Cyclodextrin polymer networks decorated with subnanometer metal nanoparticles for high-performance low-temperature catalysis

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The synthesis of support materials with suitable coordination sites and confined structures for the controlled growth of ultrasmall metal nanoparticles is of great importance in heterogeneous catalysis. Here, by rational design of a cross-linked β-cyclodextrin polymer network (CPN), various metal nanoparticles (palladium, silver, platinum, gold, and rhodium) of subnanometer size (<1 nm) and narrow size distribution are formed via a mild and facile procedure. The presence of the metal coordination sites and the network structure are key to the successful synthesis and stabilization of the ultrasmall metal nanoparticles. The as-prepared CPN, loaded with palladium nanoparticles, is used as a heterogeneous catalyst and shows outstanding catalytic performance in the hydrogenation of nitro compounds and Suzuki-Miyaura coupling reaction under mild conditions. The CPN support works synergistically with the metal nanoparticles, achieving high catalytic activity and selectivity. In addition, the catalytic activity of the formed catalyst is controllable.

INTRODUCTION

Ultrasound metal nanoparticles (NPs) have attracted attention in many areas, including catalysis, sensing, biomedicine, electronics, and optics (1–4). Because of their small size and large surface-to-volume ratio, they often have unusual properties that markedly differ from their respective bulk counterparts (5, 6). In the field of heterogeneous catalysis, the size, shape, and size distribution of NPs significantly affect the catalytic performance (7, 8). Small metal particles usually have high catalytic activity since they have much more accessible active sites. To achieve the highest possible metal accessibility, the NPs’ size should be about 1 nm, forming clusters of a few tens of atoms (9, 10). However, as the particle size decreases, the NPs tend to aggregate and fuse together owing to their high surface energy. This results in decreased catalytic activity and impeded recyclability, thus restricting their practical use. Therefore, it is still a great challenge to obtain ultrasmall NPs with narrow size distribution as well as good stability.

Numerous attempts to synthesize stable NPs have been made on the basis of surface-capping ligands, supporting substrates, and dendrimer and cage architectures (11–20). One simple and efficient method is the use of size-controlling supports. The NPs are confined within the support structure and become stabilized by their interaction with the ligands. The reactivity and stability of these catalyst systems are highly dependent on the substrates. Ideally, the substrate would work synergistically with the metal NPs to further promote the catalysis capabilities. To date, many substrate materials have been studied, such as metal organic frameworks, covalent organic frameworks, zeolites, silica, and carbon materials (15–21). However, these support materials are usually chemically or mechanically unstable, or they lack the necessary flexibility for modification or synergetic effects. Therefore, the rational design and synthesis of more suitable substrate materials are of great importance in heterogeneous catalysis.

Insoluble polymer networks of cyclodextrin (CD), an inexpensive, naturally produced macrocycle of oligosaccharide, have been extensively studied for the removal of micropollutants via adsorption and membrane separation (22–24). Cyclodextrin is capable of capturing a large number of organic molecules, of appropriate size and shape, to form well-defined host-guest complexes (24). To date, many studies have been reported using cyclodextrin monomers and cyclodextrin-containing polymers as stabilizing agents or supports (24–27). However, without preferential binding sites and a proper confinement structure, large metal NPs are produced, which are unfavorable for heterogeneous catalysis. To limit the NP size during nucleation and growth, strong coordination sites and restricted space inside the support are necessary. Furthermore, simplifying the synthesis of cyclodextrin-containing supports with suitable coordination sites would expand the toolbox for metal NP chemistry and enable more efficient utilization of precious metals in catalysis.

