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Enhanced Emission of Silver Nanoclusters Through Quantitative Phase Transfer

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Silver nanoclusters composed of only a few metal atoms present appealing properties such as fluorescence. We have previously reported on aqueous solutions of this fluorophore using poly(methacrylic acid) as scaffold and their sensing properties. Here we report on the preparation of organic solutions of fluorescent silver nanoclusters by quantitative transfer from aqueous solution to an immiscible organic solvent. The fluorescent silver nanoclusters in the organic phase present enhanced emission properties and increased purity, which may expand the range of applications of this promising fluorophore.

1. Introduction

Fluorescent silver nanoclusters as stable entities in water solutions have been studied since 2002,[1] and have gained importance due to their appealing properties such as photostability[2] and high fluorescence quantum yield.[3] Compared to organic dyes and semiconductor quantum dots, the sub-nanometer size of silver nanoclusters (just a few atoms large) and their biocompatibility[4] suggest that they can have a bright future in applications such as biolabeling and biosensing[5a] (for a recent review on fluorescent silver nanoclusters, see the book chapter by Díez and Ras[5b]). Efforts have been made to synthesize silver nanoclusters in different conditions and studies demonstrate that the optical properties and stability of silver nanoclusters are strongly influenced by the local environment, including scaffolds[6–9] and solvents.[10] Fluorescent silver nanoclusters are always prepared starting from an aqueous environment. To study the nanoclusters in non-aqueous environment, two approaches have been reported: 1) mixing of an aqueous nanocluster solution with an organic solvent,[11] and 2) precipitation of silver nanoclusters and redissolution in the organic solvent.[10] Here we demonstrate a novel and attractive approach to convey clusters to an organic solvent, namely phase transfer. Phase transfer from water to organic solvents is a common processing step for nanomaterials such as metal clusters,[12] metal nanoparticles,[13,14] graphene sheets[15] and semiconductor quantum dots,[16] since it allows to expand their range of applications.[17] Here we report on the efficient phase transfer of sub-nanometer luminescent silver clusters between two immiscible liquids without addition of a phase transfer agent. The phase transfer of silver nanoclusters as demonstrated from water to butanol is a simple method for purification, for increasing the silver nanocluster concentration, and importantly to enhance their optical properties such as fluorescence quantum yield.

2. Results and Discussion

The formation of silver nanoclusters in aqueous phase using poly(methacrylic acid) (PMAA) as a scaffold was previously described in detail.[10] In short, a colorless aqueous solution of silver salt and PMAA was irradiated with visible light, until pink and fluorescent nanoclusters formed. During irradiation, part of the silver ions was reduced to form silver nanoclusters composed of only a few silver atoms. The unreacted silver ions remained in the silver nanocluster solution.

Addition of butanol to an equal amount of aqueous solution of silver nanoclusters forms two distinct phases, which upon even gentle agitation by shaking lead to a rapid and complete transfer of the fluorophores to the organic phase. The droplets created during shaking, rapidly coalesce to form within seconds, two distinct phases as shown in Figure 1 A (right). The efficient relocation of fluorescent nanoclusters in the butanol phase can be observed from the photographs in Figure 1 A taken under visible light and UV light. The images show the two phases, aqueous in the bottom and organic on top of the samples before (left) and after (right) shaking. The images clearly point to two details. Firstly, the silver nanoclusters have been transferred to the organic phase where they remain luminescent. Secondly, no fluorescence signal could be obtained from the water phase after separation of the two phases. These two observations indicate the total phase transfer of silver nanoclusters from an aqueous phase to an organic phase without the use of any added phase transfer agent.

The same behavior could be observed when the starting aqueous nanocluster solution was prepared with various silver to methacrylate (Ag:MAA) molar ratios ranging from 100 % to 600 %, where for instance 200 % means that there are two

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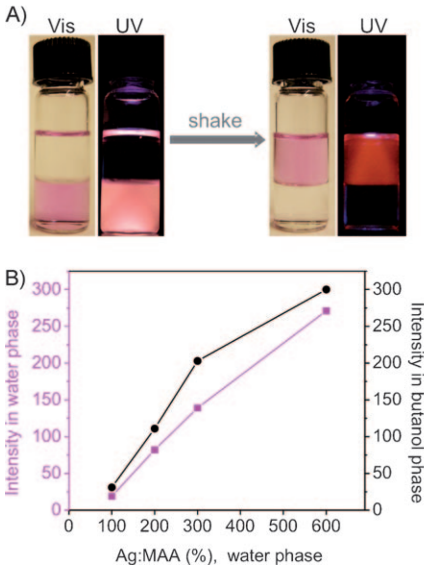

Figure 1. A) Photographs under visible and UV light of silver nanoclusters (pink) in a two-phase system containing equal amount of water and butanol. Before shaking the silver nanoclusters are in the water phase (bottom phase) after shaking they are in the butanol phase (top phase). B) Emission intensity of silver nanoclusters in water phase before transfer (pink squares) and in butanol phase after transfer (black circles) as a function of silver to methacrylate molar ratio.

