Metal Nanoparticles

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Highly Stable, Water-Dispersible Metal-Nanoparticle-Decorated Polymer Nanocapsules and Their Catalytic Applications**

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Abstract: *A facile synthesis of highly stable, water-dispersible metal-nanoparticle-decorated polymer nanocapsules (M@CB-PNs: M = Pd, Au, and Pt) was achieved by a simple two-step process employing a polymer nanocapsule (CB-PN) made of cucurbit[6]uril (CB[6]) and metal salts. The CB-PN serves as a versatile platform where various metal nanoparticles with a controlled size can be introduced on the surface and stabilized to prepare new water-dispersible nanostructures useful for many applications. The Pd nanoparticles on CB-PN exhibit high stability and dispersibility in water as well as excellent catalytic activity and recyclability in carbon–carbon and carbon–nitrogen bond-forming reactions in aqueous medium suggesting potential applications as a green catalyst.*

Metal nanoparticles (NPs) have attracted great attention because their unique properties such as high surface to volume ratio, quantum confinement, and surface plasmon effect can contribute to diverse applications in catalysis, nanoelectronics, molecular imaging, biosensors, and nanomedicine.[1] Many of these intriguing properties strongly depend on the size[2] and surface area[3] of the NPs. In addition, support materials (or stabilizers)[4] such as polymers,[5] dendrimers,[6] silica,[7] and metal oxides,[8] which are required for some applications (e.g. heterogeneous catalysis), also affect the properties of NPs. Although NPs on solid supports have been successfully employed in catalysis, most systems suffer from shortcomings such as passivation of the NP surface,[9] lack of long-term stability,[10] low dispersibility,[11] deactivation or constant leaching,[12] and low recyclability which limit their capacity and applications.[13] For example, NPs supported on mesoporous/modified silica are unstable, which leads to a rapid decay of the catalytic activity under the reaction conditions.[12] Furthermore, the catalytic activity and stability of NPs in environmentally benign media such as water has important environmental, economical, and safety implications, which are crucial in green chemistry.[14] However, to date, catalysis using NPs on solid supports has seldom been explored in water.[15]

Cucurbit[*n*]uril (CB[*n*]: *n* = 5–8, 10) exhibits remarkable recognition abilities with high affinity and selectivity towards organic and inorganic species[16] and stabilizes NPs by forming a passive layer or acting as a protecting agent.[17] We recently reported hollow polymer nanocapsules (CB-PNs) with a thin shell composed of covalently linked cucurbit[6]uril (CB[6]) units,[18] which can be readily synthesized from commercially available allyloxyCB[6] and dithiol (3,6-dioxa-1,8-octanedithiol) in a one-pot reaction. Unique features of CB-PNs include facile tailoring of their surface to prepare new functional materials for various applications such as targeted drug delivery, diagnosis, and imaging.[18c,d] Moreover, CB-PNs synthesized in the presence of excess dithiol have "disulfide loops" protruding from the surface,[18a,b,19] which can be used as an internal source of dithiols to strongly bind metal NPs, passivate their surface, and stabilize them during synthesis. Altogether, these intriguing properties imply that CB-PNs could be a promising platform for synthesizing various NPs with a controlled size and stabilizing them by preventing self-aggregation. These new water-dispersible nanostructures could prove useful for many applications including catalysis in aqueous medium.

Here, we report highly stable, water-dispersible metal-nanoparticle-decorated polymer nanocapsules (M@CB-PNs: M = Pd, Au, and Pt), which can be readily synthesized in a simple two-step process employing CB-PN and metal salts (Scheme 1). The M@CB-PNs have several remarkable features including 1) high stability and dispersibility in water, 2) precise control over the NP size, 3) excellent heterogeneous catalytic properties in carbon–carbon and carbon–nitrogen bond-forming reactions in aqueous media, and 4) excellent recycling and reusability, which are likely to be beneficial for many applications.

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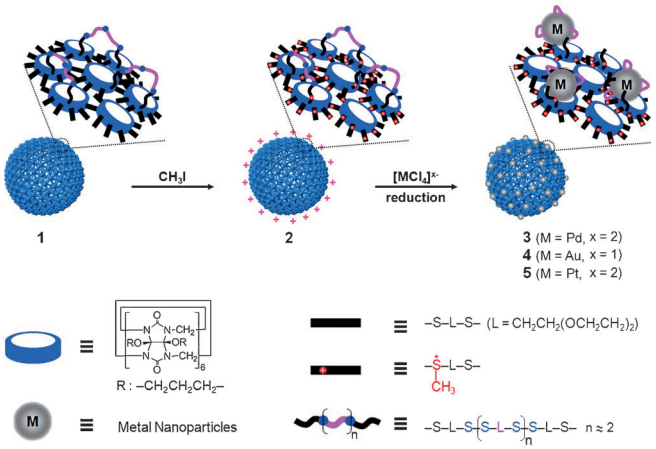


Scheme 1. Synthesis of M@CB-PNs.