In this work, the β-cyclodextrin polymer network (CPN) was designed and prepared on the basis of click chemistry. The as-prepared CPN was highly cross-linked and had excellent stability in both water and organic solvents. With the click reaction, 1,2,3-triazolyl linkages were formed, which served as connecting units for the cyclodextrins as well as effective anchoring groups to facilitate the binding of metal ions/NPs. Given the confining structure of the CPN and its strong coordination groups, we explored its potential as a support for metal NPs. Here, a series of ultrasmall noble metal [palladium (Pd), silver (Ag), platinum (Pt), gold (Au), and rhodium (Rh)] NPs were facilely synthesized by wet chemistry under mild conditions. The as-prepared CPN, decorated with ultrasmall metal NPs, showed excellent catalytic activity in various chemical reactions, including nitroarene reduction and the Suzuki-Miyaura coupling reaction, which are important for environmental and industrial applications. Furthermore, the metal NPs supported on
CPN showed high stability over multiple catalytic cycles and were easily recyclable.

RESULTS
Construction and characterization of CPN
As shown in Fig. 1A, the β-CPN was facilely synthesized by a click reaction, with per-(6-azido-6-deoxy)-β-cyclodextrins and 1,4-diethynylbenzene as monomers. Under mild reaction conditions (60°C, 2 days), the CPN was formed as a pale yellow precipitate with a yield of 77% (Fig. 1D). It is particularly worth mentioning that, in the polymer network, cyclodextrin was regioselectively cross-linked, leaving the secondary side of cyclodextrin unmodified; hence, the molecular transport through the cavity was not hindered. Both monomers had rigid structures, and the highly cross-linked CPN had excellent chemical stability. The CPN was stable in both water and different organic solvents [N,N′-dimethylformamide (DMF), tetrahydrofuran (THF), acetone, hexane, ethanol, and methanol]. The synthesis procedure had a major effect on the product obtained. Since the reaction happened on just one side of the cyclodextrin, the steric effect on the cross-linking degree must be carefully considered. Only when the ratio of per-(6-azido-6-deoxy)-β-cyclodextrins and 1,4-diethynylbenzene was larger than 3 could a precipitate form in the reaction solution. In the preliminary experiment, 1,3,5-triethynylbenzene was also used to synthesize the CPN. However, the precipitate formed by that reaction was not chemically stable in organic solvents (table S1). The detailed synthesis procedure is described in the Supplementary Materials.

The successful synthesis of CPN via a click reaction was verified by various characterization methods (see section S2 and figs. S1 to S9). The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images showed that the CPN was characterized by an irregular shape (Fig. 1, B and C). Powder x-ray diffraction (PXRD) patterns did not show crystallinity peaks for the plain CPN (fig. S10), indicating the amorphous structure of the polymer network, in which the single cyclodextrin unities were randomly distributed, without forming crystalline domains. This is consistent with the selected area electron diffraction, as shown in the inset of Fig. 1B. Besides high chemical stability, the CPN also had good thermal robustness. Thermogravimetric analysis showed that until 260°C, less than 5% weight loss occurred (fig. S11). The Brunauer-Emmett-Teller (BET) surface area of the CPN was 10.2 m² g⁻¹. The relatively low surface area was probably due to the high cross-linking degree of the CPN material.

Fig. 1. CPN synthesized by a click reaction. (A) Synthesis of the CPN from per-(6-azido-6-deoxy)-β-cyclodextrins with 1,4-diethynylbenzene. (B) TEM images of the CPN. Inset: Selected area electron diffraction of the dashed black square. (C) Scanning electron microscopy image of the CPN. (D) Photo of the as-prepared CPN powder (photo credit: Tiefan Huang, KAUST).
**Subnanometer metal NPs decoration**

Considering the spatial confinement of CPN and strong coordination of 1,2,3-triazolyl groups for various metal ions (28, 29), we explored the potential of the CPN as a substrate to induce nucleation and confined growth of metal NPs inside the confined network structure. A wet-chemistry strategy was adopted to synthesize the CPN supported metal NPs (metal NPs@CPN). As shown in Fig. 2A, the CPN was impregnated with a metal precursor and subsequently reduced with NaBH₄ in methanol to obtain a final metal NPs@CPN. For PdNPs@CPN, inductively coupled plasma (ICP) spectroscopy analyses showed that the Pd content in PdNPs@CPN was 6.0 weight % (wt%), which was consistent with the x-ray photoelectron spectroscopy (XPS) result (5.6 wt%). Since XPS can only detect Pd close to the surface, we concluded that the PdNPs were fairly homogeneously distributed throughout the support CPN. Detailed characterizations are available in section S3 and figs. S12 to S16.

