J|A|C|S COMMUNICATIONS

Published on Web 10/15/2009

Specific Peptide Regulated Synthesis of Ultrasmall Platinum Nanocrystals

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Platinum (Pt) nanocrystals (NCs) have been extensively explored because of their excellent catalytic performance in applications such as fuel cell and hydrogen generation.[1] Pt NCs of variable sizes have been synthesized using different stabilizing agents.[2] Systematic studies have shown that the size of Pt NCs has an obvious effect on their catalytic activity and selectivity,[3] especially for sub-10 nm NCs with a high ratio of atoms at corners and edges.[4] Ultrasmall Pt NCs with sizes under 5 nm are found to have a particularly high catalytic performance in some reactions.[5] To date, the synthesis of ultrasmall Pt NCs under 5 nm involves rigorous synthetic conditions such as high temperature and hazardous organic solvent. The resulting Pt NCs are often not water-soluble which makes them less accessible for catalytic reactions in aqueous solution. There have been a few reports describing synthesis of water-soluble Pt NCs in the sub-5 nm regime, but only with limited control of size and size distributions.[6]

Here we report a rational approach to synthesize well dispersed ultrasmall Pt NCs with sizes ranging from ca. 1.7 to 3.5 nm, using specifically selected peptide molecules as the stabilizing agent. We further demonstrated that the strong binding of peptides to the Pt NC surface is reversible by either pH modulation or peptide photolysis. The reported Pt NCs are synthesized in aqueous solution at room temperature, which has not been reported for such small Pt NCs. The NCs show good size distribution with size variation within 10% based on statistical analysis. Using biomolecules, such as peptides, proteins, RNA, and DNA, to regulate the formation of inorganic NCs has been an emerging field in recent years.[7] Biomolecules can be specifically selected or designed to recognize a chosen target material through the rational biomimetic evolution approach.[8] As a result, the selected biomolecules can be used as stabilizers to regulate crystal nucleation and growth and, therefore, control the size and morphology of the resulting NCs.[9] In this study, we used a phage display (Ph.D.) technique to identify peptide sequences that specifically bind to the Pt surface.[8] The sequence Thr-Leu-His-Val-Ser-Ser-Tyr (TLHVSSY, termed P7A, MW: 805.9) emerged as the specific binder after three rounds of biopanning (see Supporting Information (SI) for details), which shares a similar hydroxyl group rich motif with previously reported squences.[7] Free P7A were then synthesized with an F-moc solid phase peptide synthesis (SPPS) technique with purity >95% (see SI, Figure S1). The integrity of P7A in related salt solutions and reactions was also tested (SI, Figure S2).

The synthesis of Pt NCs with a uniform size distribution is briefly described below (see SI for details). A mixed aqueous solution of potassium tetrachloroplatinate (K_2PtCl_4) and P7A peptide was first prepared, into which a fresh 40 mM sodium boron hydride ($NaBH_4$) solution was injected in a single shot. The reaction was strongly stirred at room temperature until no color change can be observed. Blank reactions without adding peptides as well as negative control reactions with a nonrelevant peptide sequence were also performed.

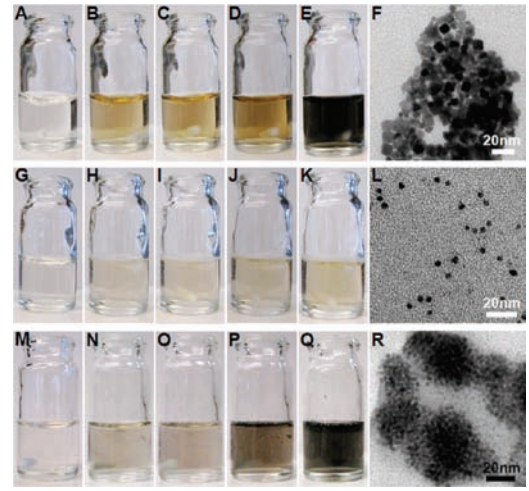

Figure 1. Color evolution of blank reaction (A−E), 50 μg/mL peptide reaction (G-K) and negative control reaction (M−Q). (A), (G), and (M) are before $NaBH_4$ addition. (B−E), (H−K), and (N−Q) are photos taken at 10 s, 30 s, 1 min, and 3 min after reductant injection. TEM images of the obtained NCs from blank reaction at 10 s (F), P7A peptide reaction after 36 h (L), and C12 peptide reaction at 10 s (R).

Figure 1 shows the color evolution and transmission electron microscope (TEM) images of the aforementioned reactions.

The quickly darkening color observed in the blank reaction indicates the reaction evolved very fast (Figure 1A−E). After ~2 h, there were obvious precipitations. TEM studies show NCs from the blank reaction typically have large sizes (>10 nm) with a wide size distribution and are usually aggregated together even at a very early stage (Figure 1F). In contrast, the reaction with P7A peptide present evolved much more slowly and is highly controllable (Figure 1G−K). The resulting solution was stable for up to a few months, indicating NCs were well dispersed in solution. TEM studies show these NCs typically have nearly spherical shapes, with a narrow size distribution, and remain well dispersed in solution even after long duration of aging (Figure 1L). The comparison with blank reaction implies that the peptides suppress the crystal growth at a very early stage and change the growth kinetics of Pt NCs. The negative control experiment with sequence His-Ser-Val-Asn-Lys-Leu-Pro-Thr-Pro-Leu-Arg (HSVNKLPTPLR, termed C12, MW: 1439.7) was carried out to confirm the specificity of P7A to Pt NCs. It was observed that reaction with the C12 sequence evolves much faster than that with P7A. (Figure 1M−Q). At 3 min, obvious precipitation was observed in solution. The TEM image in Figure 1R shows the aggregations of small NCs. The observations suggest that the free-standing peptide P7A, although selected against the platinum surface as a part of the M13 phage coat protein, retains a strong and specific binding ability to the Pt crystal surface. Although there has been no conclusive answer to date regarding the exact origin of the specific binding of peptide to a material surface,[10] the strong binding ability of P7A to Pt observed here

