Sonochemical Synthesis of Highly Fluorescent Ag Nanoclusters

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ARTICLE

ABSTRACT Highly fluorescent, stable, water-soluble Ag nanoclusters have been successfully prepared *via* a convenient sonochemical approach using a simple polyelectrolyte, polymethylacrylic acid (PMAA), as a capping agent. The optical and fluorescence properties of the Ag nanoclusters can be easily controlled by varying the synthetic conditions, such as sonication time, stoichiometry of the carboxylate groups to Ag^+, and polymer molecular weight.

KEYWORDS: fluorescence · nanoclusters · silver · sonochemistry · ultrasound

Even smaller than nanoparticles, noble metal nanoclusters consist of several to ~100 metal atoms and possess sizes comparable to the Fermi wavelength of electrons (*i.e.*, the de Broglie wavelength of the electrons at the Fermi level: ~0.5 nm for Ag and Au). Such nanoclusters have received increasing attention in recent years because their optical, electrical, and chemical properties are significantly different than their larger cousins (*i.e.*, noble metal nanoparticles).[1−5] These nanoclusters are of significant interest because they provide the bridge between atomic and nanoparticle behavior in noble metals. Silver and gold nanoclusters are generally fluorescent upon photoexcitation.[2,6−9] Silver nanoclusters are especially fluorescent and have been proved to be excellent fluorophores for chemical sensing, bioimaging, and single-molecule studies after the observation of fluorescence from Ag nanoclusters.[10−17]

The synthesis of Ag nanoclusters in aqueous solutions, however, is difficult because Ag nanoclusters tend to aggregate: Ag nanoclusters will grow continuously, forming larger nanoparticles and reducing their surface energy, until their growth is stopped by preformed templates or capping agents. DNA, polymers, dendrimers, polymer capsules, polymer microgels, and multiarm star polymers have each been used as protecting and stabilizing agents to prepare fluorescent Ag nanoclusters in aqueous solutions.[18−27] Water-soluble highly fluorescent Ag nanoclusters have been prepared from the radiolytic, chemical, or photochemical reduction of silver salts in aqueous solutions containing such capping agents.[2,28] Here we present a new and easily controlled sonochemical synthesis of water-soluble fluorescent Ag nanoclusters in aqueous solutions using a common polyelectrolyte, polymethylacrylic acid (PMAA), as the capping agent to stabilize and protect the Ag nanoclusters in the solution.

Sonochemistry has found important synthetic applications in materials chemistry.[29,30] The chemical effects of high intensity ultrasound derive primarily from acoustic cavitation: the formation, growth, and implosive collapse bubbles in a liquid irradiated with ultrasound.[31,32] Localized hot spots with temperatures of ~5000 K and pressures of hundreds of bars can be generated during ultrasonic irradiation of water.[32] As a consequence, highly reactive species, including $HO_2^{\bullet}$, $H^{\bullet}$, $OH^{\bullet}$, and perhaps e_{aq}^-, are formed during aqueous sonolysis,[33−36] similar to the effects of γ-ray or deep-UV irradiation of aqueous solutions. While there have been a number of excellent studies on the preparation of noble metal nanoparticles by sonochemical reductions in aqueous or alcohol solutions,[37−42] to the best of our knowledge, there is no prior report of the synthesis of ultrasmall metal nanoclusters using a sonochemical method.