After Pd decoration, the polymer network had a more porous structure (Fig. 2B), possibly due to the remaining azido group’s reduction. The TEM images indicated that ultrasmall PdNPs were formed and that they were highly dispersed throughout the CPN support, without any aggregation (Fig. 2, C and D). Because the formed NPs were so small, the diffraction pattern of crystalline Pd was not observed in the corresponding selected image area (Fig. 2C, inset). This is in agreement with the absence of diffraction peaks of Pd in the high-sensitivity PXRD (fig. S16). High-angle annular dark-field scanning TEM (HAADF-STEM) further confirmed the spatial

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**Fig. 2. Synthesis and characterizations of PdNPs@CPN.** (A) Wet chemistry procedure of metal NPs@CPN synthesis. (B) SEM image. (C and D) TEM images at different magnifications. Inset: Selected area electron diffraction of the dashed black square. (E and F) HAADF-STEM images at different magnifications. Inset: Size distribution of PdNPs in PdNPs@CPN. (G) EDS of PdNPs@CPN. (H) EDS mapping of composition elements Pd, C, N, and O, respectively.
confinement and uniform distribution of the PdNPs throughout the entire CPN material (Fig. 2, E and F). A histogram of NP size distribution, obtained from more than 120 randomly chosen particles, indicated an average diameter of 0.9 nm, with SDs of about 10 to 15% of the average particle size (Fig. 2F, inset). The energy dispersive x-ray spectroscopy EDS analysis indicated that only C, N, O, and Pd could be detected in the PdNPs@CPN and that there were no other impurities (Fig. 2G). The energy dispersive x-ray spectroscopy (EDS) mapping revealed that all these elements were homogeneously distributed throughout the CPN material, confirming that the PdNPs were well dispersed (Fig. 2H).

The presence of 1,2,3-triazolyl functional groups as ligands was crucial to anchor and stabilize Pd during controlled growth of NPs. To prove this, an analogous β-CD polymer (CDP) without these 1,2,3-triazolyl groups was also synthesized and used as a support under otherwise identical reaction conditions. The CDP, with a much higher BET surface (263 m² g⁻¹), was synthesized, following a previously reported procedure (22). The TEM image of PdNPs@CDP in fig. S17 revealed much larger particle sizes, with a broad size distribution and a rather low density of NPs deposited in the polymeric support. Without metal anchoring sites in the CDP, there was a lack of interaction between the NPs and the polymer network. As a consequence, few NPs favorably nucleated and grew in the network. Instead, they formed on the surface of the material and agglomerated to larger particles. As a control, unsupported PdNPs were also prepared, giving rise to severe aggregation of PdNPs (fig. S18). In this regard, the 1,2,3-triazolyl coordination groups and the confinement structure of the CPN were essential for tuning the size and distribution of the PdNPs.

Besides the synthesis of PdNPs@CPN with ultrasmall NPs and narrow particle size distribution, we used the CPN to grow other metal NPs. CPNs were successfully synthesized with ultrasmall Ag, Au, Pt, and Rh NPs via a procedure analogous to that applied to Pd. The detailed synthesis procedure and characterization are described in the Supplementary Materials. Each synthesized metal NPs@CPN displayed its characteristic color (fig. S19). Because of the varying ability of 1,2,3-triazolyl to coordinate different metal ions, the content of metal NPs loaded in the CPN support varied (table S2). The Rh content in the RhNPs@CPN was only 1.3 wt%. However, for AuNPs@CPN, 10.1 wt% of metal content was reached, even when a much lower impregnation concentration was used. Since 1,2,3-triazole is considered a soft base, based on the HSAB (hard and soft acids and bases) theory, the soft base forms more stable complexes with soft acids than with borderline and hard acids (30). Hence,
the use of metal ions classified as softer acids should lead to higher adsorption during the impregnation process and higher NP loading after reduction. True to our prediction, Au$^{3+}$, the softest acid, has the highest NP loading, while Rh$^{3+}$ has the lowest.

