Metal Nanoclusters

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Color Tunability and Electrochemiluminescence of Silver Nanoclusters**

*Isabel Díez, Matti Pusa, Sakari Kulmala, Hua Jiang, Andreas Walther, Anja S. Goldmann, Axel H. E. Müller, Olli Ikkala, and Robin H. A. Ras**

When reducing the bulk size of metals firstly to nanoparticles and further to few-atom nanoclusters, new properties appear that allow applications of these species in optical systems,[1] catalysis[2,3] and biomedical technology.[4] Metal nanoparticles have properties that are dominated by their surface plasmons, that is, the collective oscillation of conduction electrons. It is well known that the plasmonic properties of nanoparticles depend on various parameters, including size, shape, and refractive index of the environment. These properties are technologically important since they form the basis of localized surface plasmon resonance (LSPR) sensing, which allows the detection of single molecules and finds applications in, for example, immunoassays and biochemical sensors.[5] In nanoclusters, on the other hand, the particle size is further scaled down to approach the Fermi wavelength of an electron (ca. 0.5 nm for silver and gold), and the continuous density of states breaks up into discrete energy levels. Therefore, optical and electronic properties of nanoclusters are significantly different to those of nanoparticles.[6–9] However, the effect of environment on the properties of metal nanoclusters has not been reported to date. Herein, we demonstrate for the first time that metal nanoclusters also respond drastically to changes in the environment by showing strong solvatochromic and solvato-fluorochromic properties. We applied poly(methacrylic acid) (PMAA) as the stabilizer for silver clusters. The use of acrylate polymers as stabilizers in reactions where the chemical reduction was initiated by ultraviolet or γ irradiation has been reported previously.[8–11] We have used visible light to initiate the reduction of silver, which leads to solutions of silver clusters without noticeable impurities of silver nanoparticle. In addition, this is the first report of metal nanoclusters that exhibit electrochemiluminescence (ECL), that is, electrogenerated chemiluminescence, a phenomenon in which one or more of the reagents is generated in situ in an electrolytic process. ECL is an established technique for chemical sensing applications.[12,13] Emission of light by ECL is quite rare and this makes electrochemiluminescent compounds well-suited for use as interference-free labels, for example, in immunoassays and DNA-probing assays. Based on these novel findings, and together with the superior properties of nanoclusters over nanoparticles (including high fluorescence quantum yield), the present work suggests considerable potential for nanoclusters as probes in applications such as molecular sensing.

We have systematically investigated the optical properties of Ag nanoclusters in solution and their response to the environment. To produce Ag nanoclusters, a freshly prepared aqueous solution of silver nitrate was mixed with an aqueous solution of PMAA. At first, the solution was colorless and the UV/Vis spectrum showed no absorption. Subsequent exposure to visible light resulted in a gradual color change to pink and the formation of a single broad UV/Vis band that increased in intensity but did not show significant changes in shape or position as the irradiation continued. The clusters prepared according to our method are referred to as first-type Ag clusters (T1 clusters) and the relative concentrations of the solutions are denoted as a percentage value, for example, a 200 % silver/methacrylic acid (Ag/MAA) molar ratio means that there are two Ag ions per methacrylic acid unit. Interestingly, the T1 clusters exhibit a red-shift of the absorption peak when the Ag/MAA molar ratio is increased from 50 % to 400 %, whereas the shape of the peak remains largely unaffected (Figure 1 a). For example, for the 50 % molar ratio, the T1 cluster solution gives an absorption peak centered at about 504 nm, whereas for the 200 % molar ratio a peak centered at about 528 nm is obtained. No further shift was observed when the molar ratio was increased to above 400 %. The fluorescence emission peak was also red-shifted when the initial Ag/MAA molar ratio was increased from 50 % to 400 % (Figure 1 b). For instance, an emission maximum at about 614 nm is observed for the 50 % molar ratio, whereas a peak located at about 626 nm is observed for the 200 % molar ratio. As expected, the color of the solution did not turn pink upon illumination and no fluorescence was detected in the absence of PMAA. T1 samples with Ag/MAA molar ratio exceeding 800 % quickly became pink and then

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[*] Dr. I. Díez, Prof. O. Ikkala, Dr. R. H. A. Ras
Molecular Materials, Helsinki University of Technology
Puumiehenkuja 2, 02150 Espoo (Finland)
Fax: (+358) 9-451-3155
E-mail: robin.ras@tkk.fi
Homepage: http://omm.tkk.fi/en/mm/

