Facile preparation of water-soluble fluorescent silver nanoclusters using a polyelectrolyte template†

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Received (in Cambridge, UK) 15th November 2007, Accepted 14th December 2007
First published as an Advance Article on the web 10th January 2008
DOI: 10.1039/b717728c

We report a new approach for the synthesis of fluorescent and water-soluble Ag nanoclusters, using the common polyelectrolyte poly(methacrylic acid) as the template.

Recently, metal nanoclusters have gained particular research interest for their unique role in bridging the "missing gap" between atomic and nanoparticle behavior in noble metals.[1–3] Such metal nanoclusters, possessing sizes comparable to the Fermi wavelength of the electron, have been found to exhibit molecular-like properties such as strong fluorescence. These emissive metal nanoclusters have great potential applications as stable chromophores in single-molecule microscopy, biological labeling, or in optical sensing.[4–6] In particular, low-nuclearity Ag nanoclusters offer the promise to combine small size and potentially ultrabright emission in a variety of scaffolds, and thus have received considerable attention within the past few years.[7–12] Template-based synthesis has proven to be an efficient and facile method to prepare highly fluorescent Ag nanoclusters. For example, Dickson and co-workers reported the successful synthesis of fluorescent Ag nanoclusters using poly(amidoamine) (PAMAM) dendrimers[7] and DNA[8] as templates. In another report, Kumacheva and colleagues prepared fluorescent Ag nanoclusters in the polymer microgel hosts.[10] More recently, Shen *et al.* reported the successful photogeneration of fluorescent Ag nanoclusters using multi-arm star copolymers as the template.[11] Although these methods can obtain fluorescent Ag nanoclusters, several synthetic issues remain in the reported methods, such as the complicated and time-consuming preparation of templates which will lead to relatively high costs,[10,11] the simultaneous formation of larger, non-fluorescent nanoparticles,[10,11] or the use of a toxic reduction agent.[8,9] Therefore, developing alternative methods to create such materials, which can still contribute to fundamental studies and eventual technical applications of these fluorescent nanoclusters, is of great importance and interest.

Here we report a new approach for the synthesis of fluorescent and water-soluble Ag nanoclusters using a common polyelectrolyte as the template. Specifically, we show that a simple anionic polyelectrolyte such as poly(methacrylic acid) (PMAA) can function as an ideal template to generate highly fluorescent Ag nanoclusters. PMAA offers several crucial advantages as the template: (1) PMAA carries carboxylic acid groups capable of coordinating with Ag^+ ions;[13] (2) PMAA chains at low ionization exhibit necessary hydrophobicity due to the presence of methyl groups in the side chain, and previous studies found that hydrophobic regions facilitated the formation of metal nanoclusters;[6] (3) PMAA responds reversibly to variations of environmental pH, ionic strength and temperature, which can extend the application of the generated emissive nanoclusters into areas such as biomedicine.[14,15] Therefore, we expect PMAA to be an ideal template for the Ag-nanocluster synthesis.

The present approach to prepare Ag nanoclusters is very simple. A freshly prepared mixture solution of $AgNO_3$ (0.05 M) and PMAA (0.1 M) was incubated in the dark for *ca.* 10 min, then subjected to UV-irradiation at 365 nm for various time intervals. Photoreduction, which has been proved to be an effective method for preparing Ag nanoclusters, is adopted in the present study. The choice of photoreduction as the reduction method also has advantages such as controlled reduction of metal ions without introducing disturbing impurities into the products.[16] In addition, the reaction can be initiated homogeneously.

Initially, the mixture solution of $AgNO_3$ and PMAA was colorless, but the following UV irradiation with increasing time was observed to result in obvious color changes from colorless to light pink, then to purple, and finally to dark red (the inset of Fig. 1(A)). The evolution of the absorption spectra of the solution upon the irradiation for different times is shown in Fig. 1(A). Before the irradiation, the solution showed no absorption in the wavelength range from 350 to 800 nm (curve a). After 5 minutes of UV irradiation, a weak absorption band centered at 500 nm appeared (curve b). When further extending the irradiation time from 10 to 90 min, the intensity of this absorption band increased significantly, accompanying a gradual red shift on the position of the absorbance maximum to 511 nm (curves c to g). Meanwhile, a shoulder peak at *ca.* 430 nm was also observed upon the irradiation, but the intensity was rather weak. The absorption bands located at both 500 nm and 430 nm should be assigned to the absorption by the photoreduced silver nanoclusters Ag_n^+, where n varied from 2 to 8, according to previous studies.[7,10] The increase in the absorbance and the red-shift of the absorption peak indicated the gradual growth of Ag nanoclusters upon prolonged UV irradiation.

