the signal on the “dry” gel (200mM H_{Au}Cl₄ feed solution).



S14.4. Current-voltage response and Fitting of the transient current part of the signal on the “dry” gel (500mM HAuCl₄ feed solution).



S14.5. Current-voltage response and Fitting of the transient current part of the signal on the “dry” gel (600mM HAuCl₄ feed solution).