M. Pusa, Prof. S. Kulmala
Laboratory of Analytical Chemistry
Helsinki University of Technology (Finland)

Dr. H. Jiang
Nanomaterials Group
Helsinki University of Technology (Finland)

A. Walther, A. S. Goldmann, Prof. A. H. E. Müller
Makromolekulare Chemie II and Bayreuther Zentrum für
Kolloide und Grenzflächen, Bayreuth (Germany)

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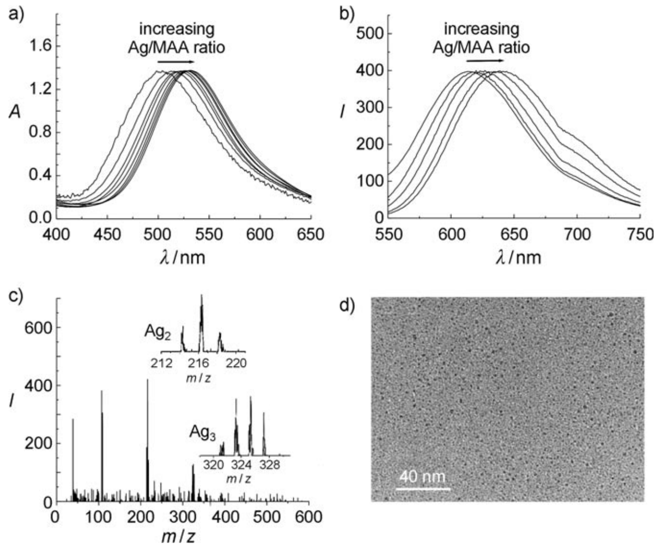

Figure 1. a) Absorption and b) emission spectra of T1 Ag nanoclusters prepared from samples with Ag/MAA molar ratios ranging from 50% to 800% under equal irradiation conditions. c) MALDI-TOF mass spectrum of T1 Ag clusters with a 200% Ag/MAA molar ratio. The high-resolution isotopic patterns are shown as insets. d) TEM micrograph of T1 Ag clusters with a 300% Ag/MAA molar ratio.

turbid, which indicated agglomeration. For T1 samples with Ag/MAA molar ratio lower than 50%, no absorption or fluorescence was observed, which indicated that an excess of polymer prevents the formation of Ag nanoclusters. This result demonstrates that PMAA is not only acting as an effective stabilizer that prevents agglomeration of the clusters, but it is also essential for cluster formation when used in the appropriate concentration. Thus, in particular for T1 samples with an Ag/MAA molar ratio below 300%, the initial Ag/MAA molar ratio determines the position of the absorption and emission maxima.

The MALDI-TOF mass spectrum of the T1 clusters shows the presence of clusters containing a small number of Ag atoms, such as Ag_2, Ag_3, and some Ag_5 (see Figure 1c), independent of the Ag/MAA ratio of the solution. Clusters of four atoms are almost never observed. It is not yet clear how each size of these Ag clusters contributes to the observed absorption and emission properties. TEM images of T1 cluster solutions show entities with sizes smaller than 2 nm in diameter (Figure 1d). No larger Ag particles or aggregation could be detected by TEM, which demonstrates that the synthesis method allows the fabrication of well-controlled nanoclusters. Importantly, the absence of large Ag nanoparticles leads to pure cluster spectra without surface plasmon bands in the region 400–450 nm (Figure 1a). It is well known that the chain conformation of PMAA is strongly dependent on the pH of the solution.[14] The pH of the solutions is around 3, which is lower than the dissociation point of PMAA. At pH 3, the carboxylic groups of poly(methacrylic acid) are in the acid form instead of ionized, which means that there are no electrostatic repulsions between COO^- groups. Instead, there are hydrogen bonds between COOH groups, which make the polymer adopt a compact coiled conformation. These coils have been claimed to favor the formation of Ag nanoclusters.[10]

The fluorescence quantum yield of T1 nanoclusters is 5–6% (relative to rhodamine 101 in ethanol). This value is independent of the initial Ag/MAA ratio. The photoluminescence lifetime measurements of T1 clusters show two main contributions, with decays of (0.96 ± 0.05) ns (82–88%) and 2.4–3.1 ns. We also observed long-lived photoluminescence emission consisting mainly of a 148–164 μs decay and also a shorter decay of 20–45 μs. The shorter components of the lifetimes compare well with those reported previously.[10,15] Additionally, the Ag T1 nanoclusters are stable over long periods when stored in the dark, neither precipitation nor changes in the absorption or emission peaks were observed in samples with Ag/MAA molar ratios lower than 800% that were stored over one year.