RESULTS AND DISCUSSION

Sonochemical reduction of Ag^+ still requires the use of a template or capping

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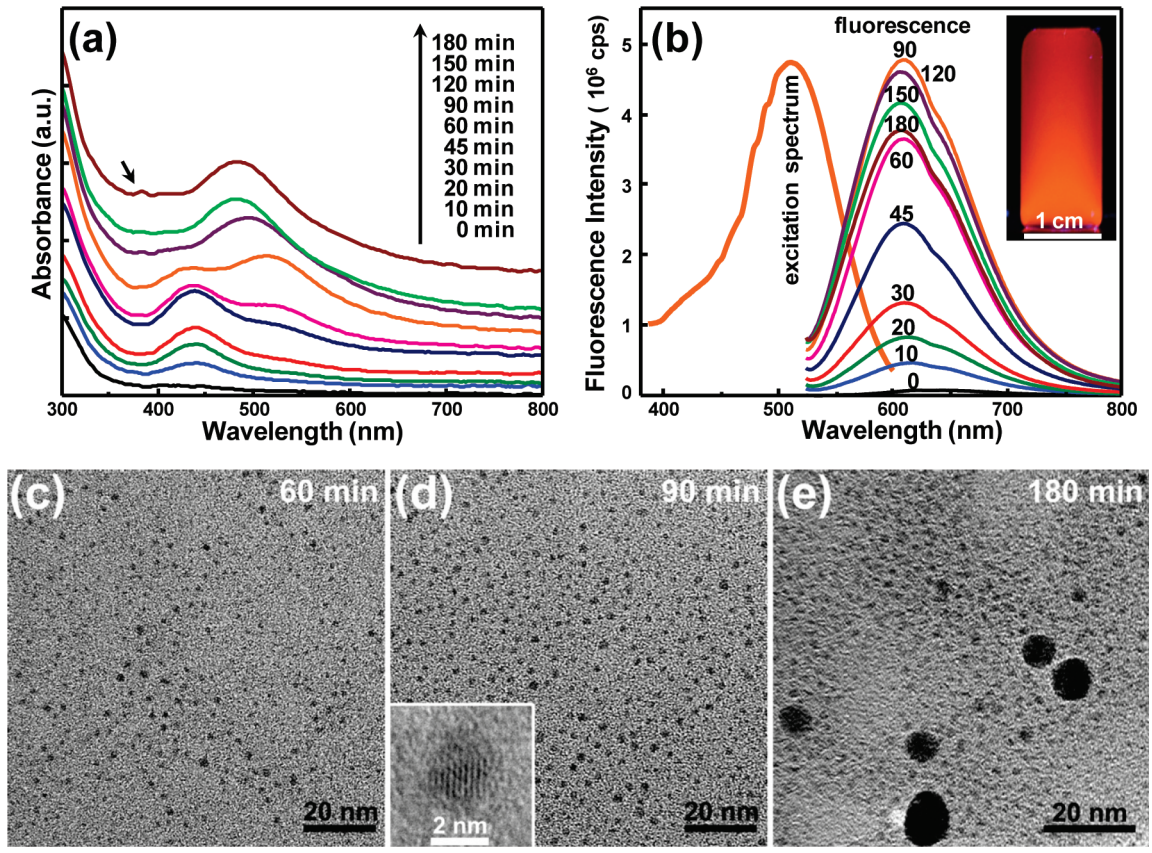

Figure 1. (a) UV−vis spectra and (b) fluorescence emission spectra of the solution containing PMAA and $AgNO_3$ after increasing length of sonication time; the excitation spectrum shown in (b) corresponds to the 90 min sample with an emission wavelength of 610 nm (inset: solution of the Ag nanoclusters illuminated by a UV lamp with 365 nm excitation). TEM images of as-prepared Ag nanoclusters from different lengths of sonication: (c) 60 min, (d) 90 min (inset shows a single magnified Ag nanocluster), and (e) 180 min.

agent to prevent the aggregation of Ag nanoclusters to form large Ag nanoparticles. PMAA (whose carboxylic acid groups have a strong affinity for silver ions and silver surfaces) has been shown to be a versatile template for preparing Ag nanoclusters under UV irradiation.[25,43] The charged carboxylate groups provide stability for Ag nanoclusters and prevent further growth of nanoclusters to large nanoparticles. PMAA also serves as $OH^{\bullet}$ radical scavengers to prevent oxidation of small silver clusters to form silver oxide.[44,45] Meanwhile, the secondary radicals formed from reaction of PMAA with $OH^{\bullet}$ exhibit strong reducing power and produce Ag atoms associated with the polymer chains.

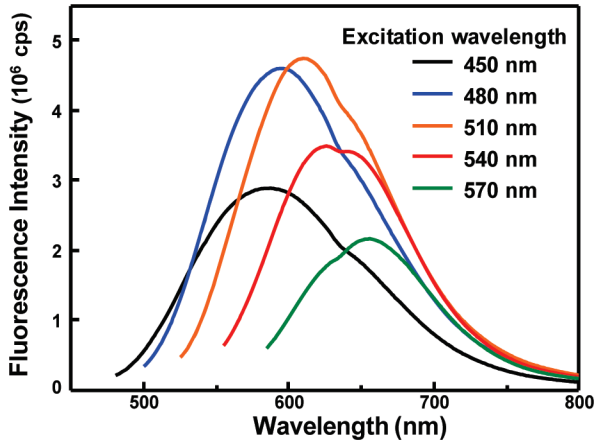

Figure 2. Fluorescence emission spectra of sonochemically prepared Ag nanoclusters (90 min sonication) at different excitation wavelengths.

