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Surfactant-free solution synthesis of fluorescent platinum subnanoclusters†

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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 Pt_{8–10} NCs stabilized on high-surface-area solid supports are 40–100 times more active for the oxidative dehydrogenation of propane than the previously studied platinum catalysts,⁸ which is responsible for their surprisingly high surface reactivity of Pt NCs. However, very few attempts have been made at the difficult synthetic route of platinum nanoclusters (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 μ L 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 of ~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.⁴ 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

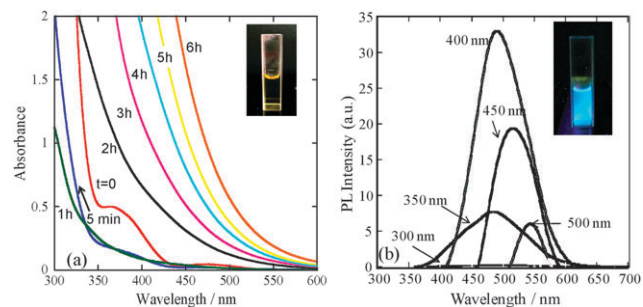


Fig. 1 (a) UV-visible spectra at different reaction times of $t = 0$ (H₂PtCl₆), 5 min, 1 h, 2 h, 3 h, 4 h, 5 h and 6 h. (b) Photoluminescence spectra of DMF-protected Pt NCs. Emission spectra for excitation at 300 nm, 350 nm, 400 nm, 450 nm and 500 nm are shown. Inset photographs show Pt NCs under (a) room light and (b) 365 nm UV light.

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† Electronic supplementary information (ESI) available: EDX spectrum of Pt nanoclusters and the UV-visible absorption spectra of Pt nanoclusters in various solvents. See DOI: 10.1039/b925117k

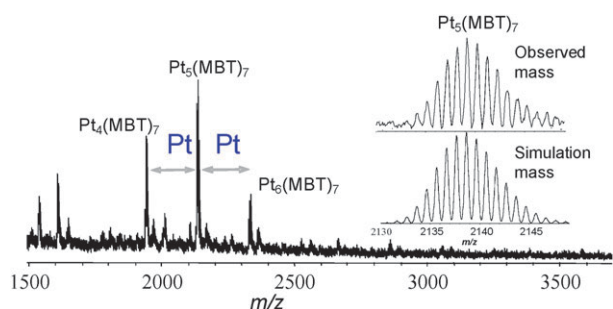


Fig. 2 MALDI mass spectrum of MBT-protected Pt NCs in the negative ion mode, obtained for DMF-protected Pt NCs by ligand exchange with 2-mercapto-benzothiazole (MBT).

observed in negative ion mode was consistent with $\text{Pt}_5(\text{MBT})_7$ nanoclusters, the simulated mass obtained in isotropic pattern analysis. These platinum atom clusters most likely give rise to the photoluminescence of Pt NCs. It is curious that the number of the MBT ligands is larger than that of Pt atoms, but we do not have the information on the exact structure of $\text{Pt}_5(\text{MBT})_7$ at present.

We also noted that the MBT-protected Pt NCs present new absorption peak at 315 nm, which may arise from MBT ligands, suggesting that the ligand-capping procedure is efficient, while the ligand exchange of DMF-protected Pt NCs with MBT did not significantly alter photoluminescence spectrum (Fig. S1, ESI[†]). The weak dependence of photoluminescence spectrum on the ligand exchange was also reported for DMF-protected Au nanoclusters.¹¹

We examined influence of metal concentration (0.1–1 mM) and reaction temperatures over 120–150 °C on photoluminescence spectra, but the spectra showed almost no change, suggesting weak dependence of the size on these changes in this synthetic method.

Transmission electron microscopy (TEM) of Pt NCs showed numerous nanoparticles of approximately 1 nm (Fig. 3a), and these small nanoparticles were confirmed to be Pt species by TEM-EDX analysis (Fig. S2, ESI[†]). The extremely small size of the nanoclusters accounts for the very low image contrast.¹² The XPS spectrum obtained from dried Pt NCs (Fig. 3b) showed a peak indicative of Pt 4f_{7/2} at 72.8 eV, suggesting the presence of Pt NCs in a more reduced state rather than Pt compounds in a high valence such as $\text{Pt}(\text{II})\text{Cl}_4^{2-}$ (74.4 eV). It is well known that the XPS peak of a metal cluster increases with reduced cluster size.^{13,14} The higher binding energy of the Pt NCs than that of bulk Pt (71.1 eV) may originate from the effect of Pt cluster size.

For metal catalysis applications, it is necessary to use different solvents, but the surface modification of metal nanoclusters using strong ligands such as thiolate-molecules may limit the catalysis applications because of lower accessibility of their surfaces. We found that the DMF-protected Pt NCs dispersed highly in ethanol or in water, under both acidic and basic conditions (pH 2, pH 12), and even at high ionic strength (1 M NaCl), without evidence of surface modification for at least one month (Fig. S3, ESI[†]). Owing to the contribution of the large dipole of the amide group in a DMF molecule, the interaction of the amide group in DMF with Pt NCs

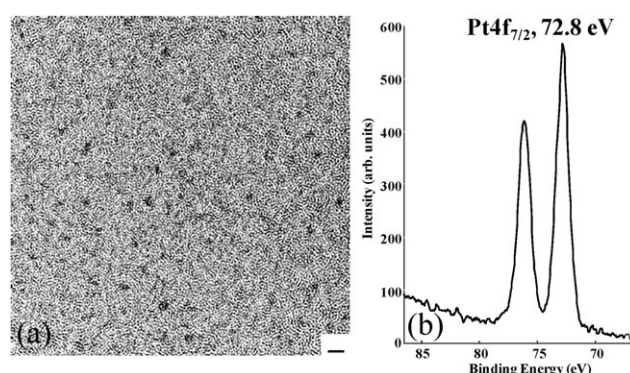


Fig. 3 (a) TEM image of DMF-protected Pt NCs. Scale bar: 2 nm. (b) XPS spectrum for dried Pt NCs indicative of Pt 4f_{7/2}.

is considered to play an important role in the stabilization of Pt NCs.

Based on the results of first-principles molecular dynamics, the formation of a Pt(I)–Pt(II) intermediate has been suggested to be critical for Pt cluster formation without going through a zero-valent state.¹⁵ In this model, the process would be expected to require the presence of mild reducing agents. These partially reduced Pt(I)–Pt(II) intermediates likely exist as early intermediates toward the formation of Pt NCs. In the synthetic method reported here, the use of DMF as a mild reducing agent and the presence of the intermediate complex formed during the very slow reduction process may both have been important for the successful synthesis of Pt NCs in surfactant-free solution.

In summary, we have demonstrated the first synthesis in surfactant-free solution of fluorescent Pt nanoclusters consisting of 4 to 6 Pt atoms. The as-prepared Pt NCs are highly stable in organic, aqueous, or salt solutions. These surfactant-free Pt NCs were readily dispersible in a variety of solvents. The property will greatly facilitate their use in metal catalysis and bioimaging applications. This synthesis strategy should be applicable to other platinum group metals. Preliminary results indicate that stable Pd nanoclusters with a small size of around 1–2 nm can be prepared in the heated DMF solution by this synthetic method. Further studies focusing on the catalytic function of the Pt NCs as well as methods for the synthesis of nanoclusters of other platinum group metals are under way.

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