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## ARTICLE

# In situ one-step synthesis of metal-organic frameworks encapsulated naked Pt nanoparticles without additional reductants

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The encapsulation of metal nanoparticles (MNPs) into metal-organic frameworks has generated recent research because of the promising novel physical and chemical properties originating from synergetic interactions between MNPs and MOFs. However, the development of a facile one-step approach for the incorporation of tiny MNPs within MOFs without additional stabilizing agents and reductants remains a great challenge. Herein, we report a new and general synthesis strategy for MNPs@MOFs that allows preferential self-assembly of MOFs around the in-situ formed MNPs surface by directly mixing both the reactive metal (e.g.,  $\text{H}_2\text{PtCl}_6$ ) and MOFs precursors in DMF. This in situ one-step assembly approach is applicable to various MOFs, affording well-defined Pt@MOFs composites with highly dispersed naked Pt NPs in narrow diameter distribution. The resulting Pt@MOFs nanocomposites exhibit excellent stability, significantly enhanced catalytic activity and selectivity as compared to the commercial Pt/C in liquid-phase aerobic oxidation of alcohols.

## Introduction

Metal-organic frameworks (MOFs) are an emerging class of porous materials assembled by metal ions and organic ligands.<sup>1</sup> Owing to their fascinating features including diverse chemical compositions, large surface areas, and well-defined pore structures, MOFs have been demonstrated to be very promising for a wide range of applications such as gas storage/separation,<sup>2</sup> drug delivery,<sup>3</sup> sensing,<sup>4</sup> and heterogeneous catalysis.<sup>5</sup> Particularly in the field of catalysis, MOFs as unique host matrices can offer a platform for incorporating metal nanoparticles (MNPs), generating MOFs-based MNPs composites with novel chemical and physical properties.<sup>6</sup>

Consequently, considerable efforts have been devoted to the preparations of MNPs@MOFs composites. These synthetic methods generally comprise two or even multi-steps, which are normally based on reduction of a metal precursor doped in already-formed MOFs<sup>7</sup> or construction of MOFs around the pre-stabilized MNPs.<sup>8</sup> The former approach could obtain small and naked MNPs or clusters, but it possesses inherent limitations such as aggregation of MNPs on the external surface, poor control over the size of MNPs, and potential damages to the MOF structures during the post-reduction process. Thus, the latter is recently gaining increasing attention because this method can avoid the intrinsic problems of the former one. Nevertheless, in order to prevent MNPs aggregation and induce

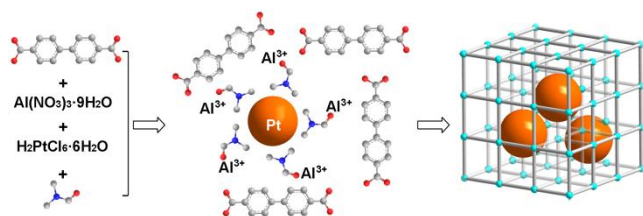
anisotropic growth of MOFs preferentially on the MNPs surface, this approach often requires certain protective agents such as surfactants, capping agents, or even ions for the stabilization of pre-synthesized MNPs. These stabilizing agents are difficult to be fully removed, which may have a negative effect on the catalytic performance of MNPs for most catalysis application.<sup>8a,9</sup> Therefore, it is highly desirable to develop a facile one-step strategy to prepare MOFs encapsulated naked MNPs in the absence of any stabilizing agents.

