

Supporting Information

Simultaneous SERS and Metal-Enhanced Fluorescence of Au-Ag Alloy Nanoparticles and SiQDs Co-Encapsulated within Polymer Nanoparticles

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General Experimental

All chemicals were purchased from Sigma Aldrich or Alfa Aesar and were used as received without purification. Water was deionized before use (nominal resistivity 18 M Ω cm, Nanopure™ purification system, Barnstead). Divinylbenzene was refrigerated and used without purification. Membranes for purification by dialysis of polymer composite nanoparticles were obtained from Spectrum Laboratories (Spectra/Por® Dialysis Membrane Tubing, molecular weight cut-off: 3500 Da, width: 18 mm and diameter: 11.5 mm). Toluene was dried over sodium and distilled as required.

Preparation of Silicon Quantum Dots (SiQDs)

Photoluminescent SiQDs were prepared according to a modification of the procedure described by Lie *et al.*¹ Porous silicon layers were formed by electrochemical etching of boron-doped p-Si<100> oriented wafer (1–10 Ω cm resistivity, Compant Technology, Peterborough, UK) in the presence of fluoride. The Si wafers were cut into squares approximately 1.2 cm² using a diamond scribe and etched in a 1 : 1 v/v solution of 48% aqueous HF and EtOH. A porous silicon layer was obtained at high current density (10 min at 250 mA cm⁻²) supplied by a programmable power supply (Keithley 2601), and the resulting porous layer luminesced orange when observed under a handheld UV lamp (λ = 365 nm). The dry porous silicon chips were then refluxed in 25 mL of dry PhCH₃ solution containing 0.4 mL of 1-undecene under an atmosphere of N₂ for 3 h. The resulting solution emitted an orange-coloured luminescence under an UV light (λ = 365 nm). This fluorescent solution was filtered to remove undissolved silicon particles and then the solvent and unreacted 1-undecene were removed under reduced pressure. The product SiQDs were obtained as an oily/waxy residue which luminesces under UV light (λ = 365 nm) and was soluble in nonpolar solvents e.g., THF, CH₂Cl₂ and PhCH₃. It was estimated that ~100 μ g of alkyl Si-QDs were typically produced per Si chip. The particle size of the alkylated SiQDs was estimated to be 6 nm in diameter based on AFM measurements in tapping mode.

Preparation of Citrate Stabilized Au-Ag NPs

Aqueous Au-Ag alloy nanoparticles were prepared using the citrate reduction method described by El Sayed *et al.*² Au-Ag Alloy nanoparticles with gold mole fractions of 0.5 and 0.75 were prepared by substituting a predetermined number of moles of gold atoms by the equivalent number of moles of

silver atoms in the form of AgNO_3 . To boiling distilled water (95 mL) was added $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (2.50 mg) and AgNO_3 (2.16 mg) to afford a cloudy solution. A solution of 1% sodium citrate was added and the colour changed yellow. The solution was further boiled for 30 min and then left to cool to room temperature. The resultant aqueous dispersion of Au-Ag alloy NPs was used without any purification. The average hydrodynamic diameters of the resulting aqueous Au-Ag NPs were determined by DLS to be 30.0 ± 3.9 nm. A TEM image of Au-Ag NPs is shown in S1(a).

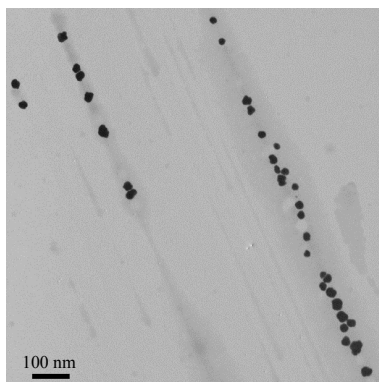
Preparation of polymer-stabilized Au-Ag NPs encoded with SERS reporter molecules (PS/Au-Ag@SERS)