The TEM (fig. S20) and HAADF-STEM images (Fig. 3, A to D) of these metal NPs@CPN revealed that all metal NPs present in the CPN support were well dispersed, without large aggregations. The EDS mapping also revealed a homogeneous distribution throughout the support (fig. S21). The average size of all formed NPs is less than 1 nm in diameter. In particular, for the AgNPs@CPN, an average size of about 0.5 nm was estimated. Considering that the radius of a silver atom is 160 pm, we speculated that only about four silver atoms aggregated. To the best of our knowledge, these are the smallest particles that have ever been prepared by wet chemistry on a support material (table S4). The results from different metals also confirmed the superior performance and general applicability of the CPN as a substrate for the nucleation and confined growth of noble metal NP, which can be attributed to the strong coordination capability of the abundant triazolyl groups in the polymer network as well as the confining function by its structure.

**Catalysis performance**

Ultrasmall NPs are usually favorable for catalysis. Therefore, we investigated the PdNPs@CPN as a catalyst in some important

![Catalytic performance of PdNPs@CPN for 4-nitrophenol reduction.](image)

(A) UV-Vis spectra of 0.1 mM 4-nitrophenol (4-NP) aqueous solution before and after addition of NaBH$_4$. Time-dependent UV-Vis spectra of the reduction of 4-NP (0.1 mM) in NaBH$_4$ (10 mM) aqueous solution catalyzed by (B) CPN, (C) Pd black, and (D) PdNPs@CPN. Inset: Optical images of reaction mixtures at 0 and 3 min. (E) Recyclability of the PdNPs@CPN for seven cycles of 4-NP reduction reactions. (F) Time-dependent UV-Vis spectra of the reduction of 4-NP (0.1 mM) catalyzed by PdNPs@CPN with the addition of 1-adamantane-carboxylate sodium salt (ACNa).
activities of the metal-free CPN. As a comparison, the addition of even after a 60-min reaction, implying the extremely low catalytic absorption of the reaction mixture at 400 nm did not change much, Pd-free CPN was evaluated as a control experiment (Fig. 4B). The decay of the catalytic activity was observed. As a comparison, Pd/C catalyst was stable under the reaction conditions, and no gradual version of 4-nitrophenol, indicating excellent recyclability. The et al 2019; Huang Sci. Adv., eaax6976 1 November 2019

because it can be conveniently tracked by ultraviolet-visible (UV-Vis) spectroscopy (31). The UV-Vis absorption peak of the 4-nitrophenol aqueous solution appeared at 317 nm, which red-shifted to 400 nm upon the addition of NaBH₄, and the color changed from light yellow to bright yellow (Fig. 4A) as a result of the formation of 4-nitrophenolate ions. First, the reduction of 4-nitrophenol by Pd-free CPN was evaluated as a control experiment (Fig. 4B). The absorption of the reaction mixture at 400 nm did not change much, even after a 60-min reaction, implying the extremely low catalytic activity of the metal-free CPN. As a comparison, the addition of PdNPs@CPN significantly accelerated the reduction reaction. Within 3 min, the peak at 400 nm completely disappeared, whereas a new peak appeared at 300 nm, signifying the 4-aminophenol production. The reduction reaction was also visually observed as the yellow color disappeared (Fig. 4D, inset). The extremely high catalytic activity of the PdNPs@CPN can be explained by the highly dispersed ultrasmall PdNPs present in the CPN support. For comparison, the catalytic efficiency of commercial Pd black was tested (Fig. 4C). Even when a large amount of Pd black was introduced (1.2 mg), only after 30 min, the 4-nitrophenol reduction was nearly complete.