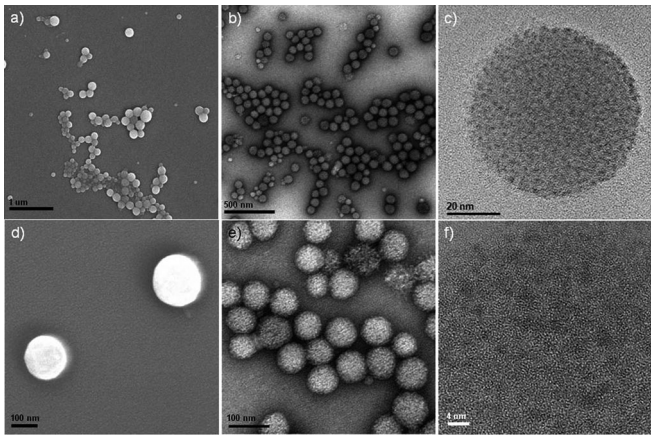


Figure 1. Electron microscopy images of Pd@CB-PN **3**. SEM images (a, d), LR-TEM images after uranyl acetate staining (b, e), HR-TEM images (c, f). Scale bars in a: 1 μm, b: 500 nm, c: 20 nm, d: 100 nm, e: 100 nm, f: 4 nm.

Pd@CB-PN **3** was prepared by a two-step process from CB-PN **1** which had been synthesized as described before:[18a,b] treatment of **1** with methyl iodide, followed by addition of K_2PdCl_4 in the presence of $NaBH_4$ as a reducing agent (Scheme 1). Although **1** has relatively low propensity to aggregate in aqueous solution, an aqueous dispersion of **1** lacks long-term stability.[19] We thus treated **1** with an excess of methyl iodide to produce water-dispersible CB-PN **2**.[20] The methyl iodide treatment resulted in partial alkylation of the thioether units on **1**, converting them into sulfonium groups. However, no appreciable change in the "disulfide loops" of CB-PN took place upon methyl iodide treatment, which was indicated by little change between the allyloxy-CB[6]/dithiol ratios of **1** and **2** (ca. 1:9.8 vs. ca. 1:9.3; Scheme S1 and Table S1 in the Supporting Information). No change in the morphology and size of **2** was observed even after the methyl iodide treatment, which was confirmed by dynamic light scattering (DLS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) studies (Figure S1), whereas the zeta potential changed from (-13.0 ± 8.7) mV for **1** to (72.9 ± 10.0) mV for **2**. The positive zeta potential indicates that the sulfonium groups are mainly distributed over the surface of **2**, allowing **2** to attract negatively charged species, such as $[PdCl_4]^{2-}$ by electrostatic interaction. Upon addition of K_2PdCl_4 (Pd/CB = 3:1 molar ratio), the zeta potential of **2** decreased to (48.4 ± 7.0) mV, which indicates that $[PdCl_4]^{2-}$ anions assemble on the surface of **2**. Treatment of the mixture of **2** and K_2PdCl_4 with $NaBH_4$ at room temperature followed by dialysis produced a clear brown solution of **3**, which is well-dispersible and highly stable without forming any precipitate up to 6 months.

DLS studies (Figure S2) revealed the colloidal particle nature of Pd@CB-PN **3**, which have an average diameter of (130 ± 40) nm. SEM studies of **3** confirmed their spherical shape (Figure 1 a,d). The hollow sphere surrounded by a thin shell of **3** was confirmed by low-resolution transmission electron microscopy (LR-TEM) (Figure 1 b,e). High-resolution transmission electron microscopy (HR-TEM) studies of **3** revealed that Pd NPs are uniformly distributed on the surface of **3** with a narrow size distribution of (1.9 ± 0.2) nm (Figures 1 c,f and 2 b,e). The amount of Pd in **3** was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), which showed that 81 % of K_2PdCl_4 formed Pd NPs (5.5 wt %) on the surface of **3**. X-ray photoelectron spectroscopy (XPS) data also identify Pd NPs on **3** (Figure S3). The scanning TEM (STEM) images of Pd NPs on the surface of **3** and fast Fourier transform (FFT) of a selected area are shown in Figure S4. All these images showed that the Pd NPs are of single-crystalline nature with a face-centered-cubic (fcc) structure. The crystalline domains are assigned to the (111) plane of fcc metallic Pd^0. These Pd NPs are uniformly distributed and well dispersed over the surface of **3**, leading to a unique morphology.