Au-Ag NPs displaying SERS reporter molecules on their surfaces were synthesised using a modification of a literature method.³ A solution of 2-naphthalenethiol (2.5 μL , 1.6 mM) in THF was added to an aqueous solution of Au-Ag alloy NPs. We term the resultant SERS-encoded nanoparticles Au-Ag@SERS. Thiol-terminated polystyrene⁴ (5 mg) was dissolved in inhibitor free THF (50 mL) and mixed with an aqueous solution of Au-Ag@SERS (50 mL) in a separating funnel, resulting in a colour change from yellow to brown. CHCl_3 (25 mL) was added and the organic and aqueous layers separated. The organic layer was collected and evaporated to dryness to afford a brown film. This film was re-dissolved in a small volume of inhibitor free THF and the desired grafted nanoparticles isolated by using centrifugation (7000 rpm for 30 min) as a brown solid. DLS analysis revealed the particles to possess hydrodynamic diameters of 32.6 ± 0.4 nm. We term the polymer-stabilized Au-Ag NPs encoded with SERS reporter molecules as PS/Au-Ag@SERS.

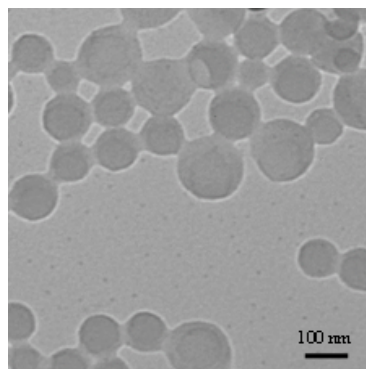
General Procedure for Miniemulsion Polymerizations

Polymer composite nanoparticles were prepared according to a modification of the route described by Hawker *et al.*⁴ 2,2'-Azobis-(2-amidinopropane) dihydrochloride (V-50) (7.5 mg) and cetyltrimethylammonium bromide (CTAB) (1.5 mg) were dissolved in 2 mL of deionized water. PS/Au-Ag@SERS were dispersed in the monomer phase (55 mg of divinylbenzene containing dispersed SiQDs), and the resulting mixture was added into the aqueous solution and emulsified by stirring vigorously (600 rpm) for 1 h. The emulsion mixture was then subjected to sonication over an ice bath for 15 min using a high intensity ultrasonic processor at 30% amplitude (VC750220, Fisher Scientific, tapered microtips, power: 750 W). The reaction vessel was fitted with a condenser inlet and the polymerization was performed at 50 °C under an atmosphere of N_2 with continuous stirring for 4 h. The resulting polymer nanocomposites were purified by dialysis against deionized water (overnight) and the purified polymer composites were stored as dispersions in aqueous solution. A TEM image of polymer nanoparticles prepared in the absence of metallic or SiQDs is shown in S1(b).

a)



b)



S1.(a) TEM image of Au-Ag alloy nanoparticles. (b) TEM image of polymer nanoparticles prepared in the absence of any metallic NPs or SiQDs.

Gel Permeation Chromatography (RAFT Polymer and Thiols Polymer)

Gel permeation chromatography (GPC) was performed using DMF/LiBr (1 gL^{-1}) as solvent at a flow rate of 0.6 mL min^{-1} on a Varian ProStar instrument (Varian Inc.) equipped with a Varian 325 UV-vis

dual wavelength detector (254 nm), a Dawn Heleos II multiangle laser light scattering detector (Wyatt Technology Corp.), a Viscotek 3580 differential RI detector and a pair of PL gel 5 μm Mixed D 300 x 7.5 mm columns with guard column (Polymer Laboratories Inc.) in series. Near monodisperse polystyrene standards (Polymer Laboratories) were used for calibration. Data analysis was achieved with Galaxie software (Varian Inc.) and chromatograms characterized with the Cirrus software (Varian Inc.) and Astra Software (Wyatt Technology Corp.).

