

Electronic Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

for

Template-Directed Synthesis of Uniformly-Sized Silver Nanoparticles with High Colloidal Stability

Maitane Salsamendi, Peter A. G. Cormack* and Duncan Graham

Corresponding author address:

Maitane Salsamendi: Polymat, University of the Basque Country, Joxemari Korta *I+D+i* center, Avda. Tolosa 72, 20018 Donostia-San Sebastián, Spain.

Fax: +34-943-017065; Tel: +34-943-018475; E-mail: maitane.salsamendi@ehu.es

EXPERIMENTAL PROCEDURES

Materials

All the materials were purchased from Sigma Aldrich unless stated otherwise. All of them were used as received.

Synthesis of poly[(*N*-ethyl-3-hydroxymethyl)triazole methacrylate] (PEHTMA)

Step 1 (Synthesis of poly(2-chloroethyl methacrylate) PCIEMA): 3 g of poly(2-hydroxyethyl methacrylate) (polyHEMA) with average $M_v \sim 20000$ (23.1 mmol -OH groups) were dissolved in 30 ml of dry DMF and the solution was cooled for 3 hours in an ice bath. *p*-toluene sulfonylchloride (8.8 g, 46.2 mmol) and pyridine (3.3 ml, 46.2 mmol), each one solved in 15 ml of dry DMF separated flask and were simultaneously added drop-wise to the previous solution. The reaction was stirred under nitrogen at 50 °C for 3 days. The polymer was precipitated into H₂O and washed with H₂O and Methanol. After filtration, the filtrate was dried under vacuum to give a white powder (3.03 g, 89%). The substitution of hydroxyl groups to deliver chloroethyl-containing polymer was 100% (See FTIR spectra). ¹H-NMR (DMSO-*d*₆): 4.16 (b, 2H, OCH₂), 3.82 (b, 2H, CH₂Cl). Elemental analysis: C, 48.5; H, 6.06; Cl, 23.88; S, 0; found: C, 48.99; H, 6.09; Cl, 22.57; S, 0.66%.

Step 2 (Synthesis of poly(2-azidoethyl methacrylate) PAEMA): PCIEMA (2.8 g, 18.9 mmol -Cl groups) and sodium azide (2.5 g, 37.8 mmol) were mixed in 60 ml of dry DMF. The reaction was stirred under nitrogen at 60 °C for 2 days. The polymer was precipitated into H₂O. The product was filtered and dried under vacuum to give a slightly orange powder (2.6 g, 88%). The nucleophilic substitution of chlorine groups with azide to yield PAEMA was 100 % (See FTIR spectra). ¹H-NMR (DMSO-*d*₆): 4.06 (b, 2H, OCH₂), 3.54 (b, 2H, CH₂N₃).

Step 3 “click” reaction (Synthesis of poly[(*N*-ethyl-3-hydroxymethyl)triazole methacrylate] PEHTMA): PAEMA (50 mg, 0.3 mmol -N₃ groups) and propargyl alcohol (19 μl, 0.3 mmol) were solved in 15 ml of dry DMF. Then, a solution of copper acetate (11.7 mg, 0.065 mmol) and triphenylphosphine (33.8 mg, 0.13 mmol) in 5ml of dry DMF was added drop-wise. The reaction was stirred under nitrogen at room temperature for 2 hours. A column extraction of Cu(II) was carried out by a porous chelating resin based on poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate and pendant 2-aminomethylpyridine groups). The polymer was precipitated into ethyl acetate. The crude was filtered and dried under vacuum to give a slightly yellow powder (49 mg, 72%). The azide-alkyne cycloaddition to obtain hydroxyethyl triazole groups was quantitative (See FTIR spectra). ¹H-NMR (DMSO-*d*₆): 8.04 (b, 1H, *triazole* ring), 5.22 (b, 1H, OH). Elemental analysis: C, 51.18; H, 6.16; N, 19.91; Cl, 0; found: C, 49.15; H, 5.73; N, 15.37; Cl, 0.38%. ICP-MS: Initial copper concentration 176 mg/l, final copper concentration 27 mg/l (84% Cu(II) is extracted).

