Photochemical generation of small silver nanoparticles involving multi-functional phosphonated calixarenes

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Silver nanoparticles less than 5 nm in diameter are accessible by a simple photochemical reduction in water, templated by *p*-phosphonated calix[4]arene and its O-alkyl derivatives, in a way depending on the pH of the reagent solution.

The synthesis of very small metal nanoparticles less than 5 nm in diameter is of interest for various applications, including in biomedical, optoelectronic and catalytic studies.[1] Their synthesis usually involves the use of strong and toxic reducing agents, such as sodium borohydride or hydrazine. In addition, the use of thio- and amino-alkanes are required, as well as phase-transfer agents, which features in the Brust method.[2] More benign routes for preparing nanoparticles are becoming important as part of a drive to develop sustainable technologies for the future. This is highlighted by the number of different greener methods being reported to generate metal nanoparticles.[3–8] One of these methods for generating small metal nanoparticles, for example, involves the use of sodium citrate and tannic acid for the production of gold nanomaterials with a diameter of approximately 6 nm.[9] Recently, we reported a method for preparing small silver nanoparticles with a diameter of 2 to 4 nm incorporating green chemistry principles using hydrogen gas as a reductant, in the presence of phosphonated calix[*n*]arenes, **1**, or polyphosphate templates.[10] The latter method has been extended to using a continuous-flow narrow channel reactor, which affords particles with a diameter of 3 to 5 nm.[11] In both of these methods alkaline conditions and elevated temperatures are required for the reactions to occur at an appreciable rate, and to be of practical convenience.

We now report an attractive green chemistry method for the synthesis of small silver nanoparticles involving photochemical reduction in the presence of water-soluble phosphonated calix[*n*]arenes, Fig. 1. Photochemical techniques have previously been reported for the synthesis of fluorescent silver nanoclusters using poly(acrylic acid) and poly(methacrylic acid),[12,13] for the production of silver nanoprisms,[14,15] and other morphologies where the shape is dependent on the wavelength of irradiation for samples containing small silver seed nanoparticles.[16–18]

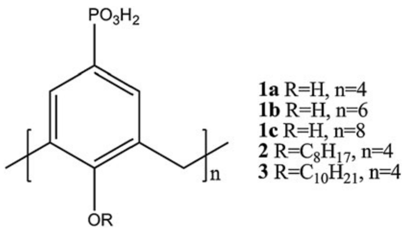

Fig. 1 General structure of the phosphonated calix[*n*]arenes.

The new synthesis herein of the silver nanoparticles was effected by exposing a small volume of aqueous solution (3 mL) containing silver nitrate and phosphonated calix[*n*]arene at a specific pH, to a high-intensity 100 W UV-lamp emitting 365 nm light. This was compared to a control solution of the same composition which was stored in a dark environment where there was no evidence for reaction between the *p*-phosphonated calix[*n*]arene and silver ions over one week.

Samples were irradiated for various times (10 to 60 min), and the extent of the reaction was monitored using UV-Vis absorption spectroscopy. The study mainly focused on using the parent compound *p*-phosphonated calix[4]arene, **1a**,[19,20] and for two different alkyl chain lengths, **2** and **3**. This was deemed appropriate given that these compounds can then decouple any effect of the O-alkyl substitution *versus* O–H at the so-called lower rim of the calixarene, for molecules that are all accessible in the cone conformation, and then to ascertain the effect of varying the length of the alkyl chain.

The initial conditions used were similar to those previously reported for the aforementioned hydrogen reduction method, namely 0.25 mM phosphonated calix[4]arene and 1 mM $AgNO_3$ at pH 9.[10] The size of the silver nanoparticles produced was established using transmission electron microscopy (TEM), the average size being 3.6 ± 1.2 nm after 60 minutes irradiation, Fig. 2(a). The particle size did not vary significantly over time, which is also confirmed by the consistency of the UV-Vis absorption spectra, Fig. 3. The optical properties of the colloidal solution over time are shown in Fig. 3, and clearly show the presence of a silver plasmon absorption peak that increases in intensity with extended reaction time.