UV-Visible Spectroscopy

UV-Visible absorption spectra of the aqueous Au-Ag NPs, PS/Au-Ag@SERS, Au-Ag polymer composite nanoparticles and Si/Au-Ag polymer composite nanoparticles were obtained using a Cary 100 Bio UV-visible spectrophotometer with 1 cm path length quartz cuvettes.

Dynamic Light Scattering

Particle size and particle size distributions of the monomer droplets and polymer nanoparticles were determined by dynamic light scattering (DLS) measurements using a HPPS (Malvern) instrument at 25 ± 0.1 °C and a scattering angle of 173° (backscatter detection). The monomer emulsion droplets or polymer nanoparticles (0.5 μL) were diluted with 10 mL of 2.47 mM SDS solution to avoid the diffusion of surfactant and monomer molecules from the monomer droplet into water. The sample solutions were then placed in low volume disposable PMMA cuvettes or in glass cuvettes (for Raman-active Au-Ag NPs in THF) and measurements were performed five times. Data is presented (T1).

Nanoparticle	Droplets		Purified Latex	
	D_h (nm)	PDI	D_h (nm)	PDI
Composite NPs absent in SiQDs	219.8 ± 3.7	0.32 ± 0.05	221.4 ± 2.5	0.30 ± 0.06
Composite NPs	206.3 ± 2.9	0.29 ± 0.08	205.8 ± 1.3	0.17 ± 0.01

T1: Dynamic light scattering measurements for the composite NPs absent in SiQDs (entry 1) and composite NPs (entry 2) (D_h = Hydrodynamic diameter ; PDI = polydispersity index)

Transmission Electron Microscopy (TEM)

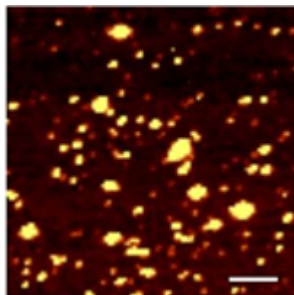
Samples for TEM were prepared by drop casting 20 μL of the polymer nanoparticle emulsion onto the surface of plastic film (parafilm). The face of a glow discharge-treated carbon support film on 400 mesh copper EM grid was then placed in contact with the sample solution and the polymer emulsion solution transferred onto the grid was then diluted by placing in contact with water droplets on the plastic film. The edge of a filter paper was used to wipe-off the excess sample solution on the TEM grid and the samples left to dry in air for approximately 5 min. Transmission electron microscopy (TEM) measurements were performed at ambient temperature using a Zeiss EM900 operated at 80 kV. Electron micrographs were recorded on Kodak type 4489 electron image film.

Confocal Microspectroscopy (Luminescence & Raman)

Luminescence and Raman spectra were obtained using a confocal Raman microscope (WiTec model CRM200, Ulm, Germany). A high intensity argon ion laser (Melles-Griot) with output power 35 mW at a wavelength of 488 nm was used as the excitation source. The collected light was analysed by a spectrograph equipped with a CCD detector; a grating with 150 lines per mm was chosen in order to capture the full spectrum including all Raman and luminescence bands of interest. Some higher resolution Raman spectra were obtained by using a grating with 600 lines per mm. All experiments were performed at scan size of 50×50 μm with 100 lines at 100 pixels per line and an integration time of 0.2 s per pixel. An emulsion solution of polymer composite nanoparticles dispersed in aqueous solution was drop cast onto glass cover slips for observation by confocal microspectroscopy.

S2. Confocal luminescence spectrum image of composite NPs. The colour scale represents the integral of the spectral intensity from a Raman shift of 200 cm^{-1} to 7000 cm^{-1} , which corresponds to a

mixture of luminescence and Raman signals which are analysed below. Scale bar = 10 μm and scan size = 50 x 50 μm .



References

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- 2) S. Link, Z. L. Wang and M. A. El-Sayed, *J. Phys. Chem. B.*, 1999, *103*, 3529-3533.
- 3) Z. Merican, T. L. Schiller, C. J. Hawker, P. M. Fredericks and I. Blakey, *Langmuir* 2007, *23*, 10539-10545.
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