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Synthesis of Ultrafine and Highly Dispersed Metal Nanoparticles Confined in a Thioether-Containing Covalent Organic Framework and Their Catalytic Applications

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ABSTRACT: Covalent organic frameworks (COFs) with well-defined and customizable pore structures are promising templates for the synthesis of nanomaterials with controllable sizes and dispersity. Herein, a thioether-containing COF has been rationally designed and used for the confined growth of ultrafine metal nanoparticles (NPs). Pt or Pd nanoparticles (Pt NPs and Pd NPs) immobilized inside the cavity of the COF material have been successfully prepared at a high loading with a narrow size distribution $(1.7 \pm 0.2 \text{ nm})$. We found the crystallinity of the COF support and the presence of thioether groups inside the cavities are critical for the size-controlled synthesis of ultrafine NPs. The as-prepared COF-supported ultrafine Pt NPs and Pd NPs show excellent catalytic activity respectively in nitrophenol reduction and Suzuki-Miyaura coupling reaction under mild conditions and low catalyst loading. More importantly, they are highly stable and easily recycled and reused without loss of their catalytic activities. Such COF-supported size-controlled synthesis of nanoparticles will open a new frontier on design and preparation of metal NP@COF composite materials for various potential applications, such as catalysis and development of optical and electronic materials.

INTRODUCTION

Ultrafine and highly dispersed metal nanoparticles (NPs) have attracted extensive research interests within the past few years due to their unique optical, electronic and mechanical properties.¹⁻² Provided high surface area and surface-tovolume ratio, ultrafine noble metal nanoparticles (Pt, Pd, etc.) are of particular interest for the applications in heterogeneous catalysis. These nanoparticles have been wildly used in various reactions, such as dehalogenation,³ hydrogenation,⁴⁻⁵ coupling reactions,⁶ showing excellent catalytic activity, high atom utilization, and easy recyclability. It has been proved that ultrafine NPs with smaller sizes generally exhibit remarkable catalytic activities.⁷⁻⁸ However, ultrafine NPs easily aggregate due to their high surface energy, with greater aggregation tendency for smaller particles. As a result, they gradually lose their catalytic activity over time, hampering reusability and thus limiting their practical applications. In order to obtain stable nanoparticles with constant high catalytic activity, researchers developed various supporting substrates,⁹⁻¹⁰ including porous silica,¹¹ carbon materials,¹² graphene,¹³ metal oxide,¹⁴ polymers,¹⁵ and metal organic frameworks (MOFs).¹⁶ However, it remains a challenge to obtain ultrafine NPs with high stability and a narrow size distribution.

In the past decade, an impressive number of covalent organic frameworks (COFs) have been reported as crystalline

organic porous polymers with well-defined pore structures.¹⁷⁻²¹ They have shown interesting potential applications in gas storage and separation, heterogeneous catalysis, optoelectronic materials and energy storage.²²⁻²⁶ However, only recently have they been reported as promising hosts to support NPs.²⁷⁻³² COF-based supports potentially could have several unique advantages: (1) COFs have pre-designable well-defined pore structures which can be used to confine nanoparticle growth and thus control the size of NPs; (2) the pore channels in COFs are well-isolated, thus the aggregation of entrapped NPs can be minimized; (3) the chemical structures of COFs can be easily tailored and surface functional groups that can anchor metal NPs can be easily installed; (4) many COFs are stable and thus would be resistant to decomposition under various reaction conditions. Banerjee and coworkers reported COFsupported Au NPs and Pd NPs hybrid materials, which show high catalytic activity in nitrophenol reduction and Sonogashira-coupling, respectively.³⁰⁻³¹ However, relatively larger size of NPs (5 \pm 3 nm for Au NPs and 7 \pm 3 nm for Pd NPs) compared to the pore size of the COF support (~1.8 nm) were obtained with broad size distribution, which indicates surface deposition of NPs rather than encapsulation inside the pores. The lack of control of the nanoparticle size is likely due to weak interactions between COF support and metal NPs.³³ Excellent size control $(2.4 \pm 0.5 \text{ nm})$ and even distribution of Pd NPs in a COF have