In addition to the remarkable activity of the ultrasmall metal particles, the cyclodextrin in the CPN also played a role in the catalytic reaction. The complexation of 4-nitrophenol with cyclodextrin in the polymer network favored the adsorption of 4-nitrophenol to reach the confined PdNPs (32, 33). This increased the local concentration of 4-nitrophenol near the PdNPs surfaces, which led to an increase in the reaction rate. Furthermore, since β-CD was cross-linked in the polymer network, the substrate had unencumbered access to the CD cavity and passed through it to interact with the PdNPs inside the polymer network. To confirm this, a reduction reaction of 4-nitrophenol to 4-aminophenol was conducted with 1-adamantane-carboxylate sodium salt (ACNa). ACNa is well known to complex with β-CD with a high association constant and therefore can be used as a competitor to other molecules (34, 35). When ACNa was added into the reaction solution, the catalytic activity of PdNPs@CPN substantially decreased. After 20 min, only a 62% conversion of 4-nitrophenol into 4-aminophenol was reached (Fig. 4F). Since ACNa has a much higher association constant with cyclodextrin compared to 4-nitrophenol (36), it competitively blocked the cyclodextrin cavity and slowed down the access of 4-nitrophenol to the PdNPs@CPN. Thus, the presence of the CD within the CPN not only participated in construction of confined space for NP formation but also provided available channels for molecule transport, leading to high reaction activity.

Besides their catalytic activity, the reusability and stability of catalysts are important parameters that determine their practical use in industrial applications. An additional experiment was carried out to examine the recyclability of PdNPs@CPN. The PdNPs@CPN were easily recovered by simple filtration. After one cycle was completed, the catalyst was retained by a syringe filter (0.45 μm, Whatman) and reused with fresh reactants (10 ml of 0.1 mM 4-nitrophenol and 10 mM NaBH₄). The reaction was monitored as before. As shown in Fig. 4E, after seven cycles, the PdNPs@CPN maintained 100% conversion of 4-nitrophenol, indicating excellent recyclability. The catalyst was stable under the reaction conditions, and no gradual decay of the catalytic activity was observed. As a comparison, Pd/activated carbon (Pd/C) was also tested as a catalyst in this reaction. It showed a comparable catalytic activity and can complete the reaction in a very short time as well. Activated carbon is known to have a much larger specific surface area (>1000 m²/g). This indicated that the catalytic active sites of PdNPs@CPN in this work had higher catalytic activity than that of Pd/C. Furthermore, the recyclability of Pd/C was not as good as PdNPs@CPN (fig. S22). More than 4% of catalytic activity was lost after only two cycles, probably due to the partial occupation of active catalytic sites by adsorbates. The TEM images showed that the reused PdNPs@CPN maintained its structure, and the PdNPs were still highly dispersed, without any significant aggregation (fig. S23). ICP–optical emission spectrometry analysis showed that the Pd leaching was inappreciable; only 0.10 parts per million of Pd was detected in the filtrate, which was considered negligible since 6 wt% of PdNPs@CPN was freshly added. These features were attributed to the high chemical stability of the cross-linked polymer network and its ability to stabilize the PdNPs.