Further experiments showed that the Ag clusters have dynamic properties. A pink T1 cluster solution with a 300% Ag/MAA molar ratio was mixed with PMAA solutions, thus lowering the final nominal Ag/MAA molar ratio. UV/Vis spectra of these samples were recorded after two days of mixing in the dark, at which point a new equilibrium was reached. Interestingly, the new absorption and emission bands are blue-shifted with respect to the original 300% T1 sample and the new positions of the optical bands (Figure 2, squares) correspond well to the data obtained from T1 solutions with the corresponding lower initial Ag/MAA molar ratio (Figure 2, crosses). Thus, the addition of polymer after irradiation leads to the formation of samples with the same optical properties as the samples with equivalent Ag/MAA ratio before irradiation. On the other hand, the dilution of a T1 cluster solution with water only affects the intensity of the absorption peak, but not the position. The gradual spectral shift after dilution with a polymer solution suggests that the clusters are not strongly bound to the polymer and can be redistributed over the exposed polymer chains. This reversibility indicates a dynamic behavior in which the optical shifts

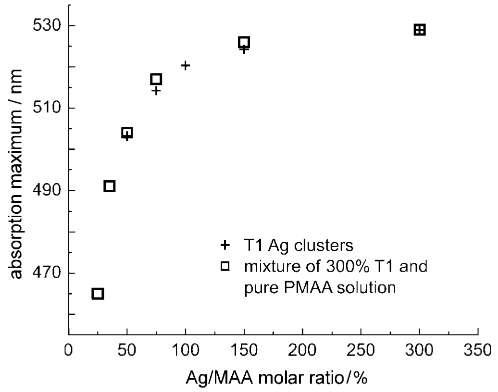

Figure 2. Comparison of the absorption maxima of T1 Ag nanocluster solutions with different initial Ag/MAA molar ratio (crosses) and the absorption maximum of mixtures of T1 Ag nanocluster solution with a 300% Ag/MAA molar ratio mixed with different volumes of a PMAA solution (squares), which indicates cluster redistribution.

are not related to the cluster size. In the new equilibrium, the clusters are still protected by the polymer, hence they are stable over prolonged periods, that is, they do not degrade, oxidize, or aggregate to form large nanoparticles. The chromatic shift of the T1 clusters with increasing Ag/MAA molar ratio (Figure 1a and 1b) and the reversibility arising from redistribution (Figure 2) may be caused by a subtle change in the local environment of the clusters. The dynamic behavior shown in Figure 2 suggests that the nanoclusters are weakly bonded to the polymer.

The weak bonding is also demonstrated by the addition of tetrahydrofuran to a solution of T1 clusters, which results in the formation of a strongly colored precipitate and a turbid colorless supernatant. It is likely that the supernatant contains polymer without clusters whereas the precipitate is rich in Ag nanoclusters. The aggregation of clusters in the T1 solution by the addition of THF is reversible; addition of water to reduce the proportion of THF resulted in redispersion of the aggregated clusters to reform a pink solution.

We applied this procedure to separate the clusters from the solution. After precipitation, the violet clusters were removed from the solution and gently pressed with a spatula to remove the absorbed liquid. After quickly rinsing with water, the clusters were immediately redissolved in selected solvents. Such solutions of redissolved clusters are referred to as second-type Ag (T2) clusters. The spectral properties of the T2 cluster solutions can be tuned to a great extent by selecting appropriate solvents. This solvatochromic effect is shown in Figure 3a. In the same way, we can prepare cluster solutions with tunable absorption and emission properties by mixing solvents. For instance, photographs, under visible and UV light, of T2 cluster solutions prepared in different water/methanol mixtures are shown in Figure 3b,c. The normalized absorption and emission curves of the same samples are shown in Figure 3d,e.