Unlike the hydrogen reduction method, the photochemical reduction can take place over a wide pH range. For the reduction to occur at a reasonable rate using hydrogen, the Ag^+ ions are first bound to the phosphonated calixarene, which occurs in alkaline conditions, and during the reaction protons are formed and the solution becomes acidic. During

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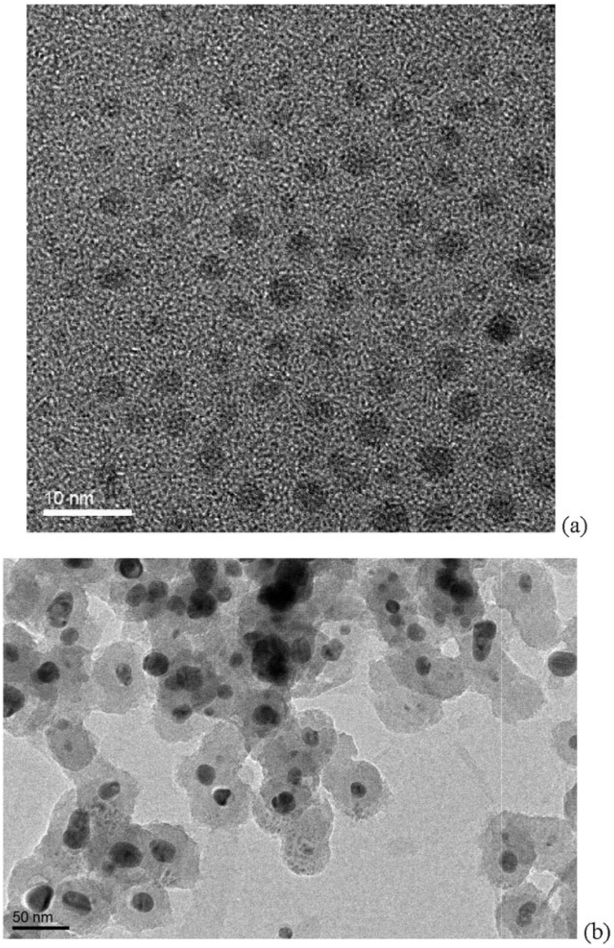

Fig. 2 Silver nanoparticles produced using 0.25 mM *p*-phosphonated calix[4]arene, **1a**, after 10 minutes exposure to 365 nm light; (a) pH 9, (b) pH 2.

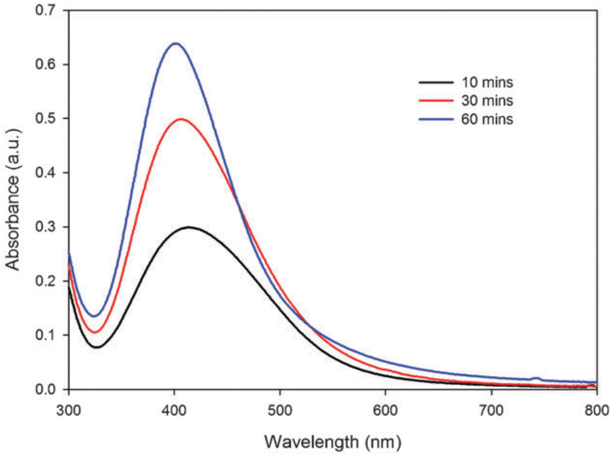

Fig. 3 UV-Vis spectra of photochemically produced Ag nanoparticles using 1 mM $AgNO_3$ and 0.25 mM *p*-phosphonated calix[4]arene, **1a**, at pH 9.