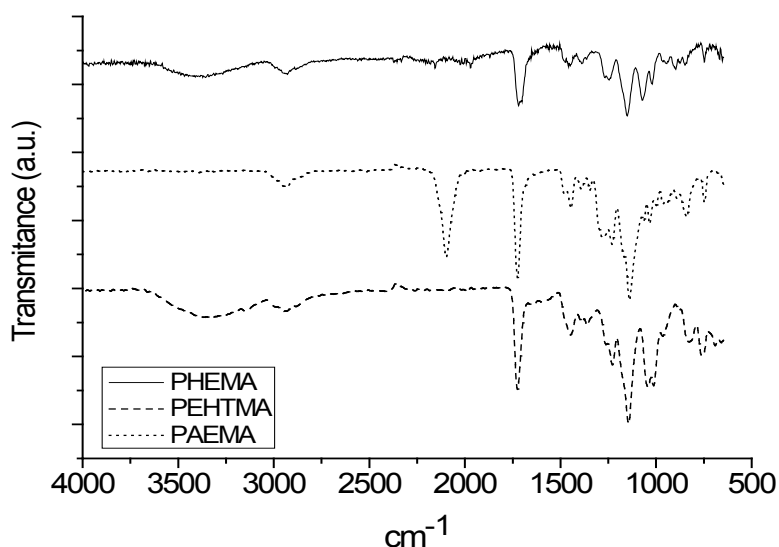
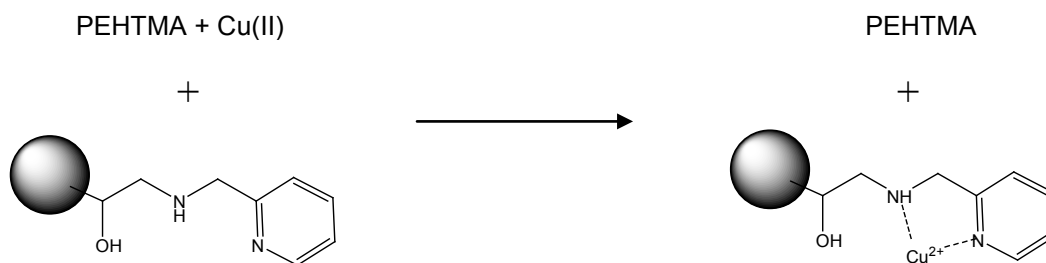


Figure S 1: Comparison of FT-IR spectra of PHEMA, PAEMA and PEHTMA.

The total conversion of initial hydroxyl groups to azide groups first (in the first two steps) and to hydroxymethyltriazole groups later on, was studied by FT-IR spectroscopy. The hydroxyl band at 3390 cm^{-1} in polyHEMA was disappeared and a new peak at 2102 cm^{-1} corresponding to azide groups was obtained in PAEMA. After a “click” reaction, the complete disappearance of the azide group peak was observed, and a new band again at 3380 cm^{-1} in PEHTMA was appeared due to the generation of the new hydroxyl groups.

Removing Cu(II) from PEHTMA

A porous polymer resin (poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate)) with a chelating ligand (2-aminomethylpyridine) attached on it was used to extract the Cu(II) from the PEHTMA solution. The resin with a ligand was developed at the University of Strathclyde^[1, 2] in collaboration with BP.



The column extraction of the copper was characterized by the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (the results are mentioned above).

Synthesis of silver-citrate nanoparticles (Ag-Citrate)

All glassware was cleaned with aqua regia and thoroughly rinsed with distilled water. Ag-Citrate nanoparticles were prepared according to the Lee & Meisel procedure.^[3] A clean three necked round bottom flask was filled with 500 mL of Milli Q water. The solution was heated to 45 °C with a Bunsen burner under continuous stirring with a glass stirrer. Then silver nitrate (90 mg dissolved in 10 mL of Milli Q) was added. The solution was heated further to 98 °C. Tri-sodium citrate (100 mg in 10 mL Milli Q) was added and the solution was kept at 98 °C for 90 minutes and afterwards allowed to cool to room temperature.

Synthesis of silver-PEHTMA nanoparticles (Ag-PEHTMA)

Reaction parameters			
Temperature (°C)	RT	60	100
Triazole, AgNO ₃ Concentration (mM)	0.5	1.5	
Solvent ratio DMF:H ₂ O	7:3	5:5	3:7
Ag:Triazole ratio	1:1	10:1	50:1

The optimization of the synthesis conditions was carried out carefully by the extinction spectroscopy. All the reaction parameters varied for that purpose are summarized in the table above. The parameter values in bold are the best ones in terms of stability, reaction duration or narrow particle size distributions.