We demonstrate that sonication of aqueous $AgNO_3$ solutions with dissolved PMAA results in the formation of Ag nanoclusters. To prepare Ag nanoclusters, a freshly prepared solution of $AgNO_3$ was mixed with an aqueous PMAA (M_w = 9500, sodium salt) solution. The molar ratio of carboxylate groups (from the methacrylic acid units) to Ag^+ was 1:1. The pH value of the resulting solution was adjusted to 4.5 to form a compacted coil conformation of PMAA, which has been claimed to favor the formation of Ag nanoclusters.[43] The solution was sparged with Ar for 2 h and then sonicated for various time intervals. As shown in Figure 1a, upon sonication, the initially colorless solution gradually turns pink (90 min) and then dark red (180 min). The resulting Ag nanoclusters are highly fluorescent (Figure 1b) and have been characterized by transmission electron microscopy (TEM) (Figure 1c−e), which shows that the sonochemically prepared Ag nanoclusters are less than 2 nm in diameter. These ultrasmall Ag nanoclusters are

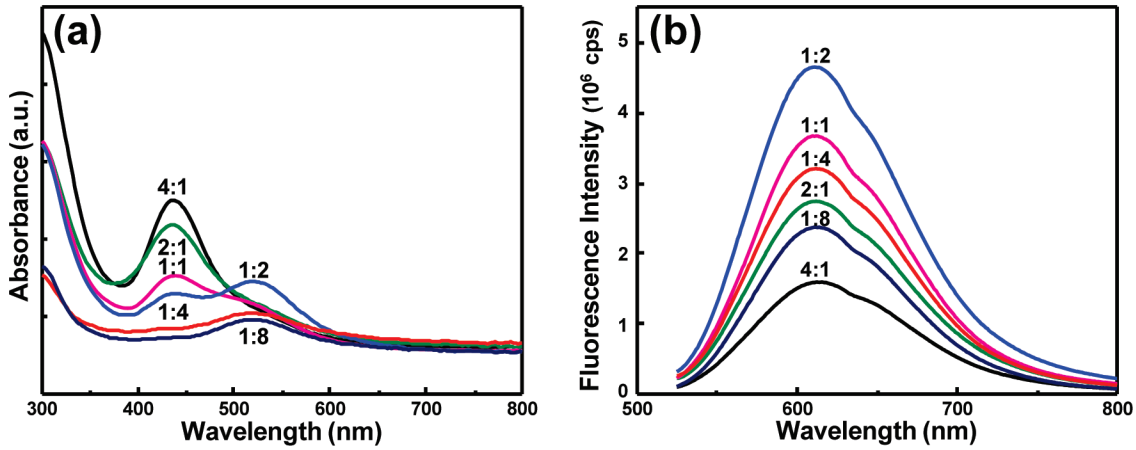

Figure 3. (a) Absorption spectra and (b) fluorescence emission spectra of sonochemically prepared fluorescent Ag nanoclusters (60 min sonication) from samples with different ratios of polymethylacrylic acid carboxylate groups to Ag^+, as labeled. The excitation spectra are identical to that of Figure 1b.

more clearly visible with a dark-field image, as shown in Figure S1 in Supporting Information.

The evolution of absorption and fluorescence of the sonochemically prepared Ag nanoclusters with duration of sonication has proved interesting. Before sonication, the solution showed no absorption in the range of 300−800 nm. After 10 min sonication, a peak around 440 nm appeared and further sonication increases the intensity of this peak. As sonication continues (Figure 1a), a shoulder at 520 nm grows in, the peak at 440 nm gradually disappears, the 520 nm peak gradually blue shifts to 490 nm, and finally a new absorption peak around 390 nm begins to emerge after sonicating for 180 min. A similar trend has been observed in UV-irradiated formation of Ag nanoclusters in polymer microgels.[21] Absorbance in the region from 440 to 520 nm has been observed previously and ascribed to the formation of Ag nanoclusters, with shorter wavelength corresponding to smaller nanoclusters.[21] The peak at 390 nm is the characteristic surface plasmon band of larger Ag nanoparticles.