To further investigate the applications of PdNPs@CPN to other nitroarene hydrogenations, a series of nitroarenes (Table 1) with different solubility and electronic properties were examined. The reactions were performed in the presence of only 0.25 mol% PdNPs@CPN at room temperature. For the water-soluble nitroarenes, the reactions were performed using water as a green solvent. In 3 min, a 99% product yield was obtained (entries 1 to 3). The fast reaction was accompanied by a large amount of hydrogen generation and temperature elevation. In a control experiment using 3-nitrophenol in the absence of PdNPs@CPN, the yield of the corresponding product after 60 min was only 5% (entry 4). The other nitroarene hydrogenation reactions were performed in water/methanol mixtures owing to solubility problems. All the components were completely reduced to the corresponding amines, with 99% yield achieved in 5 min under mild conditions. The catalytic efficacy of the PdNPs@CPN was not sensitive to the substituent groups of substrates. Nitroarenes containing electron-releasing or electron-withdrawing groups were reduced efficiently. In addition, PdNPs@CPN showed an outstanding hydrogenation selectivity. For 4-nitrochlorobenzene and 2-nitrochlorobenzene (entries 5 and 6), only the nitro group was reduced; the chlorosubstitution was not affected. Chloroaniline was obtained with a yield of 99%. No dehalogenation of the product was observed. Also, 4-nitrobenzonitrile was selectively reduced to 4-aminobenzonitrile with 99% yield, leaving the –CN group unchanged (entry 10). However, less than 90% of yields were obtained, when Pd/C was used as the catalyst (entries 7 and 8). Although Pd/C also exhibited high conversion, it had a low catalytic selectivity, leading to the generation of a substantial product with undesired dehalogenation. We speculated that, unlike Pd/C, in which all active catalytic sites, i.e., PdNPs, were on the surface of the pore wall of activated carbon, PdNPs@CPN had all PdNPs confined and surrounded by cyclodextrins in the support, which can offer a protective environment for substrates from possible over-reduction during catalytic reaction.

We further investigated the catalytic activity of PdNPs@CPN for the Suzuki–Miayaura coupling reaction, which is among the most widely used protocols for the formation of carbon–carbon bonds (37). A series of aryl halides was reacted with phenylboronic acid in 50% ethanol-water, a green solvent, in the presence of only 0.1 mol% Pd of catalyst (table S3). Most of the reactions listed in table S3 were very efficiently completed under mild experimental conditions, producing the corresponding biphenyl compounds, including aryl
Table 1. Catalytic performance of PdNPs@CPN in the hydrogenation reactions for various nitroarenes.

| Entry | Reactant | Product | Solvent | Time (min) | Yield* (%) |
|-------|----------|---------|---------|------------|------------|
| 1°    | HO-NO₂   | HO-NH₂  | H₂O     | 3          | >99        |
| 2°    | HO-NO₂   | HO-NH₂  | H₂O     | 3          | >99        |
| 3°    | HO-NO₂   | HO-NH₂  | H₂O     | 3          | >99        |
| 4°    | HO-NO₂   | HO-NH₂  | H₂O     | 60         | 5          |
| 5°    | Cl-NO₂   | Cl-NH₂  | H₂O     | 5          | >99        |
| 6°    | Cl-NO₂   | Cl-NH₂  | H₂O     | 5          | >99        |
| 7°    | Cl-NO₂   | Cl-NH₂  | H₂O     | 5          | 89         |
| 8°    | Cl-NO₂   | Cl-NH₂  | H₂O     | 5          | 86         |
| 9°    | Cl-NO₂   | Cl-NH₂  | H₂O     | 5          | 64         |
| 10°   | Cl-NO₂   | Cl-NH₂  | H₂O     | 5          | 81         |
| 11°   | Cl-NO₂   | Cl-NH₂  | H₂O     | 5          | >99        |
| 12°   | Cl-NO₂   | Cl-NH₂  | H₂O     | 5          | >99        |
| 13°   | Cl-NO₂   | Cl-NH₂  | H₂O     | 5          | >99        |

*Gas chromatography–mass spectrometry result. †Reaction conditions: nitroarenes (2.3 mmol), PdNPs@CPN (0.25 mol%), H₂O (4 ml), room temperature. ‡Without PdNPs@CPN. §Nitroarenes (1 mmol), PdNPs@CPN (0.25 mol%), and 50 ml of H₂O/methanol (3:2) as the solvent. ¶Pd/C as the catalyst. ¶Pt/alumina as the catalyst.
iodides and aryl bromide, with excellent yields (>96%) (entries 4 to 7). However, for the relatively inactive aryl chloride, only 62% yield was reached after a 24-hour reaction. The activation of the C—Cl bond required harsher reaction conditions than the activation of either the C—Br or the C—I bond in a heterogeneous catalysis system (38, 39).