Preparation of the sample Ag-Citrate-PEHTMA

50 µl of PEHTMA solution in DMF (15 mM) were poured in the vial and 50 µl of Ag-Citrate in H₂O was added. The mixture was diluted in 500µl of DMF and H₂O in order to fix the DMF:H₂O ratio in 7:3.

The synthesis of silver NPs was not templated in this case by PEHTMA, but the polymer was added to the as-synthesised Ag-Citrate solution. The multidentate polymer PEHTMA should remove the citrate from the silver surface and form a chelate complex with the nanoparticles covering and stabilizing them.

CHARACTERISATION METHODS FOR Ag-PEHTMA, Ag-Citrate AND Ag-Citrate-PEHTMA

Nuclear Magnetic Resonance (NMR)

¹H NMR spectra were recorded, unless stated otherwise, at room temperature on Bruker Avance 400 instrument at 400 MHz; chemical shifts are given in ppm.

Elemental Analysis

Elemental analyses were conducted on a Perkin Elmer 2400.

FT-IR Spectroscopy: Attenuated Total Reflectance (ATR)

IR spectra were recorded on an ATR Shimadzu spectrometer.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The mass spectra were recorded on Agilent 7700 inductively coupled plasma mass spectrometer.

UV-Visible (UV-Vis) spectroscopy

UV-Vis spectroscopy was carried out on a Varian Cary 300 BIO spectrophotometer using 1 cm path quartz cells. Nanoparticle concentrations were calculated by Beers law using the extinction coefficient for silver nanoparticles of $2.87 \cdot 10^{10} \text{ M}^{-1} \text{ cm}^{-1}$, derived from literature.^[4]

Transmission electron microscopy (TEM)

The TEM imaging was carried out in a Leo in-column EFTEM with OMEGA spectrometer operating at an accelerating voltage of 120 kV.

To determine the particle size, the diameter of 40 different particles were measured by the software of the TEM and the relative standard deviation (RSD) was calculated.

Scanning electron microscopy (SEM)

For the particle sample depositions silicon wafers (Agar Scientific) were cleaned with methanol and oxygen plasma (Diener electronic femto oxygen plasma cleaner, 72 cm³/min gas flow) to produce a negatively charged surface for better adhesion of the cationic particles. Imaging was carried out on a Sirion 200 Schottky field-emission electron microscope (FEI) operating at an accelerating voltage of 5 kV. Image analysis was carried out using Image J, v1.43u.

ζ-potential

The ζ (Zeta) potential measurements were carried out using a Malvern 2000 Zetasizer, using the default method protocol and a minimum sample volume of 3 ml. Before each measurement a standard solution of -68.0 ± 6.8 mV was measured.

CHARACTERISATION OF SILVER NANOPARTICLES

Characterisation by Scanning Electron Microscope (SEM)