A distinctive feature of our Ag nanoclusters is their strong fluorescence, which is *not* observed for Ag nanoparticles. An intense fluorescence emission band around 610 nm is observed upon excitation at 510 nm (Figure 1b). The maximum emission intensity occurs for Ag nanoclusters produced by sonication for 90 min. Prolonged sonication led to the gradual decrease of the fluorescence intensity as formation of large nonfluorescent Ag nanoparticles occurred (as confirmed in the absorption spectra plasmon band at 390 nm and by direct observation in the TEM, Figure 1e). The corresponding fluorescence excitation spectrum at 90 min was recorded, which exhibited a peak at 510 nm and a weak shoulder around 400−440 nm (Figure 1b). This dual peak in the excitation spectrum indicates that Ag nanoclusters of different sizes contribute to the emission at 610 nm. The quantum yield is substantial, ≈11%, calculated by use of Rhodamine B in ethanol as a reference. Furthermore, the Ag nanoclusters sonochemically prepared are stable under Ar; essentially no change in fluorescence intensity was observed even after 1 month storage in the dark (under Ar).

There is a strong relationship between a Ag nanocluster size and its fluorescence excitation and emission wavelengths.[23,43] We clearly have a distribution of Ag nanocluster sizes present, as revealed in Figure 2, which shows the emission spectra of Ag nanocluster solutions at various excitation wavelengths. For excitation wavelengths between 450 and 570 nm, the maximum emission is observed at an excitation wavelength of 510 nm. The emission maximum was found to shift to longer wavelengths with increasing excitation wavelengths, which confirms a distribution of Ag nanoclusters with different numbers of Ag atoms.[23,43] Note that essentially all Ag nanoclusters prepared to date by any synthetic method show a similar phenomenon; that is, the emission maximum shifts as the excitation wavelength varies. The ability to control nanocluster distribution to a single nanocluster size has not yet been achieved.

The stoichiometry of the carboxylate groups (RCO_2^-) to Ag^+ also plays an important role in the preparation of water-soluble fluorescent Ag nanoclusters. Figure 3 shows the absorption and emission spectra of Ag nanoclusters with different RCO_2^-/Ag^+ ratios produced under the same sonication time with the same Ag^+ concentration. Excess carboxylate groups (RCO_2^-/Ag^+ = 4/1 or 2/1) lead to the formation of smaller Ag nanoclusters with an absorption peak around 440 nm, while fewer carboxylate groups (RCO_2^-/Ag^+ = 1/4 or 1/8) yield larger Ag nanoclusters with an absorption peak around 520 nm. In the middle region (RCO_2^-/Ag^+ = 1/1 or 1/2), both types of Ag nanoclusters are formed. For solutions sonicated for 60 min, the color is yellow with excess carboxylate groups and pink with a lower RCO_2^-/Ag^+ ratio. In contrast to a prior photochemical preparation,[25] when the RCO_2^-/Ag^+ ratios are changed,

we observe no obvious shift in the emission maximum; likewise, in Figure 1b, the fluorescence does not shift as a function of nanocluster size distribution. The change in absorbance wavelength, *but not in fluorescence emission*, shows that there is one dominant fluorescing nanocluster, regardless of the change in the overall nanocluster distribution, which does affect the absorbance spectra. The fluorescence intensity increases as the ratio of RCO_2^-/Ag^+ decreases with a maximum at $RCO_2^-/Ag^+ = 1/2$. Further decreasing the carboxylate groups leads to a decrease in total fluorescence intensity, possibly because of Ag nanocluster agglomeration in the absence of sufficient carboxylate groups to stabilize the nanoclusters.

The effect of the polymer was also examined in its effect on the formation of Ag nanoclusters. The molecular weight of PMAA may be varied (M_w = 4500, 15 000, and 100 000, sodium salt) in the preparation of fluorescent Ag nanoclusters. The fluorescence intensity, however, decreases as the molecular weight increases for the same length of sonication (Figure 4). Presumably, this is because of slower diffusion of reactive species produced by sonolysis into the interior of the longer chain length polymers. Other commercially available polymers were also tested in our sonochemical synthesis of Ag nanoclusters. PAA and poly(acrylic acid-*co*-maleic acid) also led to the formation of water-soluble fluorescent Ag nanoclusters. Polymers containing other functional groups that have a high coordination affinity for Ag^+ (*e.g.*, polyvinylpyrrolidone, polyvinyl alcohol, polyethylenimine, and poly(*N*-isopropylacrylamide)) did not lead to fluorescent Ag nanoclusters; with those polymers, only large, nonfluorescent Ag nanoparticles (Figure S2 in Supporting Information) with a characteristic surface plasmon absorption band around 400 nm were obtained.

