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Etching Colloidal Gold Nanocrystals with Hyperbranched and Multivalent Polymers: A New Route to Fluorescent and Water-Soluble Atomic Clusters

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Metal and semiconductor nanoparticles are a topic of considerable interest in chemistry, biology, and materials sciences. This broad and interdisciplinary interest arises not only from their novel size-dependent electronic and optical properties but also from their dimensional similarities with biological molecules such as nucleic acids and proteins.[1,2] For semiconductors with well-defined energy band gaps, strong quantum-size confinement is observed when the particle sizes are smaller than the exciton Bohr radius (about 4−5 nm for CdSe). This has allowed the development of semiconductor quantum dots as a new class of fluorescent labels with unique properties and applications that are not available from traditional organic dyes and fluorescent proteins.[3−5] In contrast, metallic materials such as silver and gold do not have a discrete band gap, and quantum-mechanical properties are only observed in atomic clusters that are smaller than the Fermi wavelength (less than 1 nm) of the conduction electrons.[6] As a result, metal nanoclusters consisting of only several to tens of atoms are likely to behave as "artificial atoms," showing discrete and size-tunable electronic transitions. Due to this stringent size requirement, progress has been slow in developing fluorescent metal particles, and current synthetic routes are limited to chemical reduction of silver or gold precursors in the presence of stabilizing ligands such as triphenylphosphine,[7] thiols,[7,8] and poly(amidoamine) dendrimers.[9]

Here we report a ligand-induced etching process for preparing highly fluorescent and water-soluble metal nanoclusters. Specifically, we show that ligand exchange reactions using multivalent coordinating polymers such as polyethylenimine (PEI) are able to "etch" preformed colloidal gold nanocrystals, leading to atomic gold clusters that are highly fluorescent upon UV light excitation. Surprisingly, these "as-prepared" fluorescent clusters appear to be in an oxidized electronic state, with their excitation and emission maxima located at 421 and 505 nm, respectively. Upon treatment by strong reducing agents such as NaBH$_4$, the cluster's excitation and emission peaks are shifted to 353 and 445 nm. Electrospray ionization (ESI) mass spectrometry data (Supporting Information) indicate that the light-emitting species are small atomic nanoclusters consisting of only 8 gold atoms (Au$_8$). There is also evidence to suggest that a ligand-to-metal electronic transition in the ultraviolet is superimposed on the cluster absorption spectra, but it is not directly related to the intrinsic fluorescent properties of these atomic clusters.

Au nanocrystals were synthesized using a method based on a modified Brust−Schiffrin method.[10,11] Transmission electron microscopy (TEM) (Figure 1A) showed highly monodispersed nanocrystals about 8 nm in diameter, with a strong surface plasmon resonance peak at 523 nm (Figure 1B). Hyperbranched PEI (M_n = 1800 g/mol) was used as a multivalent polymer for ligand exchange reactions with the original capping molecule dodecylamine.[11] After ligand exchange, two absorption peaks were observed at 345 and 518 nm, and separation of the reaction mixture by ultracentrifugation (75000 rpm, 30 min) produced a yellow supernatant and a red deposit. The red deposit was associated with the 518-nm absorption (Figure 1B), and was identified as PEI-coated gold nanocrystals. These PEI-etched nanocrystals are about 7 nm in size (a reduction from 8 nm before etching, and a 5-nm blue-shift in plasmon resonance) (Figure 1C) and are well dispersed on the TEM grid. When stained by phosphotungstic acid, the PEI polymer layer surrounding the nanocrystals is clearly visible in the TEM images.[11]

