Supplementary Material (ESI) for Chemical Communications

Simultaneous Templating of Polymer Nanocapsules and Entrapped Silver Nanoparticles

Sergey Shmakov and Eugene Pinkhassik

Supplementary Information

Chemicals

All solvents used were HPLC grade. 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) was purchased from Avanti Polar Lipids, Inc. as a dry powder. p-divinylbenzene (DVB), tert-Butylstyrene (tBuSt), methanol and Sephadex G-50 (medium) were purchased from Sigma-Aldrich. DVB and tBuSt were passed through alumina column to remove the inhibitor. Sephadex G-50 (10 g) was swollen in 120 mL of water in a glass screw-capped bottle for at least 5 h at room temperature and stored at 4 °C until required for use. All other chemicals were not further purified before use.

Synthesis of nanocapsules with entrapped silver nanoparticles

Nanocapsules with entrapped silver nanoparticles were prepared by the following procedure: tert-Butylstyrene (24 μL, 1.33×10^{-5} mol), p-divinylbenzene (19 μL, 1.33×10^{-5} mol), and 2,2-dimethoxy-2-phenylacetophenone, DMPA, (UV initiator; 0.33 mg, 1.3×10^{-6} mol) were added to a solution of DMPC (60 mg, 8.85×10^{-5} mol) in $CHCl_3$. The monomers were purified on a column of neutral alumina prior to addition. The $CHCl_3$ was evaporated using a stream of purified argon to form a lipid-monomer film on the wall of a culture tube. The film was further dried under vacuum for 30 min to remove traces of $CHCl_3$. The dried film was hydrated with 10^{-2} mol solution of $AgNO_3$ in deionized water to give a dispersion of multilamellar vesicles, which was then extruded at 35 °C through a polycarbonate Nucleopore track-etch membrane (Whatman) with 0.1-m pore size using a Lipex stainless steel extruder (Northern Lipids). Prior to polymerization, unloaded silver ions were removed from the mixture by size-exclusion chromatography on Sephadex G-50 column. Oxygen was removed by passing purified argon through the solution. The sample was irradiated (λ=254 nm) in a photochemical reactor equipped with a stirrer (10 lamps of 32 W each; 10-cm distance between the lamps and the sample) for 60 min. Methanol (10 mL) was added, and the precipitate was washed 3-5 times with methanol.

For DLS measurements and UV-spectroscopy prepared nanocapsules were resuspended in Triton X-100 solution in water (0.5 mL, 2 %) by stirring for 1 h at ambient temperature.

For XRD study nanocapsules were resuspended in benzene, and freeze-dried.

X-Ray Diffraction Measurements

XRD spectra were collected on a Bruker D8 Advance X-ray diffractometer using Cu Ka radiation at 40 kV and 40 mA. The diffraction pattern were obtained in the 2θ scan range 30-75^{o} with a step size of 0.05 and a time/step of 0.2 s.

Transmission Electron Microscopy (TEM)

TEM images were acquired on a JEOL JEM1200EXII microscope. Samples were negatively stained with phosphotungstic acid (pH 5.9) on a carbon grid.