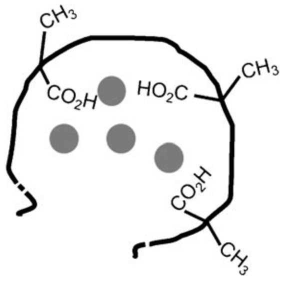

Figure 2. Schematic drawing of the proposed arrangement of a PMAA chain, with the carboxyl groups pointing towards the silver nanoclusters (dots) and the methyl groups pointing outwards. The hydrophobic methyl groups are exposed to the solvent, making butanol a preferred solvent for the silver clusters.

silver ions per methacrylic acid unit. It was noticed that the global transfer of silver nanoclusters to the butanol phase comes along with an increase in the emission intensity of the nanoclusters for all the molar ratios considered (Figure 1 B). Comparing the nanoclusters in the initial water phases and in the final butanol phases, the increase in the intensity is larger than the 10 % correction for the refractive index of the solvent.[18] The greatest enhancement in the intensity is observed for the molar ratio Ag:MAA 300 % in the starting aqueous solution. In this case the emission intensity of the silver nanoclusters in butanol was 46 % higher than for the aqueous silver nanocluster solution. The increase in intensity coincides with a small red shift of the emission band. The higher emission intensity in butanol phase is caused by the higher fluorescence quantum yield with respect to water phase. The original aqueous solution of silver nanoclusters prepared using PMAA has a fluorescence quantum yield of about 6 %,[10] whereas the nanoclusters in the butanol phase have a quantum yield of about 9 %, compared to rhodamine 101 in ethanol.

The transfer to butanol phase of silver nanoclusters protected by PMAA was not anticipated since neither silver nitrate nor PMAA are soluble in butanol. We rationalize the phase transfer as follows. Considering the affinity of the carboxyl groups towards silver ions,[19,20] it is reasonable to assume that the silver nanoclusters are surrounded by the carboxyl groups of PMAA. In PMAA the carbon of the polymer backbone to which the carboxyl group is attached also has attached a methyl group. This means that locally the methyl groups from methacrylate units are directed towards the solvent (Figure 2). When the clusters in aqueous solution are mixed with butanol, the hydrophobic methyl groups facing the external side of the nanodomains would be easily accessible to butanol molecules. When butanol and water phase separate, the composite silver nanocluster–PMAA surrounded by butanol molecules prefers to go to the butanol phase.

Spherical aberration corrected high angle annular dark field scanning transmission electron microscopy (HAADF–STEM) images of the silver nanoclusters in butanol phase are presented in Figure 3. Two distinct features are observed in the higher magnification image in Figure 3 B: small isolated dots of about 0.1–0.2 nm and small features of approximately 2 nm that do not show crystallinity. The small isolated dots are individual silver ions. The 2 nm features likely are assemblies of silver ions and silver clusters in the coiled polymer scaffold. The image recorded at low magnification (Figure 3 A) confirms the absence of large nanoparticles, and corresponds well to the image of silver nanoclusters prepared in water solution presented in our previous publication.[10]

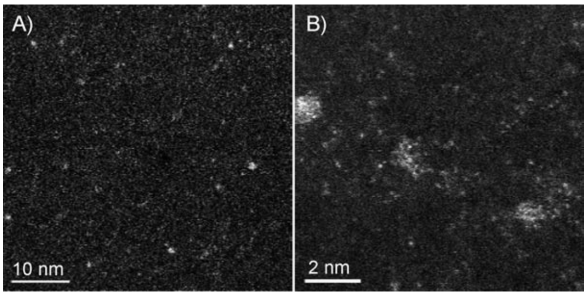

Figure 3. Spherical aberration corrected HAADF–STEM images of silver nanoclusters casted from butanol phase.

