

## Preparation of Monodisperse Platinum Nanocrystal Core–Poly(amidoamine) (PAMAM) Dendrimer Shell Structures as Monolayer Films

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Hybrid nanoparticles of carboxyl-terminated generation 4.5 (G4.5) poly(amidoamine) dendrimers with platinum nanocrystals encapsulated inside them were prepared in water. The obtained nanoparticles were treated by size-selective precipitation to refine the size distribution. On a carbon-coated copper grid, the nanoparticles formed a monolayer film when observed by TEM. The sizes of the hybrid nanoparticles were evenly dispersed, with an average diameter of 4.0 nm. The Fourier transform power spectrum proved that the monolayer film had short-range order, and locally hexagonal packing was present. High-resolution transmission electron microscopy showed that the encapsulated Pt atoms were gradually rearranged as metal nanocrystals after a period of time.

Nanoparticle materials with an ordered structure have attracted much attention for years, and research on them has led to many important applications, because of their intriguing optical, electronic, and magnetic properties. For instance, the orderly structure of a nanometer-scale metal particle array has demonstrated great potential in producing single-electron devices, surface catalysts, and magnetic materials.<sup>1–5</sup> Recently, there have been many reports on the superlattice of various metal nanoparticles with organic surfactants<sup>6–8</sup> or amphiphilic block co-polymers.<sup>9,10</sup> However, few reports have involved the orderly array of polymer nanoparticles 1–10 nm in diameter, because of the difficulty in precisely controlling the size and shape of the nanoparticles.<sup>11</sup> Therefore, the exploration of novel methods and compounds for the formation of evenly sized and regularly shaped polymer nanoparticles, as well as an ordered nanometer structure, still remains a great challenge. A new class of macromolecules—dendrimers—is considered to be a superb candidate for preparing nanoparticles, because of their unique properties.<sup>12–14</sup> Dendrimers have an intrinsically well-defined globular structure and highly modifiable surface groups. Therefore, they are monodispersed building blocks, as well as ideal guest-molecule carriers,<sup>15</sup> promising biocompatible materials,<sup>16</sup> and excellent templates for generating metal nanoparticles within their spacious interior.<sup>17–21</sup>

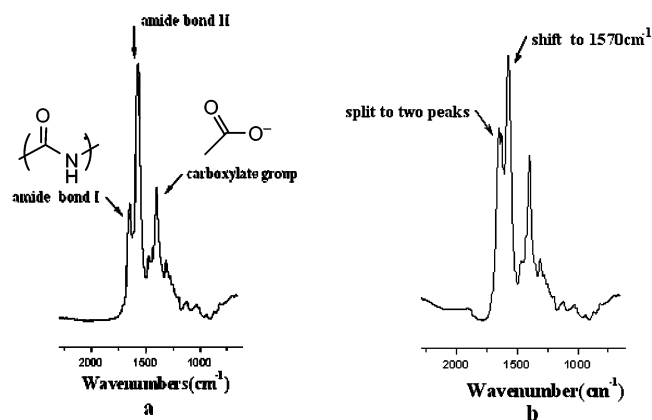
Crooks et al. made a study on the formation of platinum, gold, copper, and palladium nanoparticles with dendrimers as templates.<sup>22–24</sup> Tomalia et al. demonstrated that zerovalent transition metals can be encapsulated inside poly(amidoamine) (PAMAM)<sup>25</sup> dendrimers in a variety of architectures.<sup>26–28</sup> Watanabe and Regen reported on the construction of dendritic multilayers with generation 6 (G6) PAMAM dendrimers as building blocks and  $K_2PtCl_4$  as the layer linkers, by the interaction of terminal amine groups of dendrimers and  $K_2PtCl_4$ .<sup>29</sup> Tsukruk and co-workers have published papers on the

monolayer structure and the self-assembled multilayer films of PAMAM dendrimers.<sup>30,31</sup> Here, we describe, for the first time, the preparation of size-monodisperse hybrid nanoparticles of carboxyl-terminated generation 4.5 PAMAM dendrimers (ethylenediamine core) (G4.5– $COO^-$ ) that encapsulate platinum nanocrystals inside them, and the formation of monolayer films from the obtained nanoparticles as globular building blocks that make the array of dendrimers readily observable by transmission electron microscopy (TEM). The combination of platinum and PAMAM was investigated using UV–Vis spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The structure of the films was observed with TEM/high-resolution TEM (HRTEM) and the Fourier transformation method.

G4.5 poly(amidoamine) dendrimers were synthesized according to the literature<sup>25,32</sup> and were hydrolyzed with a stoichiometric amount of KOH in methanol, to yield carboxyl-terminated G4.5 PAMAM.<sup>33</sup> The product was purified through a dialysis membrane (molecular weight cutoff of 12 000), to remove impurities and narrow the dendrimer particle size distribution. Similar to the process reported by Crooks et al.,<sup>22,23</sup> the platinum nanoparticles were prepared by partitioning  $PtCl_6^{2-}$  into the interior of G4.5– $COO^-$  dendrimers, followed by a chemical reduction. The pH of the solutions was controlled at 9.0 during the preparation.

