

Growth Mechanism of Metal Clusters in Ligand Exchange Processes

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Two-phase system is exploited for the preparation of thiol-stabilized Pd clusters, which involves ligand exchange reactions of polymer-protected clusters dispersed in aqueous phase. The thiol-stabilized Pd clusters prepared by this method exhibit a variety of distributions in size and shape depending primarily on the concentrations of thiols used in the ligand exchange reactions, while the average size of the clusters increases significantly after extraction to the organic phase. Based on these observations, we propose a two-step mechanism for the cluster growth where the metal clusters are transferred into the organic phase with a low ligand coverage, followed by coalescence into more stable forms.

Key words: metal clusters, ligand exchange, coalescence, thiols

1. INTRODUCTION

Several methods have been proposed for the chemical preparation of colloidal metal dispersions with a narrow distribution of size [1-7] and shape [8]. The process common to all those methods involves the reduction of the relevant metal ions in the presence of a ligand reagent, which stabilizes the resultant clusters and prevents further coalescence. Under such preparation conditions, the cluster size and shape can be controlled by adjusting the ratio of the amount of the ligands over that of the metal ions. One may also furnish the clusters with additional properties by choosing the kind of ligand reagent. This is further accomplished by applying ligand exchange reactions to the preformed clusters [9-12]. For example, Toshima and Liu have shown that the ligand exchanges from poly(*N*-vinyl-2-pyrrolidone) (PVP) to triphenylphosphine (TPP) and from TPP to diphenylphosphinobenzene sulfonate (DPPS) [9, 10] take place readily around noble metal clusters, which result in the drastic change in the solubility of the dispersed clusters. Brown and Hutchison have reported on the substitution of the ligands of Au₅₅(PPh₃)₁₂Cl₆ with alkyl- or aryl-thiols to increase the stability of the gold clusters [11]. In those processes, the ligand exchange proceeds with retaining the particle-size distribution. Recently, the growth of the Au clusters has been reported during exchange reactions into primary amine ligand [12]. This suggests the possibility for preparing size-controlled metal clusters with desired surface properties by utilizing the ligand exchange reactions, while the underlying growth mechanism has not yet been unraveled.

In this paper, we report on the preparation of thiol-stabilized Pd clusters via ligand exchange reactions followed by solvent extraction: the Pd clusters stabilized by PVP [2, 3] are extracted from an aqueous solution to toluene containing thiols. The efficiency of extraction, the size and shape distributions of the clusters extracted into the organic phase are investigated as a function of thiol

concentration by the combination of UV-VIS absorption spectroscopy and transmission electron microscopy.

2. EXPERIMENTAL

2.1 Preparation of PVP-protected Pd clusters

The polymer-protected Pd clusters were prepared following the recipe given by Toshima and coworkers [2, 3]. To ethanol solution (50 mL) of PdCl₂ (11.7 mg, 0.066 mmol), 302 mg of PVP (averaged MW 40000) was added. The ethanol solution was mixed with 50 mL of water and the mixture was subsequently refluxed at 90 - 100 °C for 1 hour under ambient air. The color of the mixed solution changed from clear yellow to a transparent dark brown at the beginning of the reflux, due to the formation of Pd clusters. After removing all the water-ethanol solvent, an aqueous solution of the PVP-protected Pd clusters was obtained by redissolving the residual into 100 mL pure water. For further convenience, this aqueous solution is referred to as *sample 1*, hereafter.

2.2 Ligand exchange from PVP to *n*-dodecanethiol

To the hydrosol (25 mL of sample 1) of the PVP-protected Pd clusters, toluene (25 mL) having various concentrations of *n*-dodecanethiol (DT) was added to form two immiscible layers. The concentration of DT in toluene was varied in the range 0.01 - 4 mM. The mixture was heated up to 90 - 100 °C under stirring for 30 min. This treatment gave us three forms of two-phase mixture, depending on the DT concentration. At a small DT concentration below 0.1 mM, the color of the aqueous layer faded, while the organic layer was not colored. The clusters flocculated at the interface of the two layers. The dark-brown floccules were carefully taken out by a pipette from the two-phase interface and further separated by centrifugation. Trituration in a small amount of acetone gave a dark-brown suspension of the floccules (*sample 2*). When the DT concentration is in the range 0.1 - 0.2

mM, the color of the aqueous layer became faint, while the organic layer turned dark gray. Dark-brown floccules were also formed at the interface. The colored organic layer was separated and evaporated to 2 mL (sample 3). When the DT concentration was further increased to >0.3 mM, the aqueous layer became completely discolored. The Pd clusters were extracted into the toluene phase without any formation of floccules. The dark-brown organic layer was evaporated to 2 mL (sample 4) after a separation.