The phase transfer of silver nanoclusters from aqueous to organic solution was also studied as a function of relative phase volumes for a given aqueous nanocluster solution with molar ratio Ag:MAA of 200 %. The relative volumes water to butanol used were 1:5, 1:2, 1:1, 1:0.5 and 1:0.2. The emission spectra (Figure 4 A) of the nanoclusters in the original water solution (grey) and in the final butanol phase (black) show that the shape of the spectra is not affected by the solvent. In contrast,

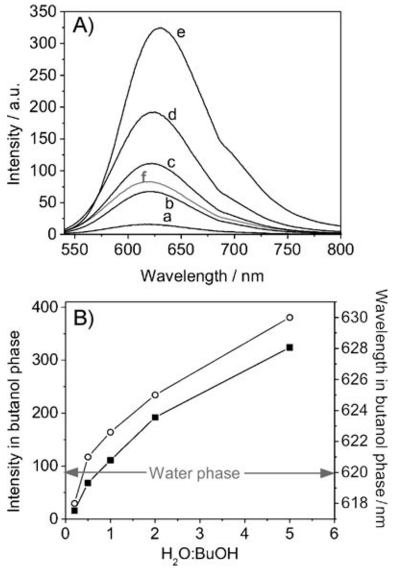

Figure 4. A) Emission spectra of silver nanoclusters in water phase before transfer (curve f) and in butanol phase after transfer using the volume ratios water to butanol a) 1:5, b) 1:2, c) 1:1, d) 1:0.5 and e) 1:0.2. B) Intensity (black squares) and emission wavelength at maximum (white spheres) of silver nanoclusters in butanol phase after phase transfer using the same volume ratios as in (A). The intensity and wavelength at maximum of the clusters in water are marked with an arrow.

the intensities of the nanoclusters show great dependence on the relative volumes of the solvents, which is due to a concentration effect (Figures 4A, B). For instance when the nanoclusters were transferred to an equal volume of butanol, the intensity of the nanoclusters emission increases slightly as described previously. For this case with Ag:MAA molar ratio of 200%, the intensity changes from 82 in water (Figure 4A, curve f) to 111 (curve c), which implies an increase of 36%. When the nanoclusters in aqueous phase (curve f) are transferred to a five times larger volume of butanol, the emission intensity in the new phase decreases as expected due to dilution (curve a), thus, the intensity in the butanol phase is 16, which is one fifth of the intensity in the original aqueous solution. Considering the intensity of the starting water phase, the maximum intensity enhancement for nanoclusters was obtained when transferring the nanoclusters to a very small volume of butanol phase, like when using volume ratio water to butanol 1:0.2. In this case the intensity of the clusters could be greatly enhanced from 82 (Figure 4B) in water phase to 324 in butanol phase, which means four times higher intensity.

Remembering that all the nanocluster solutions in butanol phase presented in Figure 4B were prepared from the same batch of aqueous silver nanocluster solution, it is worth to mention that using different volumes of butanol for the transfer affects not only the emission intensity of the nanoclusters in the organic phase but also the emission wavelength. Figure 4B collects both the intensity and the wavelength of the nanoclusters in butanol phase after extraction with different water-to-butanol volume ratios and shows similar trend in both properties. The small shift in the wavelength due to phase transfer is not constant as expected for nanoclusters transferred from the same water solution, instead the shift depends on the volume ratio of the phases. Thus starting from a water phase with emission at 620 nm, after transferring to butanol using a water-to-butanol volume ratio of 1:5 the emission wavelength is centered at 618 nm, whereas for a volume ratio 1:0.2 the emission is centered at about 630 nm. The origin of the wavelength shift is not known.

A different situation was created when, instead of shaking, the butanol was slowly added to silver nanoclusters in water solution and the two phases were kept in rest without mixing for a few days. Several hours after adding the top butanol phase it could be observed that the butanol remained colourless, and that the upper layer of the aqueous phase became colorless and not fluorescent. The colorless upper layer in the aqueous phase was expanding with time and after a few days the initial two phases, water and butanol, were still clearly separated, but now both of them were nearly colorless and nonfluorescent. Moreover, a third phase appeared at the bottom of the aqueous phase. This new phase was strongly pink coloured and luminescent as shown in Figure 5. The third phase forms a pink sphere containing the nanoclusters and its fluorescence is stable over several months. The sphere is nearly solid and could be easily isolated from the other two phases. A possible explanation could be as follows. Butanol is partially soluble in water and the butanol molecules that slowly dissolve in water are attracted by the methyl groups of PMAA creating a butanol phase into the water phase. This discovery promises to be an excellent way to concentrate silver nanoclusters, increasing enormously the emission intensity in a reduced volume.