Using a UV–Vis spectrophotometer, changes in the absorption spectra during the nanoparticle preparation process were recorded (see Supporting Information). In the absence of PAMAM, there was a strong absorption band at 255 nm that corresponded to the absorption of  $PtCl_6^{2-}$ . When PAMAM was added to the solution (dendrimer:platinum molar ratio of 1:60), a new band at 240 nm emerged, whereas the size of the band at 255 nm decreased, because of the replacement of chloride ligands by the functional groups of dendrimers. After reduction with  $NaBH_4$ , a broad absorption band was observed, which was a result of the absorption of platinum colloids. Inductively coupled plasma (ICP) measurements show that there were no

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**Figure 1.** FTIR spectra of (a) G4.5 carboxylate poly(amidoamine) and (b) the hybrid nanoparticles of G4.5 PAMAM mixed with  $\text{H}_2\text{PtCl}_6$  (G4.5 PAMAM: $\text{H}_2\text{PtCl}_6$  = 1:60).

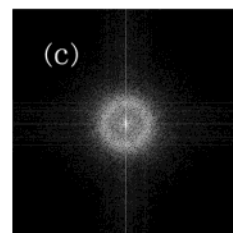
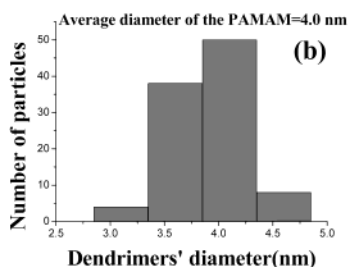
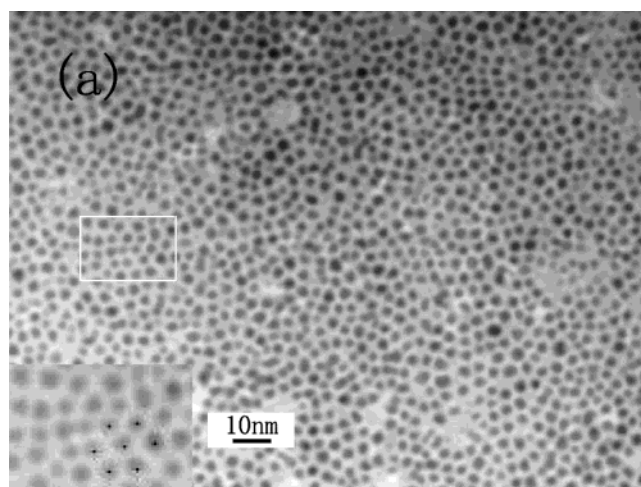
free  $\text{PtCl}_6^{2-}$  ions in the solvent. Therefore, the average number of Pt atoms in a PAMAM dendrimer was estimated to be 60 in this procedure.<sup>22,23</sup>

FTIR spectra were conducted on a Nicolet Model Magna-IR 750 spectrometer to identify the location of  $\text{Pt}^{4+}$  species. It is well-known that the two amide bands I and II, at 1650 and 1540  $\text{cm}^{-1}$ , respectively, are characteristic of the PAMAM dendrimer branches. The FTIR spectra of carboxyl-terminated PAMAM dendrimers showed three distinct peaks: at 1650 (amide band I), 1574 (overlap band of amide II and carboxylate), and 1400  $\text{cm}^{-1}$ . After PAMAM was combined with  $\text{PtCl}_6^{2-}$ , amide band I split into two peaks, at 1652 and 1625  $\text{cm}^{-1}$ , which indicated that  $\text{Pt}^{4+}$  ions had interacted with the amide groups in the interior of dendrimers<sup>21</sup> (Figure 1). Moreover, the absorption band at 1400  $\text{cm}^{-1}$ ,<sup>34</sup> which is assigned to the sodium carboxylate of the G4.5 PAMAM dendrimers, showed no changes. These experimental results demonstrate that, under our controlled conditions, most of the  $\text{Pt}^{4+}$  ions have been encapsulated inside the dendrimer molecules.

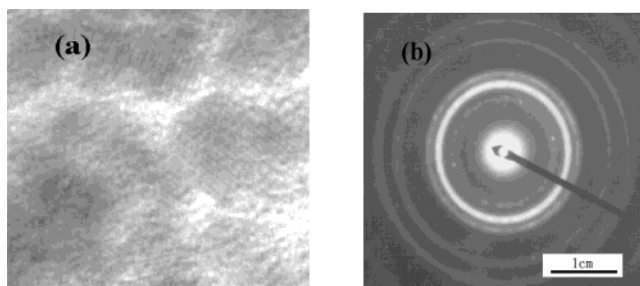
To narrow the size distribution of the hybrid nanoparticles, 0.5 unit volume of tetrahydrofuran (THF) was gradually added to one unit volume of the aforementioned prepared solution. After centrifugation at 5000 rpm for 10 min at room temperature, black precipitates were separated. Another 0.5 unit volume of THF was added again into the remaining solution. Nanoparticles of different sizes could be obtained by repeating this procedure. A precipitate yield of >80% was collected when the volume ratio of THF to the solution was 1:1. These precipitates could dissolve in KOH solution (pH = 9) readily and form a transparent brown solution. TEM image analysis showed that the size distribution of the platinum–dendrimer hybrid nanoparticles was significantly narrowed after this size-selective precipitation procedure<sup>35</sup> (see Figure 2).