Figure 1. (a) Synthesis of Thio-COF and (b) Schematic representation of the synthesis of Thio-COF supported PtNPs@COF and PdNPs@COF. Top and side views of the energy-minimized models of Thio-COF (yellow, S; blue, N; grey, C; red, O) are shown in b.

been achieved by the Fischer group through gas-phase infiltration of volatile organometallic precursors inside the cavity of the 3D COF-102 followed by photodecomposition of the precursor to form Pd NPs.²⁷

These literature precedents suggest that encapsulation and seed-growth of NPs inside the cavities are critical to confine nanoparticle growth and control the size. We envision that the presence of strong anchoring groups inside the pores would facilitate the binding of metal ions/nanoparticles and formation of nucleation sites inside the cavities, thus enabling confined growth of nanoparticles and control of their particle size. Previously, we have reported a size-controlled synthesis of narrowly-distributed ultrafine gold nanoparticles (average size: 1.9 nm) using a shape-persistent organic cage bearing thioether groups as a template.³⁴ We have demonstrated that the presence of thioether group inside the cavity is crucial for the size-controlled synthesis of Au NPs, serving as nucleation sites for the metal deposition and NPs growth. Herein, we report the synthesis of a thioether-containing COF and its application in controlled growth of ultrafine noble metal nanoparticles. The COF-supported Pd NPs and Pt NPs (PtNPs@COF and PdNPs@COF) with narrow size distribution $(1.7 \pm 0.2 \text{ nm})$ have been successfully prepared with high distribution density. The as-prepared PtNPs@COF and PdNPs@COF show excellent catalytic activities in reduction of 4-nitrophenol and the Suzuki-Miyaura coupling reaction, respectively. Advantages of these COF-NP hybrid catalysts over organic molecular cage-encapsulated NPs include their efficient exposure of active sites, high stability over multiple catalytic cycles, and easy recyclability. We also demonstrate the critical importance of crystallinity of the COF support and thioether functional groups in controlling the formation of NPs with narrow-size distribution.

EXPERIMENTAL SECTION

Synthesis of Thio-COF. To a glass tube (the outer diameter is 10 mm and the inner diameter is 8 mm) were added trialdehyde 1 (11 mg, 0.05 mmol), thioether substituted diamine 2 (31 mg, 0.075mmol), 6 M acetic acid (0.2 mL), dioxane (1.8 mL) and mesitylene (0.2 mL). The tube was flash frozen at 77 K in liquid nitrogen and evacuated to the internal pressure of ~100 mtorr, and then the tube was sealed under an open flame. The mixture was first warmed to room temperature and then the temperature was slowly raised to

120 °C over 2 h. The reaction was kept at this temperature for 3 days and cooled to room temperature over 12 h. The orange precipitate was collected by vacuum filtration, washed with a large amount of acetone and CH_2Cl_2 , and dried under vacuum to yield the thioether-containing COF (**Thio-COF**, 38 mg, 91 %). Elemental analysis calcd (%) for ($C_{15}H_{14}NOS$)_n: C, 70.28; H, 5.50; N, 5.46. Found: C, 69.97; H, 6.50; N, 5.11.

Synthesis of PtNPs@COF and PdNPs@COF. In a typical procedure, a well-dispersed suspension of as-prepared Thio-COF (4 mg) in methanol (3 mL) was mixed with a solution of metal precursor K₂PtCl₄ (5 mg, 1.2×10^{-2} mmol) or K₂PdCl₄ (4 mg, 1.2×10^{-2} mmol) in water (2 mL). The mixture was brought to dryness under vacuum with stirring to deposit metal precursors in Thio-COF support. The mixture was redispersed in a mixed solvent of methanol and water (5 mL, MeOH/H₂O, v/v = 3:2). A solution of NaBH₄ in methanol (0.25 M, 2 mL) was added dropwise and the mixture was stirred for 2 days. The product was collected through centrifugation, washed with ethanol and dichloromethane three times, and dried under vacuum for further use.