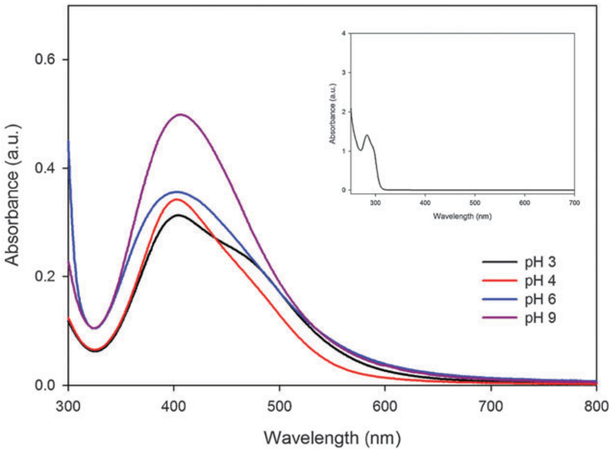

Fig. 4 Influence of solution pH on optical properties of Ag nanoparticles photochemically generated using a 1 mM $AgNO_3$ and 0.25 mM *p*-phosphonated calix[4]arene, **1a**, after 30 minutes irradiation. Inset: UV-Vis spectrum of $AgNO_3$/phosphonated calix[4]arene solution before exposure to 365 nm light.

the photochemical reduction there was no change in solution pH over time, and the particle size did not change significantly until pH 2, whereupon large Ag nanoparticles with an average size of 18.5 ± 6.3 nm were produced, Fig. 2(b). The resulting particles were surrounded by a 20–30 nm thick shell of phosphonated calix[4]arene, **1a**, and this relates to the pH approaching the pK_{a1} of phosphonic acid, that being 1.3,[21] noting that phosphonated calix[4]arene is only sparingly soluble at low pH.[17]

Although the particle size does not change significantly over a wide pH range, the absorption intensity of the plasmon peak is greater under more alkaline conditions, as observed by comparison of UV-Vis absorption spectra after a specific time, Fig. 4, and a shoulder emerges at longer wavelengths at lower pH.

In addition to varying the pH of the solution, the effect of calixarene ring size was also examined. We again found that there was little influence of the ring size on the size of the silver nanoparticles, as was the case using hydrogen as the reducing agent, and the reaction rate was also similar for all ring sizes, for calixarenes **1a**, **1b**, and **1c**.

The mechanism of this reaction is unclear, but similar experiments using related polyelectrolytes, including polyphosphates and poly(vinyl phosphonic acid), did not facilitate the photochemical reduction reaction over a wide pH range. This suggests that the calixarene, rather than the phosphonate group, is required for the reaction to proceed. Photolytic excitation of the calixarene with transfer of an electron to the silver species is likely, but the nature of the oxidised calixarene species has not been established, despite several attempts to do so. Examination of the UV-Vis absorption spectrum of a *p*-phosphonated calix[4]arene solution reveals an absorption band over a range from 330–265 nm, inset, Fig. 4. This suggests that the excitation wavelength used is outside the optimal range for photochemical reduction, and the use of shorter wavelength light is likely to lead to an increase in the rate of the reaction.

Since the presence of a calixarene is essential for the photochemical reduction to occur, phosphonated calix[*n*]arenes were replaced with another water-soluble calixarene, namely *p*-sulfonated calix[4]arene, where PO_3H_2 is substituted with SO_3H. Under the same experiment conditions for **1a**, a

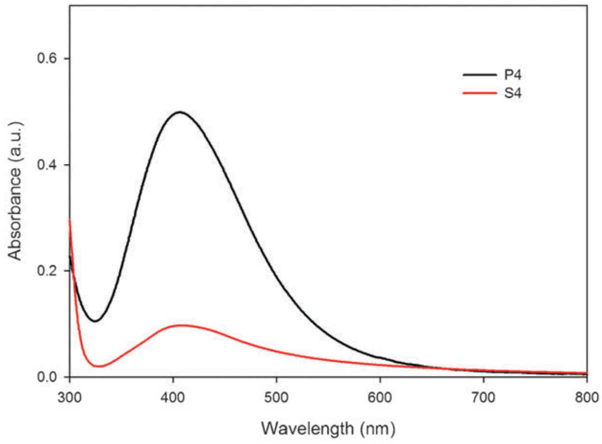

Fig. 5 Comparison of optical properties of colloidal silver solutions prepared in the presence of *p*-sulfonated calix[4]arene, and *p*-phosphonated calix[4]arene, **1a** (S4 and P4, respectively), at pH 9 after 30 minutes.