Transmission electron microscope (TEM) images of the Pd clusters were obtained with a top-entry HITACHI H-9000 electron microscope operated at 300 kV. For preparing the TEM specimens one or two drops of the solution containing the clusters (samples 1-4) were deposited on a carbon-coated collodion film supported on copper grids. The TEM images shown in this paper were recorded with a magnification of 200,000.

3. RESULTS AND DISCUSSION

3.1 Efficiency of solvent extraction

Figure 1 shows the UV-VIS spectra of the Pd clusters extracted into the organic phase at various DT concentrations; 0.07, 0.13, 0.26 and 4.20 mM. The absorption spectrum of the starting materials in the aqueous phase (sample 1) is also shown for comparison. Spectrum a shows that the Pd clusters are not transferred into the organic phase at a DT concentration of 0.07 mM. Spectra c and d almost mimic that of the starting materials, indicating that Pd clusters are extracted efficiently from the aqueous solution into the organic phase. Careful examination reveals that the shape of spectrum b (0.13 mM) differs from those of c and d; the absorbance in the longer wavelength region is enhanced to a considerable extent. This suggests that the Pd clusters extracted at a concentration of $[DT] = 0.13$ mM possess different size and/or shape distribution from that extracted at $[DT] > 0.26$ mM.

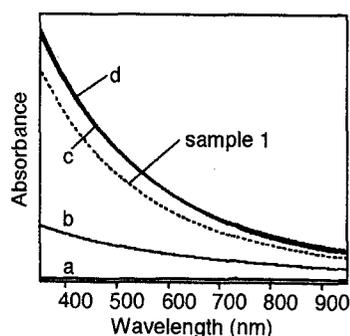


Fig. 1: UV-VIS spectra of the toluene solutions of the Pd clusters extracted at the DT concentrations of (a) 0.07, (b) 0.13, (c) 0.26, and (d) 4.20 mM.

We have estimated the extraction efficiency, Γ , by dividing the spectral intensities integrated over

the 300 - 1000 nm range at various DT concentrations by that taken at the highest DT concentration (spectrum d). The Γ values thus determined are plotted against the DT concentration in Fig. 2. The extraction efficiency is negligibly small in the low DT concentrations below ≈ 0.05 mmol dm⁻³, starts to increase at ≈ 0.07 mM, and reaches to almost unity at ≈ 0.3 mM. The efficiency levels off at the concentrations of >0.3 mM.

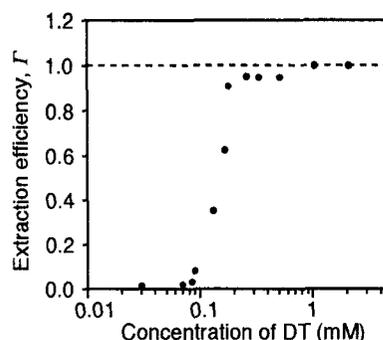


Fig. 2: Efficiency curves for the Pd cluster extraction by DT. The concentration of the Pd ions used in the preparation of sample 1 is 0.66 mM.

3.2 Morphologies of Pd clusters

Figure 3 shows typical TEM images of the Pd clusters obtained at various stages of experiment. The first glance over the TEM images reveals that these clusters differ conspicuously in size and shape. The starting materials, PVP-protected clusters (sample 1), have a spherical shape and are dispersed rather randomly (Fig. 3(a)). The size distribution of the PVP-protected clusters, depicted as a histogram in Fig. 3(a), is essentially the same as that reported by Toshima *et al.* [2, 3]; the average diameter of the clusters obtained from our TEM images is 2.6 nm with a standard deviation of 0.5 nm. As seen from Fig. 3(b), the floccules obtained as sample 2 are composed of aggregates arranged in a large network. The cluster dispersion obtained as sample 3 gives a rather funny TEM pattern: the clusters aggregate into worm-like shapes (Fig. 3(c)). On the other hand, the clusters extracted at higher DT concentrations (sample 4) are sphere in shape and nearly monodispersed (Fig. 3(d)). Obviously the each particle is larger than the starting material (sample 1): the average diameter is determined to be 3.7 nm with a standard deviation of 0.6 nm. Another notable feature of Fig. 3(d) is that each particle tends to self-assemble into cross-linked structures with a typical face-to-face spacing of ~ 1.9 nm. This separation is obviously too small to be consistent with nonoverlapping alkyl chains of DT because the chain length is estimated to be ~ 1.77 nm [13]. It thus seems that the packing of the Pd clusters also results in considerable interdigitation of the alkyl chains as observed in the gold clusters [14]. To investigate the crystalline morphology of the DT-