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10.1021/ja907235v CCC: $40.75

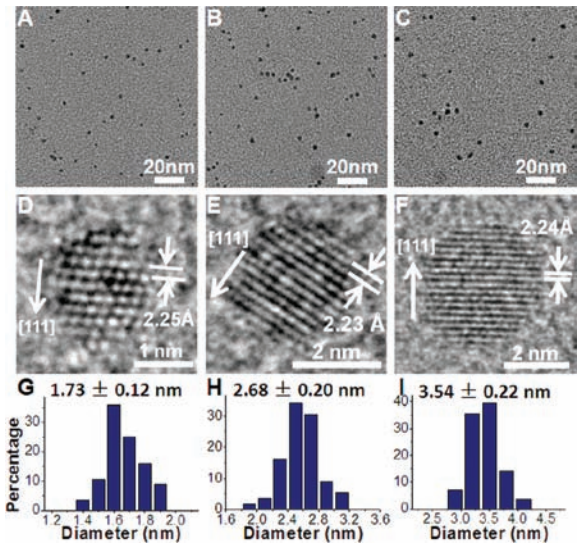

Figure 2. (A−C) TEM images of reaction samples taken at 10 s, 60 s, and 5 h. (D−F) and (G−I) are high resolution images and size distributions of the samples in (A−C), respectively.

might be attributed to the interaction between hydroxyl (i.e., threonine, tyrosine, and serine) and/or polar (i.e., histidine) residue groups and the Pt surface. Some molecular geometrical factor may also contribute by fitting the functional groups to the atomic arrangements on certain crystallographic facets.[7,11] In addition, it is important to note that the strong interaction between P7A and Pt can be readily tuned or reversed. Our studies have demonstrated that the peptide can be unbound from the NC surface by simply lowering the pH of the solution (SI, Figures S3, S4). Alternatively, the peptide can also be degraded through a photolysis process[12] (SI, Figures S5, S6). The results indicate possible approaches to recover the Pt NC surface, which is important for catalytic reactions.

We tentatively attribute the effects that peptides exert on Pt NC size and shape to its strong binding ability to the Pt surface. After the addition of $NaBH_4$, the reduced Pt atoms may form extremely small clusters or nuclei, consisting of only tens of atoms. We suggest that peptides bind to reduced Pt atoms or Pt nuclei and form a peptide coating on Pt NCs through the functional residue groups.[13] The coverage of peptides prevents NC growth from particle coalescence and slows down monomer attachment onto the NC surface.[14] Hence the Pt NC growth rate with peptide present is greatly reduced when compared to the blank reaction, resulting in much smaller NC sizes. Meanwhile, when peptides bind to the Pt NC surface, it changes the Pt NC surface energy landscape and hence its growth kinetics, which may lead to the observed different morphologies compared to blank reactions.[15]

With the greatly reduced growth rate, we were able to achieve ultrasmall NCs of variable sizes with a narrow size distribution by stopping the reaction at different times. In this experiment, aliquots of reaction solution at different times, e.g. 10 s, 60 s, and up to 36 h, were taken out and immediately put into an ice bath. Then droplets of different samples were taken to prepare TEM samples. Figure 2A−F show the TEM images of NCs taken from the reaction at 10 s, 60 s, and 5 h. In Figure 2A, the Pt NCs at 10 s after reductant injection have an average size of 1.73 nm, which is much smaller than the NCs formed at the same time in the blank reaction (Figure 1F). Figure 2B shows the Pt NCs taken out at 60 s, which have an average size of 2.68 nm. Figure 2C shows the NCs obtained from the reaction solution 5 h after the injection with an average size of 3.54 nm. High resolution TEM (HRTEM) images in Figure 2D−F show that the atomic layers in the ⟨111⟩ direction, as marked by the arrows, grow from 7 to 12 and finally to 16 layers. With this approach, ultrasmall Pt NCs of variable sizes below 5 nm can be synthesized in a highly controllable fashion. Histograms of Pt NC sizes show a highly uniform size distribution, typically with a standard deviation of less than 10% or less than one atomic layer variation on average (Figure 2G−I).

In short, we have reported the rational synthesis of monodisperse ultrasmall Pt NCs, in aqueous solution at room temperature, with specifically selected peptide molecules as stabilizers. The selected peptide molecule P7A is able to bind to the Pt NC surface and thus can function as a stabilizer to regulate Pt crystal nucleation and growth and, therefore, control both the morphology and size of the final Pt NCs. Uniform near-spherical Pt NCs with a size from 1.73 to 3.54 nm were achieved with a very narrow size distribution. Detailed studies on the Pt NCs synthesis with the stabilization of peptide molecules are underway for better size and shape control as well as elucidation of the exact growth mechanism.

Acknowledgment. We acknowledge support from the Office of Naval Research under Award N00014-08-1-0985 and partial support from AROD-MURI Grant No. 08-00678-UCLA-1.

Supporting Information Available: Selection of peptide sequence; Peptide synthesis; Integrity study of the peptide; Synthesis of Pt NCs; Recovery of the Pt NC surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA907235V