General procedure for the reduction of 4-nitrophenol catalyzed by PtNPs@COF. To a cuvette were added an aqueous solution of 4-nitrophenol $(1.0 \times 10^{-3} \text{ M}, 0.3 \text{ mL})$, water (1 mL) and an aqueous solution of NaBH₄ (0.5 M, 1 mL). A suspension of PtNPs@COF in water (0.5 mg/mL, 25 μ L or 50 μ L) was introduced, and the reaction progress was monitored with the UV-Vis spectroscopy. The initial bright yellow solution gradually turned to colorless as the reaction progressed.

General procedure for the Suzuki-Miyaura coupling reaction catalyzed by PdNPs@COF. In a typical procedure of the coupling reaction, arylhalide (1 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (1.5 mmol), and PdNPs@COF (0.1 mol%) were mixed in DMF/H₂O (3 mL, 1:1 v:v) in a Schlenk tube. The reaction tube was evaluated and flushed with N₂ gas three times. The mixture was heated at 50 °C for 3 h with stirring. The product was extracted with dichloromethane and the yield was analyzed by ¹H NMR integration of the crude product mixture.

RESULTS AND DISCUSSION

The thioether-containing imine-linked COF (**Thio-COF**) was synthesized through the condensation of trialdehyde **1** and

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Figure 2. Characterizations of **PtNPs@COF**: (a) low-magnification TEM image, the inset is the size distribution profile of Pt NPs; (b) high-magnification TEM image; (c) high-resolution TEM (HR-TEM) image; (d) high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image; (e) selected area electron diffraction (SAED) pattern; (f) energy dispersive X-ray spectroscopy (EDS) mapping of composition element, Pt, S, C and N respectively.

thioether substituted diamine 2 (Figure 1a). Under the solvothermal conditions (1,4-dioxane and mesitylene, 6M HOAc, 120 °C, 3 days), **Thio-COF** was obtained as yellow powder with an isolated yield of 91%. The COF material is not soluble in water and common organic solvents such as dichloromethane, acetone, ethanol, and tetrahydrofuran.

Thio-COF was characterized by elemental analysis, Fourier transform infrared (FT-IR) spectroscopy, solid state ¹³C NMR spectroscopy, scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA). The FT-IR spectrum of **Thio-COF** (Figure S1) shows the characteristic C=O stretch of a β -keto-enamine at ~1621 cm⁻¹. The structure of **Thio**-COF was also supported by the solid-state ¹³C crosspolarization magic angle spinning (CP-MAS) NMR spectrum (Figure S2), showing the resonance signals around 148 ppm and 185 ppm, which are corresponding to the resonance signals of enamine and ketone carbons, respectively.35-37 The scanning electron microscopy (SEM) images show irregular shaped particles of Thio-COF (Figure S3). The elemental composition detected by Energy Dispersive X-ray Spectroscopy (EDS) agrees well with the theoretical values and the element analysis result (Figure S4). TGA indicates Thio-COF has a good stability, showing weight loss of 13% at 300 °C (Figure S5).

The crystallinity of **Thio-COF** was evaluated by powder Xray diffraction (PXRD) measurement (Figure S6, black). A set of intensive peaks at $2\theta = 3.04^{\circ}$, 4.99° and 10.23° were observed in the experimental PXRD pattern, which can be