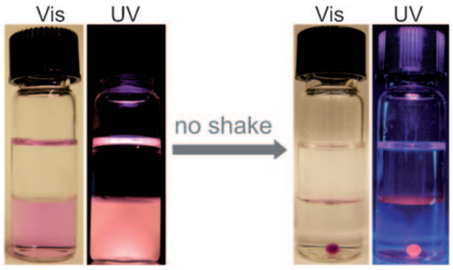

Figure 5. Photographs under visible and UV light of the silver nanocluster solution in water after slowly adding butanol in the top (left) and the same sample after reposing for few days showing the formation of a new phase as a strongly coloured droplet within the water phase (right).

Additionally, the remaining aqueous phase was characterized and we found that it contains poly(methacrylic acid) (analyzed by FTIR) and silver ions (detected by precipitation when adding chlorine ion), suggesting that the method could be used for purification by separation of unreacted precursors that were present in the starting silver nanocluster water solution.

Following the idea of purification, we prepared an aqueous mixture of silver nanoclusters (few atoms, fluorescent) and silver nanoparticles (plasmonic particles of several nm, non-flu-

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orescent). The sample was prepared by adding small amount of reducing agent, $NaBH_4$, to an aqueous silver nanoclusters solution, leading to a mixture of silver nanoparticles and silver nanoclusters. The mixture of silver nanoclusters (pink solution) and silver nanoparticles (black particles) has a dark red color as shown in Figure 6 left. Separation of nanoparticle impurities can be achieved by phase transfer. The addition of butanol, followed by vigorous shaking resulted in the separation of the nanoclusters from the nanoparticles. The pink silver nanoclusters transferred to the butanol phase, the black silver nanoparticles to the interface water-butanol and the extra silver ions remained in the water phase (Figure 6 right). In this way, the separation of silver nanoclusters from silver nanoparticles and excess precursors is an easy process that promises applications where exchange to non-aqueous phase is required.

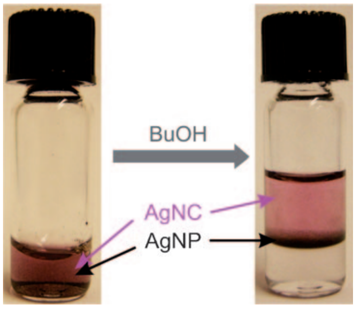

Figure 6. Left: aqueous solution of silver nanoclusters and nanoparticles. Right: after addition of butanol phase and shaking, the nanoparticles are located at the interface and the nanoclusters are located in the butanol phase (upper phase).

3. Conclusions

We have demonstrated that luminescent silver nanoclusters can be transferred efficiently from water phase to butanol phase without the use of an additional phase transfer agent. The phase transfer goes together with an enhancement of the fluorescence quantum yield (9%). Moreover, the phase transfer allows a facile process to purify fluorescent silver nanoclusters from silver ions and plasmonic silver nanoparticles, and to concentrate silver nanoclusters in small volumes, leading to increased emission intensity.

Experimental Section

Chemicals: The precursor to synthesize Ag nanoclusters was silver nitrate (Riedel-de Haën, > 99.8%). Poly(methacrylic acid) (PMAA) was supplied by Polysciences (MW = 100 000) and 1-butanol was supplied by Merck (> 99.5%). All chemicals were used as received. Water was purified by a Milli-Q system (Millipore).

Ag Nanocluster Preparation in Water (also see ref. [10]): Ag nanoclusters were synthesized at room temperature in vials by mixing equal volumes of freshly prepared aqueous solutions of silver nitrate and PMAA (5 $mg\,mL^{-1}$) in various molar ratios, for instance Ag:MAA 200%, which means that there are two Ag ions per methacrylic unit. After mixing, the colourless solutions were placed in a rotator and were subjected to light. With increasing irradiation time the solutions gradually changed from colourless to light pink. Clusters were produced by using a desk lamp with a fluorescent light source (11 W).

Ag Nanocluster Transfer to Butanol Phase: Ag nanoclusters prepared in water as described before were mixed with various volumes of 1-butanol. After short shaking the mixtures were placed in a rotator overnight. Then phase separation was allowed. Alternatively, different volumes of butanol were slowly added to clusters prepared in water, without mixing the phases. The samples were kept in repose for several days to allow slow interaction. Then the samples were imaged.

Characterization: Optical absorption spectra of the Ag nanoclusters solutions were acquired in the wavelength region from 400 nm to 900 nm using a Perkin–Elmer Lambda 950 UV/Vis/NIR spectrophotometer. Fluorescence spectra were obtained with a Varian Cary Eclipse fluorescence spectrometer. All spectra were recorded with quartz cells of 10 mm path length. High-resolution scanning transmission electron microscopy (STEM) measurement was carried out with a JEOL 2200FS double aberration corrected FEG TEM/STEM, operated at 200 kV.