Recent studies indicated that the portal of CB[6] lined with polar carbonyl groups interacts with metals.[17] The strong interaction between organosulfur compounds (thiol, disulfide, and sulfide) and various metal surfaces by metal–S bond formation is well known.[21] To define the nature of the interactions responsible for the formation of the nanostructured Pd@CB-PN, we studied Pd@CB-PN by FTIR and XPS analysis. The FTIR data showed no appreciable shift in the C=O stretching vibration (Figure S5). This, however, does not rule out the possible interaction between the carbonyl portal of the CB[6] units and the NPs since it has been reported that CB[6]-passivated Pd NPs also show no shifts in the C=O stretching vibration.[17b] The XPS data showed a red shift of the oxygen (1s) peak at 531.5 eV and a new sulfur (2p) peak at 162.8 eV in Pd@CB-PN (Figure S3), which can be assigned to the carbonyl oxygen interacting with Pd NPs[22] and sulfur in the Pd–S bond,[23] respectively. These results indicate the presence of interactions between the CB[6] unit and Pd NPs as well as formation of a new Pd–S bond. No well-defined Pd NPs were observed when the "disulfide loops" protruding from the surface of polymer nanocapsules were removed by treatment of **2** with an excess amount of ethyl vinyl ether under UV irradiation. In addition, the elemental analysis data of **2** and **3** show no appreciable change in the allyloxyCB[6]/dithiol ratio (ca. 1:9.3 vs. ca. 1:9.8), which suggests that upon reduction with $NaBH_4$, the "disulfide loops" on the surface of **2** were broken to release free thiols, which can bind Pd NPs

strongly, passivate their surface, and stabilize them on the surface of the polymer nanocapsule along with the CB[6] units (Scheme S1 and Table S1 in the Supporting Information).

The size of NPs on CB-PN **3** can be effectively controlled by varying the ratio of K_2PdCl_4 to the CB[6] units of CB-PN **2** (Pd/CB). As the ratio of Pd/CB ratio was increased to 4:1, progressive darkening of the reaction mixture was observed (Figure S6). When the ratio was increased beyond 8:1, the reaction generated a black precipitate of agglomerated Pd@CB-PN. HR-TEM studies showed that 2:1 and 4:1 ratios of Pd/CB produce Pd NPs with an average diameter of (1.7 ± 0.2) nm and (3.1 ± 0.3) nm, respectively, on the polymer nanocapsule (Figure 2 and Figure S7). In the absence of CB-PN **2**, only black precipitate was generated. These results indicate that 1) the CB-PN provides nucleation sites for NPs and stabilizes them, helping to generate uniformly sized NPs evenly distributed over the surface of the nanocapsule, and 2) there is a critical range of M/CB ratios for the formation of well-dispersed M@CB-PN.

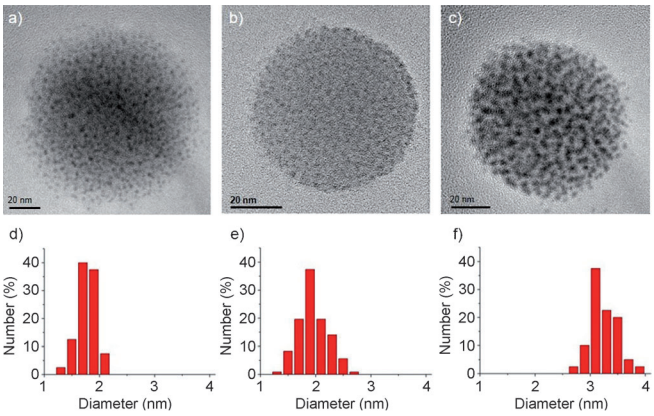
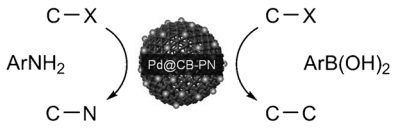


Figure 2. HR-TEM images of Pd@CB-PNs and size histograms of Pd NPs. a), b), and c) TEM images of Pd@CB-PNs (2:1, 3:1, and 4:1 Pd/CB ratio), respectively. Scale bars 20 nm. d), e), and f) Size histograms of Pd NPs (2:1, 3:1, and 4:1 Pd/CB ratio) with narrow size distribution of (1.7 ± 0.2) nm, (1.9 ± 0.2) nm, and (3.1 ± 0.3) nm based on 200 NPs, respectively.