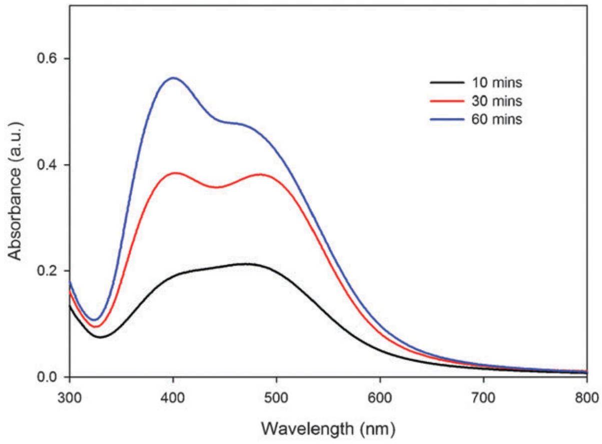

Fig. 6 Optical properties of colloid silver solutions prepared in the presence of *n*-octyl phosphonated calix[4]arene, **2**, in the cone conformation, at pH 12 after various irradiation times.

reaction took place but at a much lower rate, as established using UV-Vis absorption spectroscopy, Fig. 5. Nevertheless, the particle size is similar to that observed with phosphonated calixarenes.

In the presence of alkylated phosphonated calix[4]arenes, **2** and **3**, all in the cone conformation, different optical properties of the product were observed, now with two distinct absorption peaks in the UV-Vis absorption spectra, Fig. 6. TEM images only revealed the presence of very small particles, 2.6 ± 0.8 nm, with no anisotropic particles, such as rods or prisms, which could have explained the additional absorption at ~485 nm.[22] However, the same peak could be indicative of small silver nanoclusters that cannot be observed by TEM under the imaging conditions used, with similar UV-Vis spectra having recently been observed for fluorescent silver nanoclusters prepared by photochemical and sonochemical methods in the presence of poly(methacrylic acid).[12,13,23] Over time, the silver nanoparticle plasmon resonance peak at ~400 nm becomes dominant. Much higher concentrations of calixarene, 1 mM, were used in these cases, but similarly high concentrations of calixarenes devoid of alkyl groups did not show these unusual optical properties.

We have established the use of an alternative, simple aqueous reduction technique for the synthesis of small silver nanoparticles using a photochemical technique. In comparison to the previously reported method using hydrogen as the reducing agent, for similar size nanoparticles of silver, the photochemical reaction occurs over a wide pH range. Moreover, the photochemical reaction occurs at ambient temperature at a similar rate to the method involving hydrogen, which in contrast occurs at elevated temperatures.[10]

The presence of the phosphonated calixarene is essential for reduction to take place, and while the reaction also takes place in the presence of sulfonated calixarenes it is much slower. Clearly the phosphonate group is more effective in the photochemical reduction of silver, and presumably the process is facilitated by complexation of silver to the phosphonate group. The phosphonated calixarene then controls the growth and size of the nanoparticles, as for the hydrogen reduction method,[10] as well as stabilising the particles through complexation. Stabilisation could also involve the build up of bilayers of the calixarenes, of the type which have been established in continuous structures for Ca^{2+} complexes of *p*-phosphonate calixarene,[24] and for the parent phosphonic acid itself.[19] Indeed, the large organic shell formed around silver nanoparticles at low pH may be comprised of such layers.