CONCLUSION
In summary, we developed a highly cross-linked CPN, which contained 1,2,3-triazole groups adjacent to the cyclodextrin units. The cyclodextrin formed inclusion complexes with numerous organic compounds; the triazole formed complexes with many heavy metals. The cyclodextrin-triazole network could be loaded with high amounts of metal ions, e.g., Pd^{2+}. Because of the confinement within the highly cross-linked network, PdNPs of subnanometer size were generated after the reduction. We demonstrated that these supported PdNPs are highly efficient catalysts for low-temperature hydrogenations and the Suzuki-Miyaura coupling reaction. The synergy between the substrate-binding cyclodextrin and the ultrafine Pd particles led to unusually high catalytic activity. In addition, other highly dispersed metal NPs (Ag, Au, Pt, and Rh) were also generated in the cyclodextrin-triazole network. Their catalytic properties will be evaluated in future experiments. Considering the potential diversity of CPNs in combination with the generation of ultrasmall metal NPs, our approach will inspire further studies of novel engineered nano-material composites for potential applications in many fields, including catalysis, biomedicine, or optics.

MATERIALS AND METHODS
Synthesis of CPN
Successful fabrication of a stable CPN was achieved after many trials. We investigated the effect of cross-linkers and reactant concentration in preliminary experiments. We noticed that the ratio of cross-linker and per-(6-azido-6-deoxy)-β-cyclodextrins was determinant for the production of CPN. Only if the ratio was higher than 3 did the cross-linking reaction occur. Furthermore, a different cross-linker can affect the chemical stability of the resulting CPN. The trifunctional cross-linking reaction occurred. Furthermore, a different cross-linker can affect the chemical stability of the resulting CPN. The trifunctional cross-linker 1,3,5-triethynylbenzene led to a chemically unstable polymer network, probably due to the steric effect in the reaction. Table S1 summarizes these synthesis experiments. According to these results, we used bifunctional 1,4-diethynylbenzene as the cross-linker to synthesize CPN, and the details of the preparation is given below.

To a solution of per-(6-azido-6-deoxy)-β-cyclodextrins (1.6 g, 1.22 mmol), 1,4-diethynylbenzene (0.539 g, 4.27 mmol), and CuSO_{4}-5H_{2}O (60.8 mg, 0.243 mmol) in DMF (60 ml), sodium ascorbate (0.0966 g, 0.488 mmol) was added under a N_{2} atmosphere. The stirring mixture was heated to 60°C and maintained at that temperature for 7 days. The brown precipitate was isolated by centrifugation and then washed with DMF (2 × 50 ml), water (2 × 30 ml), THF (2 × 30 ml), and water (2 × 30 ml), sequentially. The resultant materials were freeze-dried for 3 days to afford CPN as a pale yellow powder with a yield of 77 wt%.