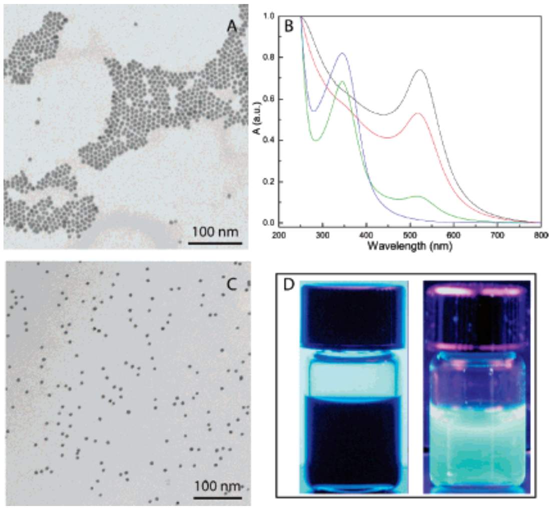

Figure 1. Ligand-induced etching of preformed gold nanocrystals with hyperbranched and multivalent PEI, and formation of highly fluorescent and water-soluble gold nanoclusters. (A, C) Transmission electron micrographs of preformed Au nanocrystals before and after ligand-induced etching. (B) Optical absorption spectra of the original Au nanocrystals (black curve), the solution mixture after etching (green curve), the etched nanocrystals after separation (red curve), and the pure supernatant after separation (blue curve). (D) Color photographs of the original Au nanocrystals in chloroform (left) and the supernatant nanocluster in water after etching and separation (right). Both were illuminated with a UV lamp (365 nm).

The separated supernatant solution emits intense green light (Figure 1D) under UV light irradiation (365 nm), suggesting the presence of fluorescent Au clusters. In contrast, neither the original nanocrystals nor the PEI-coated ones are fluorescent. In fact, the generation of fluorescent Au clusters is responsible for the size reduction of the nanocrystals after ligand exchange. Simple geometric calculations based on the size change of the nanocrystals indicate that about 30% of the Au atoms of the nanocrystals are converted into atomic clusters. These light-emitting clusters are smaller than one nanometer and are not visible under TEM. As shown in Figure 2A, luminescence of the clusters shows excitation and emission maximum at 421 and 505 nm, respectively. After chemical reduction (by adding 0.5 M NaBH$_4$ or other common reducing agents such as hydrazine to the cluster solution), a new absorption peak is observed at 295 nm (Figure 2B) while the yellow color disappears. Concomitantly, the cluster's excitation and emission spectra are blue-shifted to 353 and 445 nm (Figure 2A), respectively. Other chemicals such as strong acids, strong bases, and buffering salts are not effective. Taken together, our experimental data suggest that the as-prepared clusters are chemically

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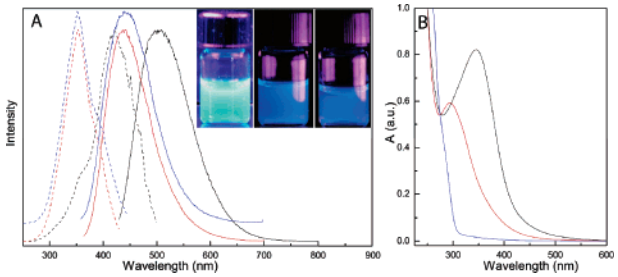

Figure 2. Comparison of the optical properties of fluorescent gold nanoclusters with different oxidation states and coordination ligands. (A) Fluorescence excitation (dashed curves) and emission (solid curves) spectra of the as-prepared clusters (black curve), clusters reduced by $NaBH_4$ (red curve), and clusters treated with concentrated mercaptoacetic acid (blue curve). (Inset) Color photos of fluorescence emission from as-prepared, reduced, and mercaptoacetic acid-treated clusters (from left to right) under UV irradiation (365 nm). (B) Corresponding optical absorption spectra of the clusters in (A).

reduced by strong reducing agents, although it is not absolute proof of the cluster's oxidation state.