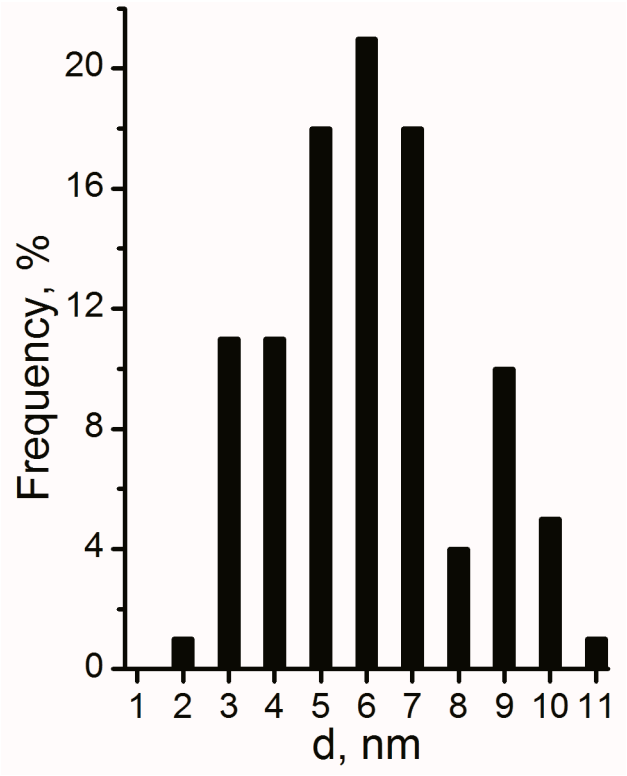

Figure 1. Size distribution of entrapped Ag NPs.

Mean diameter of Ag NPs is 5.5 and standard deviation is 2.0. Calculation was carried out for 300 NPs from 4 different TEM pictures.

Dynamic Light Scattering (DLS)

Hydrodynamic diameter measurements were performed on a Malvern Nano-ZS zetasizer (Malvern Instruments Ltd., Worcestershire, U.K.). The Helium−Neon laser, 4mW, operates at 633 nm, with the scatter angle fixed at 173°, and the temperature at 25 °C. 80 µL samples were taken from the reaction vials with a pipet and were placed into disposable cuvettes without dilution (70 µL, 8.5 mm center height Brand UV-Cuvette micro). At least 10 scans were collected from each sample.

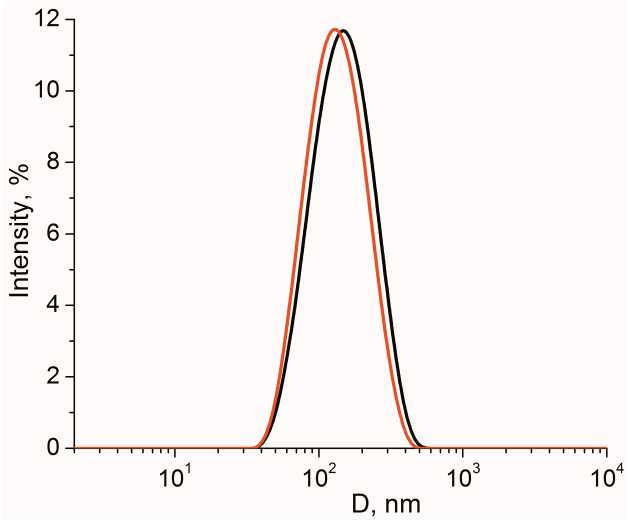

Figure 2. DLS curves for organic NCs containing silver NPs before UV irradiation (red) and after (black).

UV/VIS Spectroscopy

UV spectra were recorded on Agilent Technologies 8453 UV spectrophotometer in quartz cuvette in the range 200-700 nm.

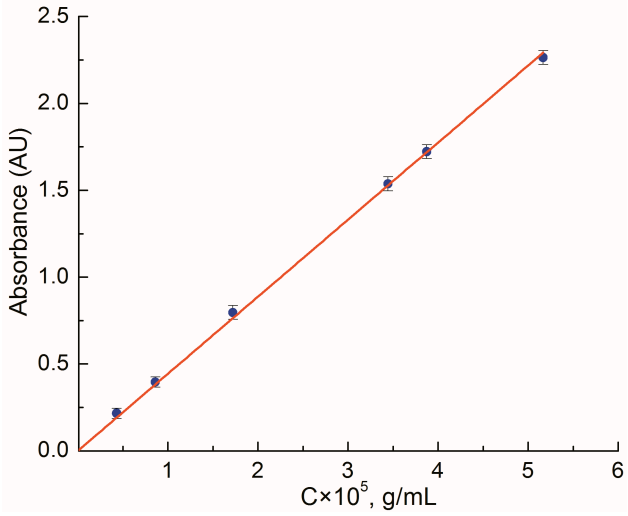

Figure 3. Calibration plot for DMPA dilution in methanol

Molar extinction coefficient (ε) for 2,2-dimethoxy-2-phenylacetophenone in MeOH was determined (at λ_{max}=253 nm) to be 12200±100 L mol^{-1} cm^{-1}.