Synthesis of metal NPs@CPN
To prepare PdNPs@CPN, Pd(OAc)_{2} (6.7 mg, 0.03 mmol) and CPN (10 mg) were added to dichloromethane (6 ml). After stirring at room temperature overnight, the precipitate was isolated by filtration. The precipitate was then washed with dichloromethane (30 ml) and re-dispersed in dichloromethane (10 ml) for 1 hour. This process was repeated two times to remove extra Pd(OAc)_{2}. Then, the precipitate was dried in vacuum at 30°C overnight to give Pd(II)@CPN as an orange solid. Pd(II)@CPN was reduced in a solution of NaBH_{4} in methanol (50 mM) at room temperature for 2 hours. After washing with an excess amount of methanol to remove extra NaBH_{4}, the final PdNPs@CPN was obtained as a gray solid. The Pd content in PdNPs@CPN was 6 wt% as determined by ICP. To prepare AgNPs@CPN, PtNPs@CPN, AuNPs@CPN, and RhNPs@CPN, AgOAc (5.3 mg, 0.03 mmol), HAuCl_{4} (2 mg, 0.006 mmol), K_{2}PtCl_{4} (6.3 mg, 0.015 mmol), and RHCl_{3} (6.3 mg, 0.03 mmol) were used as the precursors, respectively, and water was used as the solvent, with the rest of synthesis procedure the same as that of PdNPs@CPN. The metal content of each final product was 2.7 wt% for AgNPs@CPN, 5.1 wt% for PtNPs@CPN, 10.3 wt% for AuNPs@CPN, and 1.3 wt% for RhNPs@CPN as determined by ICP.

GENERAL PROCEDURE OF THE 4-NITROPHENOL REDUCTION REACTION
To a bottle of 4-nitrophenol (0.1 mM) and NaBH_{4} (10 mM) aqueous solution (10 ml), PdNPs@CPN was introduced, and the solution was stirred at 300 rpm at room temperature. The UV-Vis absorption spectra of this solution were measured at certain time intervals. The PdNPs@CPN can be recovered by simple filtration via a syringe filter. For the recyclability experiment, the recovered PdNPs@CPN was reused with fresh reactant solution, and the procedure was the same as that in the first cycle.

General procedure of the various nitroarene reduction reactions
To a Schlenk tube of nitroarene solution, PdNPs@CPN (0.25 mol%) was added, and the system was subsequently purged with N_{2} gas three times. NaBH_{4} (3 eq) was then introduced into the system. All the experiments were performed at room temperature. After the reaction, the solution was filtered and analyzed with gas chromatography–mass spectrometry to determine the yield and selectivity.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/11/eaax6976/DC1
Section S1. Materials and methods
Section S2. Characterization of CPN
Section S3. Characterization of PdNPs@CPN
Fig. S1. FT-IR spectra of β-cyclodextrin, per-(6-iodo-6-deoxy)-β-cyclodextrin, and per-(6-azido-6-deoxy)-β-cyclodextrins.
Fig. S2. 1H NMR spectra of β-cyclodextrin, per-(6-iodo-6-deoxy)-β-cyclodextrin, and per-(6-azido-6-deoxy)-β-cyclodextrins.
Fig. S3. 13C NMR spectra of β-cyclodextrin, per-(6-iodo-6-deoxy)-β-cyclodextrin, and per-(6-azido-6-deoxy)-β-cyclodextrins.
Fig. S4. Photo of as-prepared CPN.
Fig. S5. FT-IR spectra of 1,4-diethynylbenzene, per-(6-azido-6-deoxy)-β-cyclodextrins, and CPN.
Fig. S6. Molecular weight of each moiety in the CPN.
Fig. S7. XPS survey spectrum of CPN.
Fig. S8. XPS survey spectrum of CPN.
Fig. S9. Molecular weight of each moiety in the CPN.
Fig. S10. PXRD patterns of CPN.
Fig. S11. TGA curve of β-cyclodextrin and CPN.
Fig. S12. PXRD patterns of CPN.
Fig. S13. Solid-state 13C CP/MAS NMR spectra of Pd(II)@CPN and PdNPs@CPN.
Fig. S14. FT-IR spectra of Pd(II)@CPN and PdNPs@CPN.
Fig. S15. High-resolution XPS spectra of CPN, Pd(II)@CPN, and PdNPs@CPN.
Fig. S16. PXRD patterns of Pd(II)@CPN, PdNPs@CPN, Pd black, and Pd(OAc)_{2}.
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