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<td>Author(s)</td>
<td>KAWASAKI, Hideya, YAMAMOTO, Hiroko, FUJIMORI, Hiroki, ARAKAWA, Ryuichi, INADA, Mitsuru, IWASAKI, Yasuhiko</td>
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Surfactant-free solution synthesis of fluorescent platinum subnanoclusters†

Hideya Kawasaki,*a Hiroki Yamamoto,a Hiroki Fujimori,a Ryuichi Arakawa,a Mitsuru Inada b and Yasuhiro Iwasaia

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We have demonstrated the first surfactant-free synthesis of fluorescent Pt nanoclusters in N,N-dimethylformamide (DMF) solution. The Pt nanoclusters consist of 4 to 6 Pt atoms. They form highly stable dispersions in water, under both acidic (pH 2) and basic conditions (pH 12), and at ionic strengths of 1 M NaCl.

Nobel metal clusters have recently attracted considerable attention in many areas of research, including physics, chemistry, materials science, and biosciences.1 Size-dependent effects of metal clusters are observed only when the free electrons are confined relative to the Fermi wavelength (~1 nm) in the cluster conduction band.2–7 As a result, sub-nanometer-sized metal clusters (nanoclusters) consisting of several tens of atoms are likely to exhibit molecule-like behaviors, including discrete electronic states and size-dependent fluorescence.

Metal nanoclusters (NCs) are also known to possess reactivity not observed in their bulk analogs, which can make them attractive for catalysis. Platinum is perhaps one of the most important metals in catalysis applications. Recently, it has been reported that sub-nanometer Pt8–10 NCs stabilized on thiolate-organic compounds. To our knowledge, this is the first successful surfactant-free chemical synthesis of fluorescent Pt NCs in solution.9,10 Here, we report a simple, one-pot synthesis of Pt NCs in N,N-dimethylformamide (DMF) solution in the absence of any capping agents such as surfactant, polymer, or thiolate-organic compounds. To our knowledge, this is the first successful surfactant-free chemical synthesis of fluorescent Pt NCs in solution.

The preparation method described was quite simple according to a DMF reduction method for gold clusters11 and highly reproducible. A solution of 150 µL of 0.1 M aqueous H2PtCl6 was added to 15 mL of DMF that had been preheated to 140 °C, and the DMF solution was refluxed in a 140 °C oil bath with vigorous stirring for 8 h in air. As the reaction proceeded, the solution changed slowly in color from light yellow to colorless over 0 to 1 h, and finally to yellow by 2 to 6 h (Fig. 1a). The reaction was nearly complete in about 8 h, as confirmed by X-ray photoelectron spectroscopy (XPS) and by the absence of PtCl6 – ion peaks in the UV-visible absorption spectrum. The yellow solution showed a broad UV-visible absorption below 600 nm. We found the resulting DMF solution of Pt NCs to be stable for at least six months when stored in the dark, neither precipitating nor changing in spectral properties.

The Pt NCs were photoluminescent in the yellow solution after heating for more than 2 h because of their size relative to the Fermi wavelength (~1 nm), and their emission maximum depended upon the excitation wavelength (Fig. 1b). With UV excitation at 350 nm, the maximum emission wavelength was 484 nm, and with visible excitation at 500 nm, the maximum emission wavelength was 544 nm. Photoluminescence of metal clusters generally blue shifts as the clusters decrease in size.3 Thus, the different color emissions observed with excitation of the solution at different wavelengths were consistent with formation of a mixture of Pt NCs varying in size.

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) is a valuable tool to demonstrate sub-nanometer-sized metal clusters. The MALDI-MS spectrum demonstrated the existence of sub-nanometer-sized Pt NCs of 4 to 6 Pt atoms, using 2-mercapto-benzothiazole (MBT) as a novel matrix (Fig. 2). The mass of the dominant molecular ion

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Fig. 1 (a) UV-visible spectra at different reaction times of t = 0 (H2PtCl6), 5 min, 1 h, 2 h, 3 h, 4 h, 5 h and 6 h. (b) Photoluminescence spectra of DMF-protected Pt NCs. Emission spectra for excitation at 300 nm, 350 nm, 400 nm, 450 nm and 500 nm are shown. Inset photographs show Pt NCs under (a) room light and (b) 365 nm UV light.
DMF-protected Au nanoclusters. The XPS peak of a metal cluster increases with reduced cluster valence such as Pt(II)Cl₄ in a more reduced state than Pt compounds in a high valence. This work was supported by Kansai University Special Research Fund #120135 and Strategic Project to Support the Formation of Research Bases at Private Universities.

Notes and references


Fig. 2 MALDI mass spectrum of MBT-protected Pt NCs in the negative ion mode, obtained for DMF-protected Pt NCs by ligand exchange with 2-mercapto-benzothiazole (MBT).

Fig. 3 (a) TEM image of DMF-protected Pt NCs. Scale bar: 2 nm. (b) XPS spectrum for dried Pt NCs indicative of Pt 4f₇/₂.