The monolayer film was formed by evaporating the solution of the hybrid nanoparticles on a flat substrate. A drop (4  $\mu\text{L}$ ) of dilute solution (0.5 mg/mL) was deposited on a carbon-coated copper grid and allowed to evaporate slowly at room temperature. The copper grid was put in a vessel full of moisture, to ensure that the evaporation process was sufficiently slow. Generally, two more days will be necessary, which will enable the nanoparticles to have enough time to diffuse on the surface to form ordered solids. Otherwise, the nanoparticles will land on top of each other and form an amorphous solid.<sup>35</sup>

Figure 2a shows a TEM image of the monolayer film from platinum–dendrimer hybrid nanoparticles. The particles clearly are almost monodisperse and are closely packed in an orderly structure. Some parts present a hexagonal-like packing phase.



**Figure 2.** (a) TEM image of the hybrid nanoparticles monolayer film; inset is a TEM image showing the hexagonal-like packing phase selected from this picture; (b) the histogram of the nanoparticles; (c) the two-dimensional Fourier transformation of the image in Figure 2a.



**Figure 3.** (a) HRTEM image of PAMAM-Pt nanoparticles after a week; (b) electron diffraction of the platinum nanocrystals encapsulated in PAMAM.

The average distance between the centers of two neighboring nanoparticles (i.e., the average diameter of the dendrimers which encapsulate platinum nanocrystals) is 4.0 nm (Figure 2b). The average diameter of the platinum nanocrystals is 1.80 nm. Figure 2c is the optical diffraction of Figure 2a using the fast Fourier transformation method. The appearance of a diffraction ring indicates that the array formed from the hybrid nanoparticles has short-range order. The diffraction ring corresponds to an average spacing of 3.4 nm. This value is almost equal to the  $d$ -spacing of the (110) plane of the hexagonal packing of the spheres with a diameter of 4.0 nm. The result indicates that there might be several clusters that present hexagonal packing in the film. However, ordered domains are small and oriented randomly. All these features cause the wide diffraction ring.

HRTEM shows that most of the Pt atoms inside the dendrimer molecules do not exist as single crystals in freshly prepared formations (not shown). However, these atoms were gradually rearranged into metal crystals after one week (Figure 3a). From the electron diffraction pattern (Figure 3b), the spacing between

platinum crystal planes is calculated to be 4 Å, which is consistent with that of platinum metal crystals.

What initiated the formation of an orderly monolayer structure? In our experiment, the answer probably lies in the following two factors.

(1) Using molecular dynamics simulations, Alder and co-workers<sup>36,37</sup> have shown that, if interparticle attraction does not occur, separated, size-monodisperse hard spheres would form an orderly array when the particle concentration exceeded a critical volume fraction of 0.49. In the hydrolyzed PAMAM, the negative charges on the surface provide a sufficient repulsive force to counteract effects of the van der Waals attraction and hydrogen bond interaction. Therefore, the particles can be evenly dispersed in the solution during the solvent evaporation and form an orderly monolayer upon reaching and exceeding the critical volume fraction.

(2) As demonstrated by Chen,<sup>38</sup> a more orderly superlattice structure will be formed when surface pressures are increased or when particles are cross-linked via bifunctional linkers (such as 4,4'-thiobisbenzenethiol). In our case, the interaction between nanoparticles is repulsive; however, the surface tension of an aqueous solution may provide the driving force to compel the composites together. When the repulsion and conglomeration are balanced, the surface tension confines those particles to a limited space and facilitates the formation of an orderly structure. However, this force is not strong enough to form a long-range two-dimensional ordered array.

In conclusion, monodisperse hybrid nanoparticles of platinum within poly(amidoamine) (PAMAM) dendrimers were prepared. The particles were identified as core/shell nanocomposites of platinum nanoparticles and PAMAM molecules. An orderly monolayer film was fabricated with these nanocomposites. Transmission electron microscopy demonstrated the orderly structure and locally closely packed hexagonal-like phase in the monolayer. Fourier transformation proved the existence of hexagonal packing structure. Further investigations, such as three-dimensional self-assembly and exploration of the possible unique properties of these films, are in progress. It is important to note that, because the dendrimer building blocks are versatile host molecules, the method described here can be readily applicable to the preparation of various functionalized monolayer films.

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**Supporting Information Available:** Description of the preparation procedure used to form Pt-PAMAM hybrid nanoparticles, and the size distributions of platinum nanocrystals and PAMAM dendrimers encapsulated with platinum nanocrystals (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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