stabilized clusters in sample 4, high-resolution TEM (HRTEM) measurement was performed. The HRTEM images exhibit the single crystalline structure of the DT-stabilized clusters. The spacing between the [111] planes is determined to be 0.23 nm, which agrees well with that of the bulk Pd (0.2246 nm). This observation suggests that the DT-stabilized clusters in sample 4 occur with the fcc crystalline structure. By using the known value for the bulk density of Pd (12.02 g cm^{-3}), we estimate the average numbers of atoms per cluster, N_{av} , to be ~ 600 for sample 1 and ~ 1800 for sample 4. This indicates that the solvent extraction with sufficient amount of DT results in the coalescence of three preformed Pd clusters. The present observation exhibits a striking contrast to that made in the extraction by TPP: the Pd clusters were extracted by TPP without any change in the cluster size distributions, being consistent with the result by Toshima et al. [9]. From these comparisons we conclude that the cluster growth is a consequence of the ligand exchange into DT molecules.

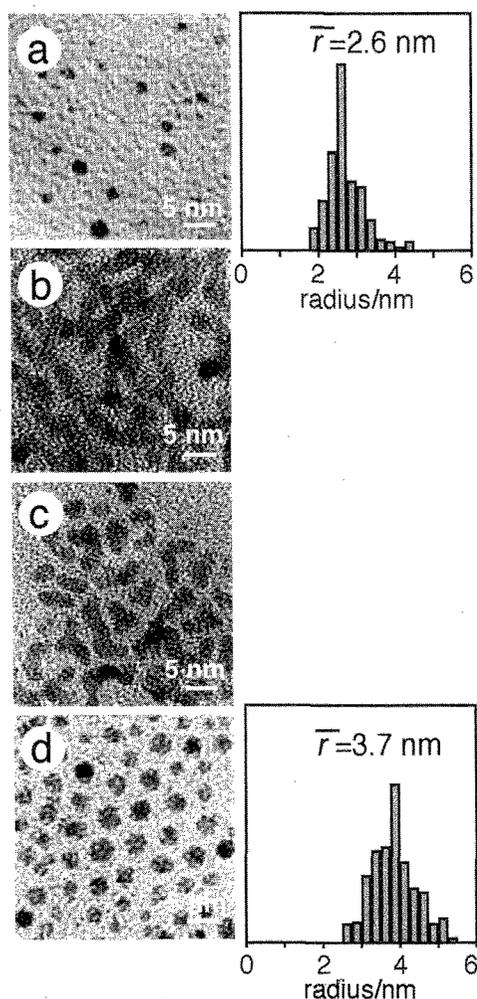


Fig. 3: TEM images and size distributions of the Pd clusters: (a) sample 1, (b) sample 2, (c) sample 3, and (d) sample 4.

3.3 Growth mechanism in ligand exchange

The most prominent findings in the present study are that (i) the Pd clusters undergo a size growth during the ligand exchange from PVP into DT, and that (ii) the size and shape distributions of the Pd clusters after the ligand exchange depend on the DT concentration employed in the extraction.