The polymer nanocapsule can be decorated with other noble metal nanoparticles on its surface. For example, gold and platinum nanoparticle-decorated polymer nanocapsules (Au@CB-PN **4** and Pt@CB-PN **5**) were successfully synthesized by mixing **2** with $KAuCl_4$ or K_2PtCl_4, respectively, at room temperature in the presence of a reducing agent (Figure S8). HR-TEM studies of **4** and **5** showed that Au and Pt NPs are uniformly distributed on the surface of the polymer nanocapsules with a narrow size distribution of (2.1 ± 0.4) nm and (1.8 ± 0.3) nm, respectively (Figure S9). Altogether, these results underscore the vast potential of the polymer nanocapsule as a versatile platform for various metal nanoparticles.

To illustrate the stability of Pd@CB-PN **3** in water and its potential in heterogeneous catalysis, cross-coupling reactions were studied. The Suzuki–Miyaura reaction is known to be a good "acid test" for examining the stability and activity of Pd NPs.[24] Thus, we decided to explore the behavior of Pd@CB-PN **3** in the carbon–carbon bond-forming model reaction of aryl iodides and arylboronic acids in water. Traditionally, these reactions have been studied in organic solvents and use of water as the sole solvent is limited.[25] The Suzuki–Miyaura coupling reaction reached completion in 1–2 h (100% of iodobenzene was converted into biphenyl; Table 1, entry 1) in pure water at room temperature in the presence of 5 mol% of **3** from a stock solution and K_3PO_4 as a base (Figure S10). No black precipitate or other indication of Pd aggregation was observed after the reaction. For comparative reactivity studies, a control experiment using Pd/C was performed in water under similar reaction conditions. Compared to **3**, Pd/C gives a much lower yield in water as only 62% of the iodobenzene reactant was converted into biphenyl (Table 1, entry 6). Furthermore, **3** was superior to water-soluble Pd NPs stabilized by PEG-modified dendrimers regarding its catalytic activity, stability, and recyclability.[25c]

Table 1: Results of C–C and C–N bond-forming reactions catalyzed by Pd@CB-PN **3**.



Entry	Ar-X	$ArB(OH)_2$ or $ArNH_2$	Catalyst	Conversion [%][a]
1	C_6H_5I	4-$(MeO)C_6H_4B(OH)_2$	**3**	100 (1st run)[b]
2	C_6H_5I	4-$(MeO)C_6H_4B(OH)_2$	**3**	100 (2nd run)[b]
3	C_6H_5I	4-$(MeO)C_6H_4B(OH)_2$	**3**	100 (3rd run)[b]
4	C_6H_5I	4-$(MeO)C_6H_4B(OH)_2$	**3**	100 (4th run)[b]
5	C_6H_5I	4-$(MeO)C_6H_4B(OH)_2$	**3**	100 (5th run)[b]
6	C_6H_5I	4-$(MeO)C_6H_4B(OH)_2$	Pd/C	62[c]
7	C_6H_5I	4-$(MeO)C_6H_4NH_2$	**3**	100[d]

[a] Conversion of aryl iodide was determined by GC-MS. [b] Recovered Pd@CB-PN **3** (3 mL from stock solution, 5.0 mol%), aryl halide (1.0 equiv), phenylboronic acid (1.2 equiv), and K_3PO_4 (1.0 equiv) in water at room temperature for 1–2 h. No Pd leaching was detected in the reaction mixture (ICP-AES). [c] A control reaction using 5 mol% of Pd/C (10 wt%, Aldrich) was carried out. [d] Phenylamine was used instead of $ArB(OH)_2$.