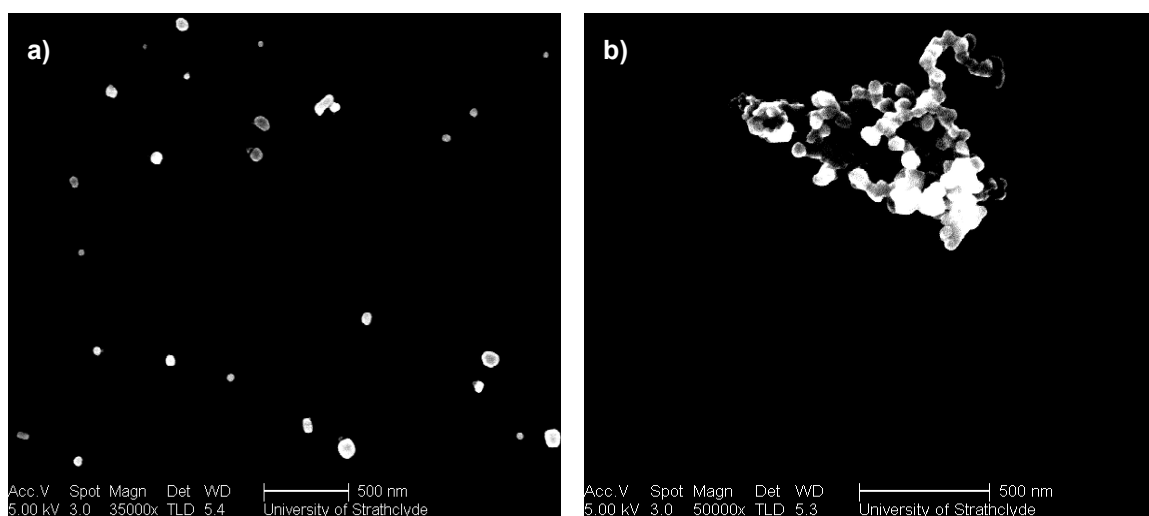


Figure S 2: SEM images of a) Ag-Citrate and b) Ag-Citrate-PEHTMA.

The SEM characterisation of Ag-Citrate and Ag-Citrate-PEHTMA was carried out. The Figure S 2a shows a broad particle size distribution obtained for the Ag-Citrate sample. The Figure S 2b shows that in the sample Ag-Citrate-PEHTMA the nanoparticles were covered by polymer chains, and that makes them not to be well focused.

Silver NP size distributions on different samples

The chemical structure of the stabilizer as well as the synthesis method, play an important role in order to control the size distribution, stability and reproducibility of the metallic particles. Here we report two different stabilizers (Citrate and PEHTMA) and three NPs synthesis/stabilization methods (templated or not templated) that are monitored by extinction spectroscopy, by SEM and by TEM in Figure S 3, Figure S 2 and Figure 1b respectively.

The silver NPs templated by PEHTMA show very narrow size distribution (FWHM = 89nm) (Figure S 3 solid) as well as a high reproducibility while the particles stabilized by sodium citrate are polydispersed (FWHM = 130nm) (Figure S 3 dot; Figure S 2a). On the other hand, Ag-

citrate-PEHTMA (synthesis of NPs is not templated by PEHTMA) showed also a broad particle size distribution (FWHM > 150nm) (Figure S 3 dash).

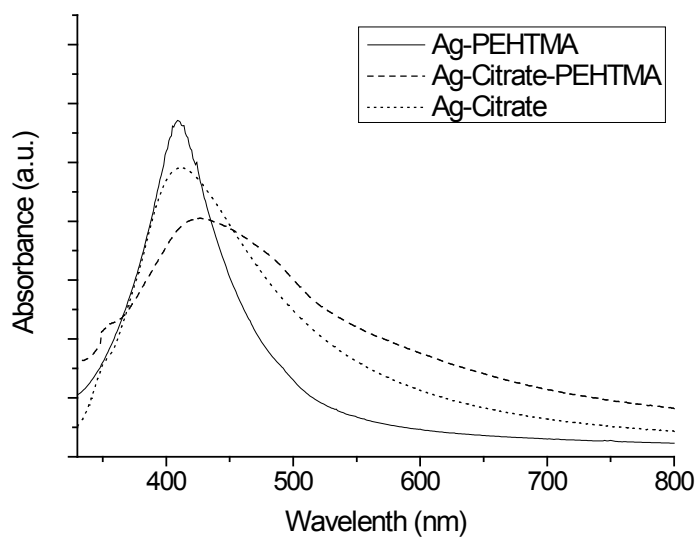


Figure S 3: The UV-vis spectrogram to compare the SPR band of Ag-Citrate, Ag-PEHTMA and Ag-Citrate-PEHTMA.

Stability of Ag-PEHTMA, Ag-Citrate and Ag-Citrate-PEHTMA in NaCl

The total volume of the samples, the concentration of the silver NPs and the concentration of the sodium chloride were fixed at 500 μ l, 11.5 pM and 0.1 M or 0.3 M respectively. The solutions were stirred and the extinction characterisation was performed every ten minutes to study the evolution of the SPR band with the time.