As opposed to larger metal nanoparticles, a distinctive feature of small nanoclusters is their strong fluorescence due

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† Electronic supplementary information (ESI) available: Experimental section, and Fig. S1. See DOI: 10.1039/b717728c

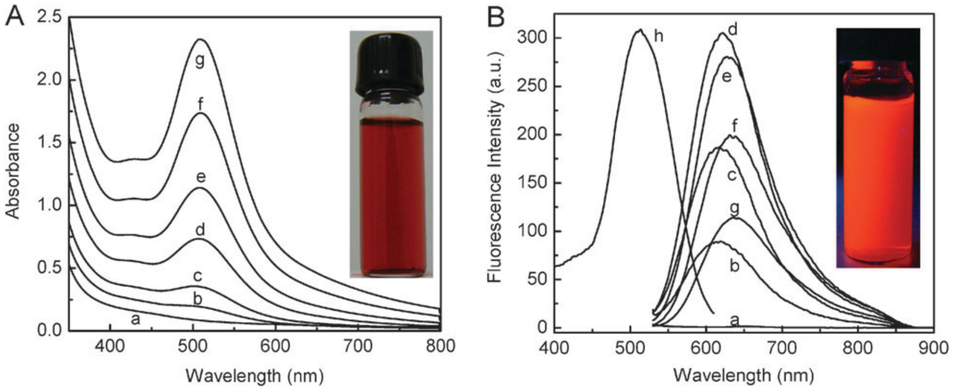

Fig. 1 UV-Vis (A) and fluorescence emission (B) spectra of the solution containing PMAA and $AgNO_3$ upon the UV irradiation at 365 nm for different times (min): (a) 0; (b) 5; (c) 10; (d) 20; (e) 40; (f) 60; (g) 90. Curve h in (B) is the excitation spectrum corresponding to the emission at 620 nm. The inset in (A) and (B) shows a photograph of the solution in the room light and UV-lamp, respectively.

to their lower density of electronic states.[17] For the present photoreduced Ag nanoclusters, strong luminescence was observed upon the excitation (the inset of Fig. 1(B)). The evolution of the emission spectra of the solution after the UV irradiation for different times is displayed in Fig. 1(B). While the initial solution exhibited no visible emission (curve a), after a 5 min irradiation, an intense emission band centered at 615 nm was observed upon excitation at 510 nm (curve b). The fluorescence intensity increased gradually with extending the irradiation time up to 20 min, and further irradiation was found to decrease the fluorescence intensity. In addition, with increasing irradiation time, the emission peak gradually shifted to longer wavelength, which mainly arose from the growth of Ag nanoclusters. Moreover, a weak shoulder emission peak at *ca.* 825 nm also appeared in the spectra, which suggested the presence of a distribution of nanoclusters with different association numbers upon the photoreduction.[11] As can be seen, the maximum photoluminescence intensity occurred at an irradiation time of 20 min, with the emission peak at 620 nm (curve d). The corresponding excitation spectrum at 20 min was recorded, which possessed a peak at *ca.* 510 nm (curve h). This clearly indicated the emissive centers to be Ag nanoclusters whose absorption band was located nearby 510 nm.[18] It is noteworthy that the photoluminescence could still be observed upon UV irradiation for up to 6 h. In addition, the luminescence intensity of as-prepared fluorescent Ag nanoclusters changed less than 3% after a storage time of 3 months in the dark, without discernable changes observed in the spectral shape. The good photostability of these emissive nanoclusters in the present study then demonstrates their possible application as bioimaging labels. The quantum yield of as-prepared Ag nanoclusters was calculated to be *ca.* 18.6% using Rhodamine B in ethanol as the reference. The luminescence lifetime was also measured, where a value of 2.3 ± 0.05 ns was obtained. Such a short lifetime agreed with a previous report for the water-soluble Ag nanoclusters.[19]

Interestingly, the silver nanoclusters could fluoresce by a wide range of excitation wavelength. As shown in Fig. 2, obvious fluorescence could be observed upon the excitation between 450 nm and 580 nm, and the maximum emission occurred at an excitation wavelength of 510 nm. This is highly reminiscent of the emissive features of metal quantum dots due to inter-band transitions from the submerged and quasi-continuum 5d band to the lowest unoccupied conduction band of Ag nanoclusters.[3,13] Behaving as quantum emitters, the fluorescent Ag nanoclusters can easily exhibit visible luminescence under a wider range of excitation. Also, the emission band of the Ag nanoclusters was found to shift significantly to longer wavelength with increasing excitation wavelength. As shown, upon increasing the excitation wavelength from 450 nm to 580 nm, the emission maximum shifted from 610 nm to 660 nm. This further confirmed the presence of a distribution of Ag nanoclusters with different association numbers.[11,20]

We further investigated the synthesis of Ag nanoclusters at different pH. The emission spectra of the mixture solution (containing PMAA and $AgNO_3$) upon the UV-irradiation for 20 min at pH 2.3 to 8.0 are shown in Fig. 3. As shown, the photoluminescence of the Ag nanoclusters generated at different pH values varied greatly. The maximum intensity was obtained at pH 4.5 (curve c), and the nanoclusters synthesized at either lower or higher pH value showed weaker fluorescence intensity. At least two factors contributed to this pH-dependence. One comes from the pH-dependent ionization of carboxylic acid groups which is crucial to sequester Ag^+ ions and confine the growth of nanoclusters. At low pH, carboxylic acid groups (pK_a = 4.25) are not fully deprotonated, thus