assigned to planes (100), (110) and (220), respectively. It indicates Thio-COF has good crystallinity with a long range ordered molecular structure. Computational simulation and Pawley refinement was performed to obtain the probable structure of Thio-COF using Materials Studio software package. Simulated models were constructed in the hexagonal system, with layers lying on the ab plane. After the geometrical energy minimization, the optimized parameters for the unit cell are a = b = 38.82 Å, c = 4.05 Å (residuals: R_{wp}) = 6.89%, $R_p = 5.37\%$). Through the comparison of the simulated PXRD patterns with the experimental profile, we determined that Thio-COF is in fully eclipsed AA stacking mode with the interlayer distance of 4.05 Å (Table S1). The theoretical pore size was determined to be 2.4 nm. Brunauer-Emmett-Teller (BET) surface area of **Thio-COF** is 50 m² g⁻¹ (Figure S7). The relatively low surface area of Thio-COF is probably due to the thin layers or small domains of the COF material, similar to case reported by Banerjee on the high crystalline COF (TpPa(MC), DaTp-CONs) with low porosity (BET surface area of 53-61 m² g⁻¹).³⁸⁻³⁹ The sample showed only a slight decrease of crystallinity after high temperature activation at 120 °C and BET surface area measurement.

Since thioether groups have strong binding interactions with metal ions, we then explored the possibility of using **Thio-COF** as a template to guide the nucleation and growth of metal NPs inside the pores. Thioether-based COFs have recently been reported to be able to detect and remove of Hg ions.^{40.42} It was thus expected that the thioether groups

pointing inside the cavity would efficiently bind metal ions and serve as the nucleation sites for confined growth of metal NPs in the well-defined pores of the COF support. We used wet-chemistry approach to synthesize **Thio-COF**-supported Pt NPs (**PtNPs@COF**) (Figure 1b). The metal precursor was deposited in the COF material by mixing K₂PtCl₄ solution with a suspension of **Thio-COF** and evaporating all the volatiles under vacuum with stirring. The mixture was redispersed and reduced with NaBH₄ in methanol to provide **PtNPs@COF**, which was thoroughly washed and dried before the characterization and further use.

The typical transmission electron microscope (TEM) images of PtNPs@COF (Figure 2a, b) reveal that the ultra-small Pt NPs were uniformly distributed in the COF material. The statistic histogram for more than 100 randomly chosen particles in the Figure 2a shows that the ultrafine Pt NPs have an average size of 1.70 nm in diameter with a narrow size distribution (inset in Figure 2a). We found the reaction conditions have significant effect on the resulting nanoparticle size. When the reduction was conducted in water rather than methanol, or the reaction temperature was raised to 50 °C, much larger size of NPs with broader size distribution were formed (Figure S8b, c). The formation of COF-supported Pt NPs was further confirmed by the high-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) image (Figure 2d), which clearly shows the presence of well-dispersed Pt NPs embedded in the COF material without any sign of agglomerization. We did not observe any un-supported Pt NPs, suggesting Thio-COF is a favorable support for the growth of NPs. The high resolution TEM image (HR-TEM) of the PtNPs@COF (Figure 2c) shows that those Pt NPs located on the surface has inter-planar spacing of 0.23 nm corresponding to the plane of a typical Pt facecentered cubic (fcc) structure. We found some Pt NPs don't show clear lattice fringes, which is likely caused by their encapsulation inside the COF cavities. The corresponding selected area electron diffraction (SAED) pattern in Figure 2e shows the polycrystalline nature of Pt NPs and characteristic diffraction rings at (111), (200), (220) and (311), which is consistent with the PXRD pattern of Pt NPs supported by Thio-COF (Figure S10).

The inductively coupled plasma (ICP) analysis reveals that the experimental Pt content in the hybrid material is 34.36 wt%, which correlates well with the theoretical Pt amount we applied (36.91 wt%). Such a high loading of ultrafine metal NPs without aggregation has rarely been observed in previous literature reports.¹⁵ This result also supports the excellent confinement ability of Thio-COF material. The composition of PtNPs@COF was further characterized by energy dispersive spectrum (EDS) elemental mapping. As shown in Figure 2f, the component elements Pt, S, C and N are all evenly distributed in the hybrid material, which again supports the excellent dispersity of Pt NPs in the Thio-COF material. The oxidation state and the interaction of Pt with S were evaluated by X-ray photoelectron spectroscopy (XPS) measurement. The spectrum of Pt 4f region shows a doublet containing a lower energy (Pt $4f_{7/2}$) band and a higher energy (Pt $4f_{5/2}$) band (Figure S12). The deconvolution of the spectrum revealed two pairs of doublets: (1) centered at 71.3 eV for Pt $4f_{7/2}$ and 74.8 eV for Pt $4f_{5/2}$, which can be assigned to Pt(0); (2) centered at 72.2 eV for Pt $4f_{7/2}$ and 76.0 eV for Pt