In addition to the Suzuki–Miyaura reaction, we also explored the Buchwald–Hartwig amination reaction[26] of aryl iodide and *p*-anisidine using **3**. In the presence of this heterogeneous catalyst (5 mol%), the Buchwald–Hartwig amination reaction gave biaryl amines (100% conversion). In this case, a mixed-solvent system (H_2O/THF = 3:1) was employed due to the poor solubility of the substrate in water. To the best of our knowledge, this is the first example of a Buchwald–Hartwig amination reaction in aqueous solution catalyzed by Pd NPs. Further studies are currently underway to understand the precise relationship between the structural details of Pd NPs and their catalytic activity and to identify the specific role of the solvents.

Recyclability and reusability of NPs are important parameters for potential applications. Considering this critical and significant issue, we carried out the Suzuki–Miyaura

coupling reaction to check the recyclability and reusability of Pd@CB-PN **3** in water. After completion of the reaction, **3** was readily recovered by centrifugation. Redispersion through sonication followed by addition of new substrates allowed the catalyst to be reused (Figure S11). During five cycles of the reaction, the conversion efficiency remained at 100% (Table 1). After recycling experiments, we removed the catalyst and analyzed the reaction mixtures of **3** by ICP-AES and HR-TEM. No traces of leached Pd species within the detection limit of ICP-AES were observed in the reaction mixtures after removal of **3**. HR-TEM studies clearly revealed (Figure S12) that the size and morphology of **3** remained the same even after exposure to the coupling reaction conditions. Furthermore, **3** can be stored without loss of catalytic activity for up to six months. On the basis of our investigations we conclude that Pd@CB-PN **3** exhibits superior heterogeneous catalytic activity in terms of stability, recyclability, and reusability in aqueous medium, compared to other existing Pd NPs on solid supports.[13,25]

In summary, we have developed a new, facile, and general method to prepare highly stable, water-dispersible metal-nanoparticle-decorated polymer nanocapsules (M@CB-PNs: M = Pd, Au, and Pt) with a narrow size distribution of NPs. The hollow polymer nanocapsule made of CB[6] provides unique properties as a versatile platform to introduce various NPs on the surface, prevent self-aggregation, and provide high stability and dispersibility in water. The key to the success of this approach is the presence of CB[6] units and "disulfide loops" on the surface of CB-PN. Illustrating their application, Pd@CB-PN shows outstanding properties as heterogeneous catalyst in carbon–carbon and carbon–nitrogen bond-forming reactions in aqueous medium with excellent recycling and reusability. With such exciting properties of M@CB-PNs, this approach may bring new inspirations to the nanoscience field in terms of the green chemistry perspective. Beyond catalysis, the highly stable, water-dispersible metal nanoparticles on polymer nanocapsules are potentially useful for other applications such as imaging and nanomedicine. Work along this line is also in progress in our laboratory.

Experimental Section

Synthesis of water-dispersible polymer nanocapsule **2**: An excess amount of CH_3I (150 μL, 2.4 mmol) was added to a colloidal solution of CB-PN **1** in methanol (10 mL). After incubation for 1 day at room temperature, the product was purified by dialysis (MWCO: 10000) against water for 2 days to give a homogeneous colloidal solution of **2** in water. Removal of the solvent under reduced pressure, followed by drying in vacuo yielded **2** (22.1 mg, 92% based on **1**). See the Supporting Information for further characterization of **2** and other experimental details.

Synthesis of Pd nanoparticle-decorated polymer nanocapsule **3**: A solution of K_2PdCl_4 in water (1.5 mM, 0.5 mL, 0.75 μmol) was added to a dispersion of **2** (0.5 mL, 0.25 μmol) and incubated at room temperature for 3 h. A solution of $NaBH_4$ in water (12.0 mM, 1.0 mL, 12 μmol) was then added at once. After incubation at room temperature for 5 h, the product was purified by dialysis (MWCO: 10000) against water for 2 days to give a homogeneous colloidal solution of Pd@CB-PN **3**. The amount of Pd in **3** was quantified by ICP-AES to be 81% of the initial Pd salt used. See the Supporting Information for further characterization of **3**.

General procedure for Suzuki–Miyaura reaction: A colloidal solution of Pd@CB-PN **3** (3 mL from stock solution, 5 mol%) was added to a vial (8 mL) containing aryl halide (1.0 equiv), arylboronic acid (1.2 equiv), and K_3PO_4 (1.0 equiv). The vial was sealed with a cap containing a septum, and stirred at room temperature for 1–2 h. After reaction, the catalyst was separated by centrifugation. The product was extracted with toluene (10 mL) and the solution dried with Na_2SO_4. The final product was analyzed by GC-MS. Homocoupling products of arylboronic acids were observed with yields less than 1–3%.

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