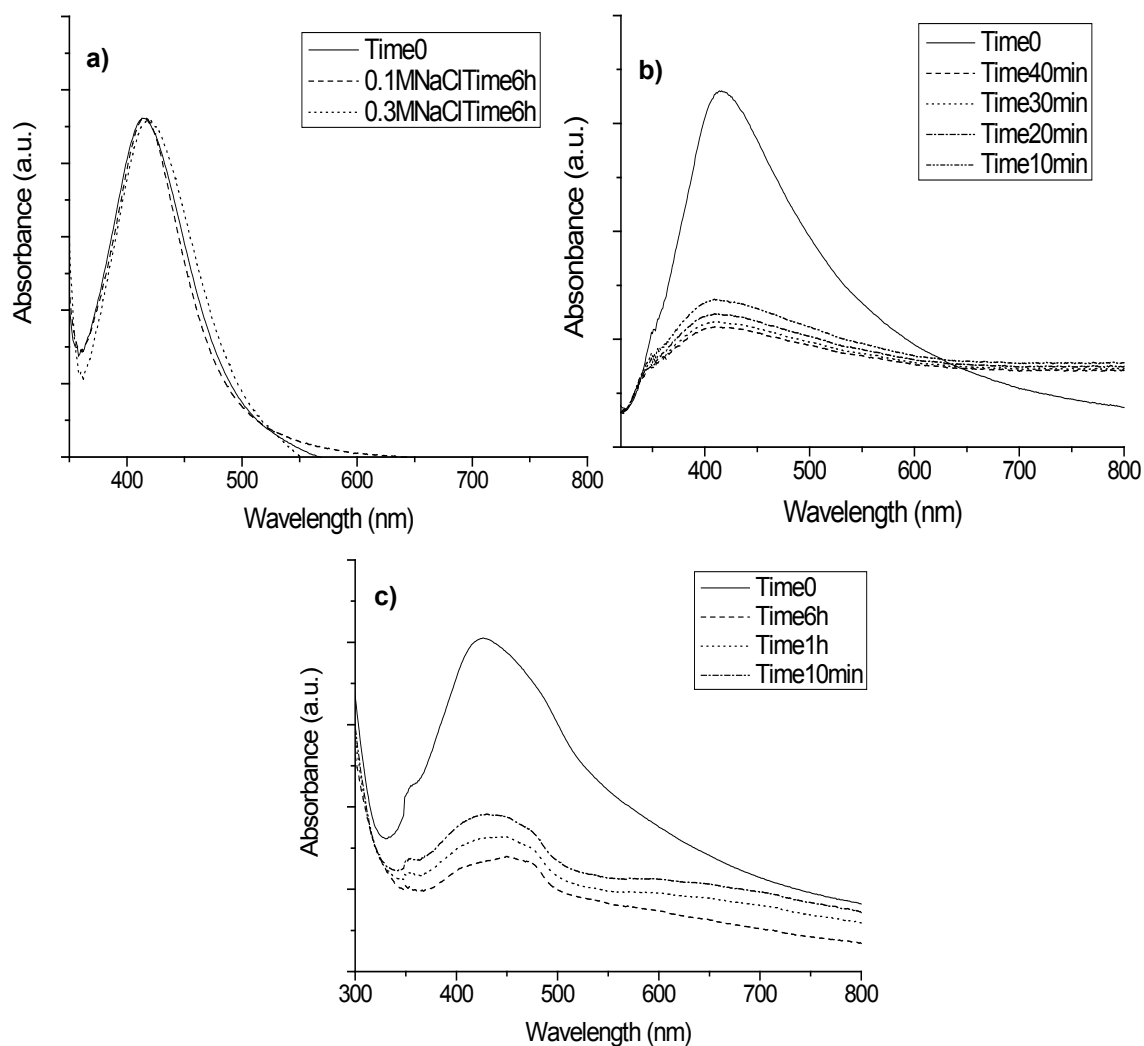


Figure S 4: UV-vis spectrogram to compare the stability of a) Ag-PEHTMA in 0.1M NaCl and 0.3M NaCl, the stability of b) Ag-Citrate in 0.3M NaCl and the stability of c) Ag-Citrate + PEHTMA in 0.3M NaCl.

PEHTMA was added to as-synthesised Ag-citrate solution in order to compare the templating effect of PEHTMA. Figure S 4a and c show that the silver nanoparticles templated by PEHTMA are more stable and less corrosive in NaCl than those synthesised in sodium citrate and then stabilised with PEHTMA.

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