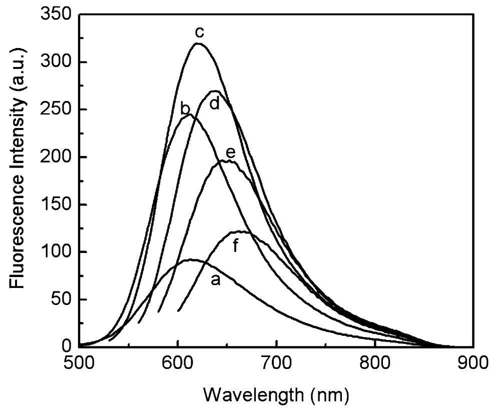

Fig. 2 Fluorescence emission spectra of as-prepared Ag nanoclusters excited at different wavelengths (nm): (a) 450; (b) 480; (c) 510; (d) 540; (e) 560; (f) 580.

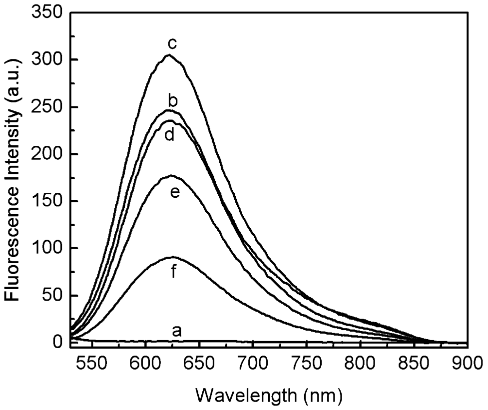

Fig. 3 Fluorescence emission spectra of Ag nanoclusters generated at different pH: (a) 2.3; (b) 3.7; (c) 4.5; (d) 6.0; (e) 6.8; (f) 8.0. The emission spectra were all recorded upon irradiation for 20 min. The excitation wavelength is 510 nm.

weaken the binding ability toward Ag^+ ions. Especially at pH 2.3, due to the complete protonation, no emissive nanoclusters were formed even upon the illumination for 60 min (curve a). The other is the pH-dependent conformational change of PMAA, which greatly influences the emission of the nanoclusters that generated within the polymers. It is known that PMAA in aqueous solution undergoes a conformational change around pH 5.[14,21] At lower pH, PMAA forms compact clusters which isolate a hydrophobic core with brush like acid layers, and such a compact structure can provide better protection of the emissive nanoclusters against quenching in solution.[19] Further increasing the pH will induce the transition to a moderately ionized extended form, thus weakening the protection. In our experiment, the optimum pH that balances the influence of both factors in the PMAA-templated synthesis of Ag nanoclusters was found to be 4.5.

A series of control experiments have been conducted to examine the present synthesis strategy. Our results indicated that PMAA, $AgNO_3$ and photoreduction were all essential to the generation of fluorescent Ag nanoclusters in the present system, since the exclusion of either component would yield no fluorescent Ag nanoclusters. In addition, reducing Ag^+ in the presence of PMAA by chemical reduction reagents (such as $NaBH_4$) other than the photoreduction, could not obtain fluorescent nanoclusters either. It is important to mention that our preliminary experiments show that poly(acrylic acid) (PAA, M_W = 8000) could also lead to fluorescent Ag nanoclusters. However, compared with PMAA under identical conditions, the fluorescence intensity of nanoclusters was much weaker, and the reaction was slower (Fig. S1, ESI†). It is obvious the additional methyl groups endow PMAA more hydrophobicity and favor the generation of emissive nanoclusters.

Our synthetic PMAA-templated Ag nanoclusters exhibit a number of attractive optical properties. For example, the fluorescent nanoclusters have large Stokes shifts (greater than 100 nm), which can prevent spectral overlap and thus favor the potential application in biological detection. Behaving as quantum emitters, the fluorescent Ag nanoclusters can easily exhibit visible luminescence under a wider range of excitation. Particularly, these emissive nanoclusters are expected to possess a stimuli-responsive property, since PMAA is known to respond reversibly to variations of environmental pH, ionic strength and temperature, which can further extend the application of fluorescent metal nanoclusters.

Compared with the method of Shen *et al.*[11] where the copolymer templates had to be pre-synthesized, the present work using a commercially available polyelectrolyte as the template appeared to be more timesaving, simple, and economical. Moreover, given there are many kinds of natural or artificial polyelectrolyte, the present work is expected to open new opportunity of preparing fluorescent metal nanoclusters using other possible polyelectrolyte templates.

In conclusion, water-soluble fluorescent silver nanoclusters have been successfully prepared using PMAA as the template under photoreduction in a very simple approach. Compared with the previous methods using polymer microgels, multi-arm star copolymers, or dendrimers as templates, the adoption of a common, commercially available polyelectrolyte, is much simpler and more economical. Furthermore, the as-prepared emissive nanoclusters exhibit good photostability, pH- and excitation-dependent emission behavior, and a stimuli-responsive property, which may offer the possibility of applications in a wide range such as optical data storage, biological labeling, and chemical and biosensing.

This work was supported by the National Natural Science Foundation of China (Nos. 20575064 and 20675076).

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