To further examine the nature of the 295-nm absorption peak, the reduced clusters are incubated in concentrated (0.5 M) mercaptoacetic acid (MA) for 3 days. During this process, mercaptoacetic acid is expected to replace multivalent PEI ligands because sulfur has a much higher affinity for gold than the PEI nitrogen atoms. As shown in Figure 2, this treatment completely eliminates the absorption peak at 295 nm but surprisingly has no effects on the fluorescence excitation and emission spectra. This intriguing finding provides strong evidence that the original absorption peak arises from metal−ligand (gold to PEI) charge-transfer transitions, and is not related to the intrinsic properties of the Au clusters. We also note that these fluorescent clusters are extremely stable; even being dispersed in 1 M HCl or 1 M NaOH has no obvious effects on their fluorescence properties. Furthermore, results from control experiments reveal that the use of neither larger PEI (M_n = 10000 g/mol) nor smaller Au nanocrystals (∼4 nm) could alter the outcome of ligand exchange reactions; that is, the same fluorescent clusters are always formed.[11]

The fluorescence properties (both wavelengths and quantum yields) of our reduced clusters are similar to those of PAMAM-encapsulated Au_8 clusters as reported in the literature.[9a] Strong evidence also comes from ESI mass spectrometry data, which showed that the PEI stabilized clusters contain 8 gold atoms.[11] Recent work by Dickson and co-workers has generated a series of atomic gold clusters such as Au_5, Au_{13}, Au_{23}, Au_{31}, with fluorescence quantum yields between 10 and 70%.[9b] It should be noted that these quantum yield data are subject to large errors because the excitation spectra for these clusters are dramatically different from their absorption spectra, and the electronic transitions responsible for fluorescence emission are still not clear. Our own data indicate that the clusters have lower quantum yields, on the order of 10−20% at room temperature. It is, however, interesting that the absolute transition energies for these clusters are found to scale with the inverse cluster size, suggesting that their electronic structures are solely determined by the Au nanocluster free-electron density and nanocluster size. They are believed to have nearly spherical electronic structures with electrons bound by an approximately harmonic potential in three dimensions. While only magic cluster sizes correspond to shell closings, their spherical electronic structures indicate that these nanocluster have behaviors similar to those of ‘‘multielectron artificial atoms.”

The detailed mechanisms of ligand-induced etching must await further investigations, but we believe that two chemical pathways could lead to the formation of atomic gold clusters. In the first, Au_8 clusters are liberated in a single step during ligand exchange and are immediately protected by a multivalent and hyperbranched PEI ligand. The PEI ligand could also function to activate Au atoms and to subtract Au_8 clusters from the nanocrystal surface. The formation of Au_8 clusters probably results from the extraordinary stability of this "magic" cluster with closed electronic shells. In the second mechanism, Au(I) ions could be released during the ligand exchange reaction. Evidence for this mechanism comes from the recent work of Hutchinson and co-workers showing the release of Au(I) complex during the ligand exchange of 1.5-nm triphenylphosphine-protected Au nanoparticles with thiols.[12] Also, it is known that Au(I) species tend to aggregate by strong "aurophilic" interactions, due to hybridization of the empty 6s/6p orbital and filled 5d orbital.[13] With a high density of binding groups, PEI could facilitate Au(I) aggregation. Work is ongoing to elucidate these detailed mechanistic steps.

In summary, we have reported a new method for preparing highly fluorescent and water-soluble metal nanoclusters based on the use of multivalent coordinating polymers to etch preformed high-quality gold nanocrystals. On the basis of mass spectrometric analysis and the previous work of Dickson and co-workers, we have identified our light-emitting species as atomic clusters consisting of 8 gold atoms (Au_8). There is also evidence to suggest that a ligand-to-metal electronic transition in the ultraviolet is superimposed on the cluster absorption spectra, but it is not directly related to the intrinsic fluorescent properties of these atomic clusters. Although the detailed mechanisms of ligand-induced nanocrystal etching need further studies, this new synthetic route holds promise for preparing new types of fluorescent metal nanoclusters for applications in catalysis and biological labeling.

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Supporting Information Available: Details of preparation and characterization of Au clusters. This material is available free of charge via the Internet at http://pubs.acs.org.

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