4f_{5/2}, which can be assigned to Pt(II) species. The presence of Pt(II) species is likely due to the reoxidation of Pt(0) to Pt(II) by exposure to air.^{5,43-44} The binding energy of Pt 4f_{7/2} peak of the Pt(0) species in the **PtNPs@COF** has a higher value compared to that of pure Pt NPs, while the binding energy of S 2p in **PtNPs@COF** has a negative shift compared to that of S in **Thio-COF** (Figure S13). These shifts are likely caused by metal-ligand interactions (e.g. the charge transfer from Pt nanoparticles to S atoms).⁴⁵ We found the molar ratio of Pt/S (1.38) determined by the XPS is much lower than the ratio (5.13) determined by the TEM-EDS (Figure S14), which suggests the majority of Pt NPs are encapsulated inside the COF pores and only limited amount of Pt NPs are deposited on the surface.

To probe the importance of structural order of the COF support for the size-controlled growth of NPs, we used amorphous thioether-containing polymer with much higher BET surface (588 m^2g^{-1}), which was obtained from the same monomers 1 and 2, as the supporting substrate for comparison (Figure S9a, b). We found rather random distribution of Pt NPs with low deposition density, indicating ordered COF structure is preferred to obtain uniform and well-dispersed Pt NPs. As a control experiment, we also prepared Pt NPs in the absence of a COF support. As expected, severe aggregation of Pt NPs was observed (Figure S9c). Interestingly, when analogous crystalline thioether-free COF was applied as a supporting substrate, domains of evenly distributed Pt NPs as well as highly aggregated Pt NPs were observed (Figure S9d). This suggests, in the absence of metal stabilization sites in the thioether-free COF, there is lack of control on the deposition sites of NPs, thus substantial Pt NPs tend to grow on the surface of COF materials and form NPs of uncontrollable random size. Only limited amount of NPs are statistically seeded in the interior of the COF support and grow in the confined space with size control and protection from agglomerization. It is therefore evident that both the structural order of supporting substrate and thioether sites are indispensable to obtain uniform and well-dispersed Pt NPs.

The as-prepared PtNPs@COF is readily dispersed in water and many organic solvents. Since well-dispersed ultrafine NPs generally exhibit high catalytic activities, next we explored the application of PtNPs@COF in heterogeneous catalysis. The catalytic activity of PtNPs@COF was examined by the reduction of 4-nitrophenol in the presence of NaBH₄. This reaction can be easily monitored by UV-Vis spectroscopy and has been widely used as a model reaction to evaluate the activity of noble metal catalysts. This reaction also has a practical significance since 4-nitrophenol is identified as a priority pollutant, while the product 4-aminophenol is an important precursor for medical industry. As a control experiment, we first conducted the 4-nitrophenol reduction in the presence of Thio-COF itself (0.17 mg/mL, 50 µL), and monitored the reaction by the UV-Vis spectra. The absorption peak at 400 nm, a characteristic peak of 4-nitrophenol and NaBH₄ mixture, remains almost unchanged after 10 min (Figure S15a), which indicates the COF alone does not have any considerable catalytic activity. By contrast, when the PtNPs@COF catalyst

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Figure 3. (a) Time-dependent UV-Vis spectra of the reduction of 4-nitrophenol (0.3 μ mol) catalyzed by 50 μ L **PtNPs@COF** (0.50 mg mL⁻¹); (b) Typical optical images of reaction mixtures at 0 min and 8 min; (c) Time-dependent UV-Vis spectra of the reduction of 4-nitrophenol (0.3 μ mol) catalyzed by 50 μ L unsupported Pt NPs (0.17 mg mL⁻¹); (d) The recyclability of the **PtNPs@COF** catalyst.