Experimental

The synthesis of silver nanoparticles was undertaken by exposing an aqueous solution containing *p*-phosphonated calix[*n*]arene **1a**, **1b**, **1c**, **2**, or **3** and 1 mM silver nitrate (3 mL) in a glass vial to 365 nm radiation for a specified period of time. The calix[*n*]arenes **1a**, **1b**, and **1c** were prepared by established literature procedures,[19,20] and the preparation of **2** and **3** is described below. A UVP Blak-Ray B-100A 100 W, 365 nm spotlight lamp was used as the source of UV radiation. TEM characterisation was carried out with a JEOL 3000F operating at 300 kV or a JEOL 2100 operating at 200 kV. Samples for TEM were prepared by diluting the product with water in the ratio of 1 : 10 and placing a 6 μL drop onto a 200 mesh copper grid covered by a holey amorphous carbon film (SPI supplies). UV-Vis absorption spectroscopy was recorded with a Varian Cary 50 Tablet UV-Visible Spectrophotometer using quartz cuvettes with a path length of 1 cm and water as the reference material.

5,11,17,23-Tetra(dihydroxyphosphoryl)25,26,27,28-tetraoctoxycalix[4]arene (2)

Compound **2** was synthesised in the same manner as previously described for the synthesis of other phosphonated calix[4]arenes with modified lower-rim functionalities,[25] using 1-bromooctane for O-alkylation of the lower-rim of the calixarene. Mp > 300 °C (decomp.); IR (KBr) 3413 (s), 2910 (s), 2854 (s), 1618 (m), 1460 (m), 1384 (w), 1271 (m), 1125 (m), 1007 (m) cm^{-1}; ^1H NMR (DMSO, 25 °C, 400 MHz) δ 6.95 (s, 8H, Ar*H*), 6.32 (br s, 8H, O*H*), 4.31 (d, 4H, ArCH_2Ar), 3.84 (t, 8H, OCH_2), 3.26 (d, 4H, ArCH_2Ar), 1.82

(m, 8H, CH_2), 1.19–1.29 (br s, 40H, CH_2), 0.83 (t, 12H, CH_3); ^{13}C NMR (DMSO, 25 °C, 400 MHz) δ 158.59, 134.19, 130.74, 74.87, 32.10, 31.52, 30.22, 29.96, 29.56, 29.22, 29.04, 26.03, 22.21, 13.78; ^{31}P NMR (DMSO, 25 °C, 300 MHz) δ 21.22; HRMS (FAB) m/z calcd for $(C_{60}H_{92}O_{16}P_4 + H)^+$ 1193.5344, found 1193.5445.

5,11,17,23-Tetra(dihydroxyphosphoryl)25,26,27,28-tetradecoxycalix[4]arene (3)

Compound **3** was prepared in the same manner as previously described for the synthesis of other phosphonated calix[4]-arenes with modified lower-rim functionalities,[25] using 1-bromodecane for O-alkylation of the lower-rim of the calixarene. Mp > 300 °C (decomp.); IR (KBr) 3445 (m), 2910 (s), 2854 (s), 1594 (m), 1464 (m), 1404 (w), 1273 (m), 1128 (m), 983 (m) cm^{-1}; ^{1}H NMR (DMSO, 25 °C, 600 MHz) δ 6.96 (br s, 8H, ArH), 6.27 (br s, 8H, OH), 4.29 (br s, H, ArCH_2Ar), 3.78 (br s, 8H, OCH_2), 3.21 (br s, 4H, ArCH_2Ar), 1.77 (m, 8H, CH_2), 1.10–1.35 (br s, 48H, CH_2), 0.78 (s, 12H, CH_3); ^{13}C NMR (DMSO, 25 °C, 600 MHz) δ 158.43, 133.99, 130.55, 74.86, 31.54, 30.57, 29.79, 29.52, 29.11, 26.17, 22.20, 13.55; ^{31}P NMR (DMSO, 25 °C, 300 MHz) δ 16.85; HRMS (FAB) m/z calcd for $(C_{68}H_{108}O_{16}P_4 + H)^+$ 1304.6566, found 1305.2571.

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