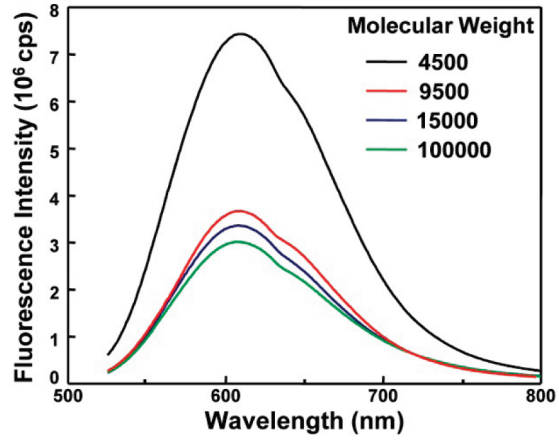

Figure 4. Fluorescence emission spectra of sonochemically prepared fluorescent Ag nanoclusters with different molecular weights of PMMA ($RCO_2^-/Ag^+ = 1/1$, 60 min sonication).

CONCLUSION

In conclusion, a convenient sonochemical method for the synthesis of water-soluble fluorescent Ag nanoclusters has been demonstrated using a simple, inexpensive, and commercially available polyelectrolyte, PMAA, for stabilization. These highly fluorescent Ag nanoclusters are very stable under ambient conditions under aqueous conditions in the absence of strong nucleophiles, and their chemical and physical properties can be easily controlled by varying the synthetic conditions. The stability and excellent fluorescent properties of these Ag nanoclusters are likely to find widespread applications in bioimaging, chemical and biosensing, single-molecule studies, and possibly catalysis. In addition, one may expect that this sonochemical method can be extended to the synthesis of other metal nanoclusters.

EXPERIMENTAL SECTION

Synthesis of Ag Nanoclusters: The polymers used in this work and $AgNO_3$ were purchased from Sigma-Aldrich and used as received. Water-soluble fluorescent Ag nanoclusters were prepared as follows: PMAA−Ag^+ solutions (30 mL) with different RCO_2^-/Ag^+ ratios were prepared using 45 mg of $AgNO_3$ in 5 mL of water, which was mixed with 25 mL PMAA solutions of different concentrations. The solution was adjusted to pH 4.5 with 0.1 M $HNO_{3(aq)}$ or $NaOH_{(aq)}$. The mixture was then transferred to a sealed vessel and sparged with Ar for 2 h at 20 °C. Sonication time using an ultrasonic horn (Sonics & Materials, model VCX-750, 1 cm^2 Ti horn at 20 kHz and 25 W cm^{-2}) was varied from 10 to 180 min under Ar flow.

Characterization of Ag Nanoclusters: UV−vis absorption and fluorescence spectra were obtained using a HITACHI 3300 double monochromator UV−vis spectrophotometer and a Jobin Yvon Horiba FluoroMax-3 spectrofluorometer, respectively. Fresh solutions (with an absorption at 510 nm of 0.1) were transferred into quartz cuvettes and spectra recorded. The quantum yield of fluorescent Ag nanoclusters was determined by measuring the integrated fluorescence intensities of the Ag nanoclusters compared to a reference solution (*i.e.*, the quantum yield of Rhodamine B at ethanol solution at 510 nm is 0.7[46]) using 510 nm excitation.[47] TEM images were taken with a JEOL 2100 transmission electron microscope with an accelerating voltage of 200 kV. Dark-field TEM images were acquired with a JEOL 2010 field emission scanning transmission electron microscope. Samples were prepared by placing a drop of solution onto copper grids with ultrathin carbon film and dried at room temperature.

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Supporting Information Available: Dark-field TEM image of Ag nanoclusters and photograph of different polymers used to prepare Ag nanoclusters under UV excitation. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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