 $(25 \ \mu\text{L}, 0.5 \ \text{mg mL}^{-1})$ was introduced into the mixture, the reduction was initiated immediately, showing the rapid decrease of the 4-nitrophenol absorption peak at 400 nm and the appearance of a new peak at ~300 nm corresponding to 4aminophenol (Figure S15b). When the dosage of **PtNPs@COF** catalyst (50 μ L, 0.5 mg mL⁻¹) was doubled, the full conversion of 4-nitrophenol to 4- aminophenol was quickly reached in 8 min with the complete disappearance of 4-nitrophenol peak at 400 nm (Figure 3a). This was even obvious to the naked eye, showing the complete discoloration of the solution from bright yellow to colorless (Figure 3b). Our catalyst loading (0.04 µmol Pt per 0.3 µmol 4-nitrophenol) is ~4500 fold less than the loading of the previously reported ultrafine Pt nanoparticles (0.2 mmol Pt per 0.3 µmol 4nitrophenol) supported by chalcogels that show a comparable reaction rate.⁵ When the same amount of unsupported Pt NPs without COF were used as the catalyst of the 4-nitophenol reduction (Figure 3c), much longer reaction time (~ 50 min) was required to reach near complete conversion likely due to their larger sizes and aggregated structures.

Stability and reusability represent important parameters to evaluate a heterogeneous catalyst for practical applications. A successive addition experiment was performed to study the stability and reusability of PtNPs@COF. After completion of the first run, a fresh starting material (4-nitrophenol, 1.0×10^{-3} M, 0.3 mL) was directly added to the reaction mixture of the first run and the reaction was monitored as before. The procedure was repeated until the completion of sixth cycle. As shown in Figure 3d, the conversation of the 4-nitrophenol for each reaction cycle was constantly near 90%, indicating the catalyst is stable under the reaction conditions and does not undergo major decomposition and lose the activity gradually. After reaction, the catalyst can be easily recycled through centrifugation or natural settling. The TEM image shows the recycled PtNPs@COF retain their structural features, still having well-dispersed Pt NPs with little aggregation (Figure S16).



Figure 4. Characterizations of **PdNPs@COF**: (a) lowmagnification TEM image; (B) the size distribution profile of Pd NPs; (C) High-resolution TEM image; (D) EDS mapping of composition elements, Pd, S, C and N respectively.

The excellent stability of Pt NPs could be attributed to the thioether-containing COF support, which facilitates anchoring and confinement of NPs within the pores, thus efficiently stabilizing these NPs.

Given the success in the synthesis of PtNPs@COF with high stability and catalytic activity, we proceeded to use Thio- COF to grow Pd NPs to demonstrate the general applicability of such COF-templated NP synthesis strategy. Pd-based catalysts are widely used in many organic reactions. It is therefore of great significance to develop active and stable Pd catalysts. The PdNPs@COF was prepared following the similar procedure described for the synthesis of PtNPs@COF using NaBH₄ as the reducing agent. The typical TEM image shows that as-obtained Pd NPs immobilized in Thio-COF generally have highly fine dispersity and ultra-small size, except for several particles of relatively large size (Figure 4a). The statistic of these Pd NPs reveals that these NPs have an average size of 1.78 nm with a narrow size distribution (Figure 4b). The Pd content in the composite material is determined to be 26.30 wt% by the ICP analysis, which agrees well with the amount of Pd we applied (24.59 wt%). These observations suggest that Thio-COF is an excellent support for Pd NPs, uptaking nearly all the Pd species and facilitating the confinement and growth of Pd NPs. High-resolution TEM image (Figure 4c) confirms that the Pd NPs are in crystalline phase with a crystal plane spacing of 0.23 nm, which corresponds to the (111) plane of Pd NPs. Similar to the case of PtNPs@COF, the EDS elemental mapping reveals even element distribution and excellent dispersity of Pd NPs within Thio-COF (Figure 4d). The oxidation state of Pd species and the interaction between Pd and S were investigated by the XPS analysis (Figure S17 and S18), which shows the presence of both Pd(0) and Pd(II) and binding of Pd NPs with thioether