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Keywords: luminescence · nanoclusters · organic solvents · quantum dots · silver

[1] J. Zheng, R. M. Dickson, *J. Am. Chem. Soc.* **2002**, *124*, 13982 – 13983.
[2] T. Vosch, Y. Antoku, J.-C. Hsiang, C. I. Richards, J. I. Gonzalez, R. M. Dickson, *Proc. Nat. Acad. Sci.* **2007**, *104*, 12616 – 12621.
[3] S. A. Patel, C. I. Richards, J.-C. Hsiang, R. M. Dickson, *J. Am. Chem. Soc.* **2008**, *130*, 11602 – 11603.
[4] J. Yu, S. Choi, C. I. Richards, Y. Antoku, R. M. Dickson, *Photochem. Photobiol.* **2008**, *84*, 1435 – 1439.
[5] a) W. Guo, J. Yuan, Q. Dong, E. Wang, *J. Am. Chem. Soc.* **2010**, *132*, 932 – 934; b) I. Díez, R. H. A. Ras in *Advanced Fluorescence Reporters in Chemistry and Biology II* (Ed.: A. P. Demchenko), *Springer Series on Fluorescence Vol. 9*, Springer, Berlin, **2010**, 307 – 332.
[6] P. R. O'Neill, L. R. Velazquez, D. G. Dunn, E. G. Gwinn, D. K. Fygenson, *J. Phys. Chem. C* **2009**, *113*, 4229 – 4233.
[7] B. Sengupta, C. M. Ritchie, J. G. Buckman, K. R. Johnsen, P. M. Goodwin, J. T. Petty, *J. Phys. Chem. C* **2008**, *112*, 18 776 – 18 782.
[8] J. Yu, S. A. Patel, R. M. Dickson, *Angew. Chem.* **2007**, *119*, 2074 – 2076; *Angew. Chem. Int. Ed.* **2007**, *46*, 2028 – 2030.
[9] I. Díez, H. Hahn, O. Ikkala, H. G. Börner, R. H. A. Ras, *Soft Matter* **2010**, *6*, 3160 – 3162.
[10] I. Díez, M. Pusa, S. Kulmala, H. Jiang, A. Walther, A. S. Goldmann, A. H. E. Müller, O. Ikkala, R. H. A. Ras, *Angew. Chem. Int. Ed.* **2009**, *121*, 2156 – 2159; *Angew. Chem. Int. Ed.* **2009**, *48*, 2122 – 2125.
[11] S. A. Patel, M. Cozzuol, J. M. Hales, C. I. Richards, M. Sartin, J. C. Hsiang, T. Vosch, J. W. Perry, R. M. Dickson, *J. Phys. Chem. C* **2009**, *113*, 20264 – 20270.
[12] a) M. A. Habeeb Muhammed, T. Pradeep, *J. Cluster Sci.* **2009**, *20*, 365 – 373; b) T. Udaya Bhaskara Rao, T. Pradeep, *Angew. Chem.* **2010**, *122*, 4017 – 4021; *Angew. Chem. Int. Ed.* **2010**, *49*, 3925 – 3929.

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[13] A. P. Kulkarni, K. Munechika, K. M. Noone, J. M. Smith, D. S. Ginger, *Langmuir* **2009**, *25*, 7932 – 7939.
[14] T. Bala, A. Swami, B. L. V. Prasad, M. Sastry, *J. Colloid Interface Sci.* **2005**, *283*, 422 – 431.
[15] T. Kim, H. Lee, J. Kim, K. S. Suh, *ACS Nano* **2010**, *4*, 1612 – 1618.
[16] Y. Wei, J. Yang, J. Y. Ying, *Chem. Commun.* **2010**, *46*, 3179 – 3181.
[17] V. Wood, M. J. Panzer, J. Chen, M. S. Bradley, J. E. Halpert, M. G. Bawendi, V. Bulović, *Adv. Mater.* **2009**, *21*, 2151 – 2155.
[18] S. I. Kotelevskiy, *J. Lumin.* **1998**, *79*, 211 – 214.
[19] Z. Shen, H. Duan, H. Frey, *Adv. Mater.* **2007**, *19*, 349 – 352.
[20] B. G. Ershov, A. Henglein, *J. Phys. Chem. B* **1998**, *102*, 10663 – 10666.

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