In order to explain these observations, we propose here a qualitative model for the cluster growth mechanism, based on the adsorption behavior of *n*-alkanethiols on bulk Au(111) surface. The STM measurements have revealed that the adsorption of the thiols to the bulk surface displays the following four-stage behavior with increase in the coverage: a two-dimensional liquid phase, a striped phase, a disordered phase, and an ordered phase with $c(4 \times 2)$ periodicity [15]. At a low coverage where the 2-D liquid or the striped phase occurs, the thiols are lying on the Au surface with the alkane chains parallel to the surface [15]. This suggests that the cluster surfaces become hydrophobic when the coverage reaches a critical value for the formation of the low-density phase of the cluster surface. The sharp onset observed in the extraction efficiency curve (Fig. 2) supports this inference. Thus the first step involves "phase transfer" of the metal clusters from the aqueous phase to the organic phase with a low coverage of DT. The nascent clusters extracted are inherently unstable against further aggregation due to the low DT coverage so that they inevitably start to "coalesce" into larger clusters. In the course of the aggregation, the effective density of the DT molecules on the surface increases because the number ratio of the surface atoms against the total atoms decreases with increase in the cluster size. Finally the coalescence terminates at the point where a self-assembled monolayer of DT is formed on the cluster surface.

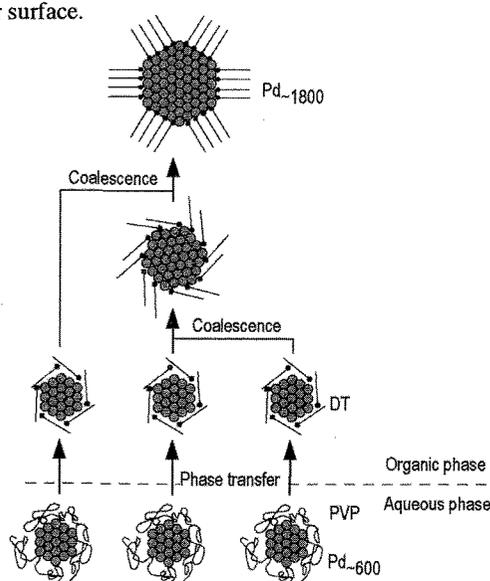


Fig. 4: Two-step model for cluster growth processes.

The proposed model well explains the TEM images of the Pd clusters obtained as sample 2 and 3: when the DT concentration is insufficient to make the cluster surface hydrophobic, the clusters coalesce at the interface of the two phases into much larger aggregates than those at higher DT concentrations.

To further confirm our model for the cluster growth, we systematically studied the ligand exchange reactions using different thiols: *n*-hexanethiol (HT: C₆H₁₃SH) and *n*-octadecanethiol (ODT: C₁₈H₃₇SH). The minimal concentration of thiols at which the extraction starts to occur increases with decrease in the chain length of the thiols: 0.04 mM for ODT, 0.09 mM for DT, and 0.20 mM for HT. This trend is consistent with the two-step model: the minimal number of molecules required to cover the cluster surface with a hydrophobic layer becomes larger for the thiols having shorter chains. As a consequence of the higher coverage for smaller thiols at the phase transfer stage, the nascent clusters emerging into the organic phase tend to be more stable against coalescence and, as a result, the final size of the cluster is expected to be smaller. Indeed, our TEM measurement (Fig. 5) shows the average diameters of Pd clusters extracted by HT and ODT are 3.1 ($N_{av} \sim 1100$) and 3.7 nm ($N_{av} \sim 1800$), respectively, which eventually correspond to the diameters for the coalescent particles of two or three Pd clusters during the phase transfer.

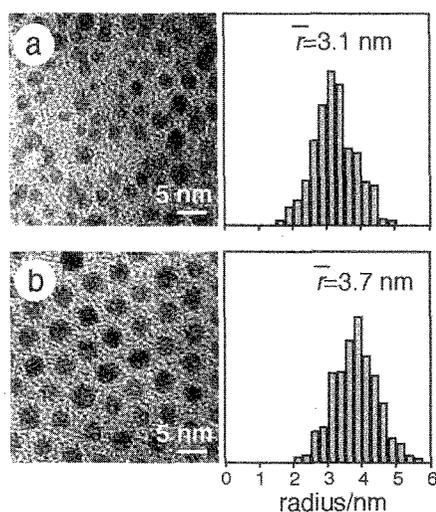


Fig. 5. TEM images and size distributions of the Pd clusters extracted by 4.2 mM of (a) HT and (b) ODT.

4. SUMMARY

We have demonstrated that the PVP-protected Pd clusters dispersed in an aqueous solution are feasibly extracted via ligand-exchange reactions into toluene containing DT. The DT-stabilized clusters coalesce into different sizes and shapes, depending on the DT concentration in the organic phase. The present study opens up a possibility for the size and

shape control of metal clusters by ligand exchange reactions.

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