Table 1 Catalytic performance of PdNPs@COF in theSuzuki-Miyaura Coulpling reaction.

x⊸	+	- — В(ОН)2 —	0.1 mol% Pd Cat. 50 °C, DMF/H ₂ O	- <
	Entry	Aryl halides	Time (h)	Yield (%) b
	1 ^{<i>a</i>}		3	>99.0
	2 ^{<i>a</i>}	∕o-√_>−ı	3	>99.0
	3 ^{<i>a</i>}	`o-√−Br	3	82.9
	4 ^{<i>a</i>}	Br	3	85.7
	5 ^{<i>a</i>}	├ ──Br	3	96.8
	6 ^{<i>a</i>}	онсВг	3	>99.0
	7 ^c		3	30.6
	8 ^{<i>d</i>}		3	74.6

^{*a*} Reaction condition: arylhalide (1 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (1.5 mmol), **PdNPs@COF** (0.1 mol % Pd loading), DMF/H₂O (1.5 mL/1.5 mL), 50 °C. ^{*b*} The yield is based on the NMR integration. ^{*c*} Pd NPs (0.1 mol %). ^{*d*} Pd(PPh₃)₂Cl₂ (0.1 mol %). The TOF numbers of **PdNPs@COF**, commercial Pd/C, and Pd(PPh₃)₂Cl₂ are 30444 h⁻¹, 185 h⁻¹, and 1048 h⁻¹, respectively, under the same reaction condition, with 0.1 mol% catalyst loading.

groups. Careful examination of the XPS spectrum showed that the Pd(II) species are re-oxidized metal species (PdO), which have been commonly observed in nanoparticle that are exposed to air.^{44, 46-48}

The catalytic activity of **PdNPs@COF** was examined in one of the representative Pd-catalyzed reactions, the Suzuki-Miyaura coupling reaction. The reactions between different aryhalides and phenylboronic acid were performed under similar reaction conditions as previously reported for polymersupported Pd catalysts.⁴⁹ A mixture of arylhalide, phenylboronic acid, K₂CO₃, and PdNPs@COF in DMF/H₂O was heated with stirring, and the crude product was analyzed by ¹H NMR spectroscopy (Table 1). Excellent catalytic activity of PdNPs@COF was observed with only 0.1 mol% Pd loading under mild conditions (50 °C, 3 h) for various substrates, including aryl iodides (>99.0% yield, entry 1 and 2) and less active aryl bromides (82.9%-99.0%, entry 3-6).

For comparison purpose, we also tested Pd NPs synthesized without the COF support (the morphology of unsupported Pd NPs is shown in Figure S19b) and the commonly used Pd catalyst, Pd(PPh₃)₂Cl₂, as a catalyst in the coupling of 1-iodo-4-methylbenzene and phenylboronic acid under otherwise identical conditions. In great contrast to the coupling reaction (>99% yield) under the catalysis of **PdNPs@COF**, significantly
 Table 2 Reusability of PdNPs@COF in the Suzuki-Miyaura

 Coulpling reaction.^a

I-	- - - +	$B(OH)_2 = \frac{0.5 \text{ mol}\% \text{ F}}{50^{\circ}\text{C, C}}$	
	Entry	Time (h)	Yield (%) ^b
	1 st batch	3	>99.0
	2 nd batch	3	98.0
	3 rd batch	3	98.0
	4 th batch	3	99.0
	5 th batch	3	98.0