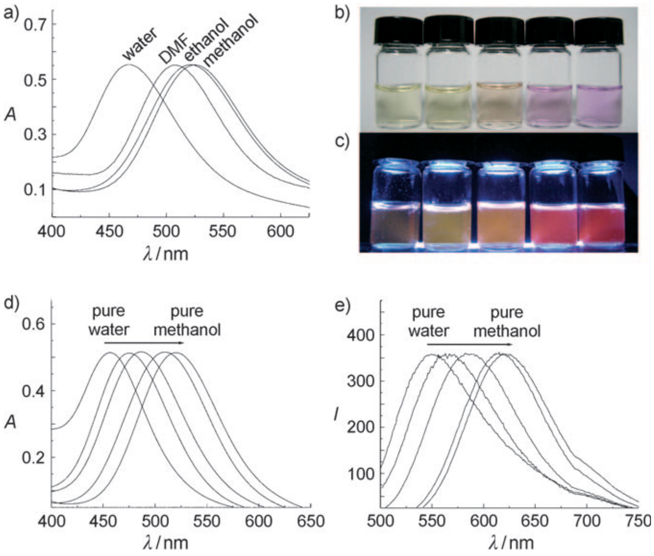

Figure 3. Solvatochromic effect of T2 Ag nanoclusters. a) Absorption spectra of T2 Ag clusters in various solvents. T2 Ag clusters b) under visible light, and c) under UV light in water/methanol mixtures ranging from pure water (left) to pure methanol (right). d) Absorption and e) emission spectra of the samples shown in (b).

The solvatochromism of the nanoclusters is analogous with that of metal nanoparticles. The solvatochromic effect is well-known for metal nanoparticles, and their photophysical properties are determined by surface plasmons.[5,16,17] On the other hand, the photophysical properties of metal nanoclusters differ in character and are controlled by quantum confinement that results in discrete energy levels, therefore it is not evident that metal nanoclusters would also have solvatochromic properties.

Another novel characteristic of our Ag nanoclusters is that they exhibit cathodic hot electron-induced electrochemiluminescence (ECL), which has not been reported to date.[18,19] The ECL spectrum of T1 clusters (Figure 4) closely matches the corresponding photoluminescence spectrum. ECL shares many advantages with chemiluminescence (CL) when used in analytical chemistry, the most important being the low detection limits that arise from the low background emission of these methods. The instrumentation required for ECL measurements is simpler than that required for photoluminescence measurements, since no expensive excitation optics are needed. The primary step in ECL at thin insulating film-coated electrodes is hot electron (e_{hot}^-) injection into the electrolyte solution by tunnel emission. This results in the subsequent generation of hydrated electrons (e_{aq}^-) and oxidizing radicals (such as sulfate radicals, $SO_4^{\bullet -}$) from added co-reactants. A co-reactant is a species that produces a highly reactive intermediate upon oxidation or reduction, which reacts with an electrochemiluminescent luminophore to either produce an excited state or commence an excitation pathway by a one-electron oxidation or reduction. The most common excitation pathway in ECL is the ox–red excitation pathway, in which the luminophore is first oxidized by a cathodically produced oxidizing radical and then reduced by one energetic electron to the excited form of its original oxidation state. At present, we believe that the Ag nanoclusters are mainly excited by the ox–red excitation pathway. The observed ECL emission of nanoclusters can quite probably be improved by optimizing the operating conditions, including evaluation of the best suitable co-reactant, appro-

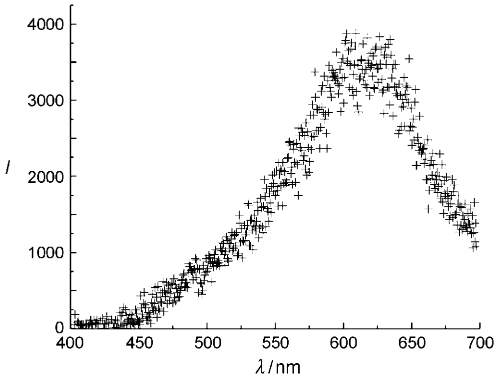

Figure 4. Electrochemiluminescence of T1 Ag nanoclusters with a 200% Ag/MAA molar ratio.

priate pH value, and excitation pulse amplitude. The nanoclusters may be used as electrochemiluminescent and photoluminescent labels in the same manner as many molecular labels, such as organic luminophores and certain metal chelates. Further work that exploits the ECL of the present and other nanoclusters is in progress.

In summary, we have demonstrated for the first time that the absorption and emission properties of few-atom metal nanoclusters respond dramatically to changes in the chemical environment, such as the Ag/MAA molar ratio and solvent. The spectral shifts are not related to a change in nanocluster size. Moreover, the Ag nanoclusters exhibit electrochemiluminescence, a property that has not been reported to date for these species. The large tunable shift in the optical characteristics, the high photoluminescence quantum yield and the electrochemiluminescence may confer remarkable advantages to these few-atom Ag clusters over larger nanoparticles in applications such as molecular sensing.

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