^{*a*} Reaction condition: arylhalide (1 mmol), phenylboronic acid (1.1 mmol), K₂CO₃ (1.5 mmol), **PdNPs@COF** (0.5 mol%), DMF/H₂O (1.5 mL/1.5 mL), 50 °C. ^{*b*} The yield is based on the ¹H NMR integration.

reduced yields, 30.6% and 74.6%, were observed when the unsupported Pd NPs and Pd(PPh_3)₂Cl₂ were used as the catalysts, respectively (entry 7-8). No conversion was observed in the presence of **Thio-COF** alone, indicating the COF material itself doesn't have any catalytic activity towards the Suzuki-Miyaura coupling reaction. The catalytic activity of **PdNPs@COF** under such mild conditions (50 °C, 3 h) and low loading (0.1 mol% Pd) surpasses many commonly used homogeneous Pd catalysts, e.g. $Pd(PPh_3)_2Cl_2$, as well as previously reported Pd-based heterogeneous catalysts, including Pd(OAc)₂ incorporated COF materials²⁴ and the Pd(II)-containing MOF materials.⁵⁰

PdNPs@COF also exhibits excellent stability and recyclability under the applied reaction conditions. The catalysts were conveniently recycled through centrifugation and washing with water and dichloromethane. The stability and reusability of PdNPs@COF were evaluated using 0.5 mol% catalyst in the reaction between 1-iodo-4methylbenzene and phenylboronic acid. After the first run, the catalyst was recycled and directly reused for the next run without any other reactivation process. The catalyst was recycled total five times, and almost complete retention of activity (≥98% yield) was observed over all five consecutive runs (Table 2), indicating the ultra-stable property of PdNPs@COF catalyst. The recycled catalyst after the 5th run was analyzed by the TEM (Figure S20). No obvious change in the size of Pd NPs and aggregation between NPs were observed. The excellent catalytic activity and stability of both PtNPs@COF and PdNPs@COF can be attributed to the following two factors: (1) the ultrafine, well-dispersed nature of these NPs is anticipated to significantly enhance their accessible active surface area, thus both Pd and Pt NPs can provide abundant catalytic sites; 2) well-defined cavities of Thio-COF materials can facilitate easy mass transfer. They can also provide protecting shell to maintain the good stability of those NPs.

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CONCLUSIONS

In conclusion, we have developed a novel COF-templated strategy for the size-controlled synthesis of stable and highly dispersed unltrafine metal NPs. The thioether-containing COF was rationally designed and synthesized for the confined growth of metal NPs. With the aid of the evenly distributed thioether groups in the ordered framework structure, ultrafine Pt or Pd nanoparticles $(1.7 \pm 0.2 \text{ nm})$ with a narrow size distribution were successfully obtained. The COF-supported ultrafine nanoparticles show excellent catalytic activities (low catalyst loading, mild reaction conditions, and high vielding) towards the reduction of nitrophenol and Suzuki-Miyaura coupling reaction. More importantly, these metal NP catalysts are highly stable and easily recycled and reused without loss of catalytic activity. The structure characterization of ultrafine metal NPs suggests that they likely reside in the pores of the COF structure, with only limited deposition on the surface. The crystalline COF structure with thioether groups in the well-defined cavity is critical for the successful synthesis of NPs with narrow size distribution, providing favorable accommodation sites for nanoparticles through metal-sulfur binding interactions, confined space for size-controlled growth of NPs, and also the protecting shell preventing the aggregation of NPs. This work will open a new frontier on design and preparation of highly stable metal NP@COF composite materials with well-dispersed NPs of narrow size distribution. Further diversifying various COF structures and different nanomaterials would provide great opportunities to prepare functional composite nanomaterials for different potential applications.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures, FT-IR spectra, solid-state ¹³C CP-MAS NMR spectrum, Gas adsorption data, TGA graph, SEM and TEM images, XPS analysis, control experiments and structural simulation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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