*N,N*-Dimethylformamide (DMF) is well-known as a uniquely versatile solvent, mainly due to its wide liquid temperature range, good chemical and thermal stability as well as wide solubility range for both organic and inorganic compounds.<sup>10</sup> Owing to these advantages, DMF has been widely employed as solvent in the synthesis of various MOFs,<sup>11</sup> and these reactions are generally performed in the temperature range of 100 °C to 150 °C. On the other hand, it has been demonstrated that DMF may also serve as a reducing agent under suitable conditions for the fabrication of metal nanoparticles with uniform shape and size.<sup>10a,12</sup> Considering that DMF is able to act as a mild reducing agent at high temperature, we proposed the possibility of preferential self-assembly of MOFs around the in-situ formed MNPs surface in one step, when both the reactive metal (e.g.,  $\text{H}_2\text{PtCl}_6$ ) and MOFs precursors are mixed in DMF directly. This achievement in the heterogeneous nucleation and growth of MOFs on MNPs takes advantage of the well-established

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hard-soft acid-base (HSAB) principle.<sup>13</sup> During the preparation process, the C-N group in DMF might preferentially adsorb on the generated MNPs surface while the C=O group of DMF would have an interaction with the hard oxophilic metal cation (e.g., Al<sup>3+</sup> and Zr<sup>4+</sup>) for MOFs.

Herein, we report, for the first time, a facile one-step approach for the incorporation of tiny Pt NPs within MOFs without the assistance of any additional stabilizing agents and reductants (Figure 1). Interestingly, the proposed methodology can be successfully applied to the MOFs constructed by aryl carboxylic ligands, which are known as the largest branch of the MOF family, even without any protecting groups (such as -NH<sub>2</sub>, and pyridyl) on the ligands for MNPs. This in situ one-step assembly strategy could afford well-defined Pt@MOFs composites with highly dispersed bare Pt NPs with narrow diameter distribution. The as-prepared Pt@MOFs exhibited extraordinary catalytic efficiency in liquid-phase aerobic oxidation of alcohols under mild base-free conditions.



**Figure 1.** Illustration of in situ one-step synthesis of Pt@DUT-5. Color coding: gray, C; red, O; blue, N; orange, Pt clusters or NPs; cyan, Al-based SBU. H atoms are omitted for clarity.

## Experimental Section

### Catalyst preparation

All chemical reagents were purchased from commercial sources and used without further purification.

**Synthesis of Pt@DUT-5.** In a typical synthesis, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.47 mmol), 4,4'-biphenyldicarboxylic acid (0.36 mmol), and the required amount of H<sub>2</sub>PtCl<sub>6</sub> was dissolved in DMF (10 mL) in a 25 mL tube. The mixture was subjected to ultrasounds (180 Watt) for 0.5 h, and then heated at 130 °C for 24 h. After the slurry was cooled to room temperature, the solid was isolated by centrifugation, washed with DMF and chloroform. Subsequently, the sample was dried under vacuum at 100 °C overnight to remove the solvents. Pt@DUT-5 composites with different Pt loadings could be obtained by altering the amount of Pt precursor added in the solution.

**Synthesis of Pt@UiO-66.** ZrCl<sub>4</sub> (0.343 mmol), 30 equivalents of acetic acid, and benzene-1,4-dicarboxylic acid (0.343 mmol) were dispersed in DMF (20 mL) under ultrasound for 5 min. Subsequently, the required amount of H<sub>2</sub>PtCl<sub>6</sub> was added into the above mixture and subjected to ultrasounds (180 Watt) for an additional 0.5 h, and then heated at 120 °C for 24 h. The resulting powder was filtered and washed with DMF and

ethanol. Finally, the solid was dried under vacuum at 150 °C overnight.

**Synthesis of Pt@MOF-253.** AlCl<sub>3</sub>·6H<sub>2</sub>O (0.625 mmol), 2,2'-bipyridine-5,5'-dicarboxylic acid (0.625 mmol), and the required amount of H<sub>2</sub>PtCl<sub>6</sub> was dispersed in DMF (10 mL) in a 25 mL tube. The mixture was subjected to ultrasounds (180 Watt) for 0.5 h, and then heated at 130 °C for 24 h. The resulting powder was filtered and washed with DMF. The solid was washed with methanol via soxhlet extraction for 24 h, and then was collected by filtration and finally dried at 120 °C under vacuum for 12 h.

**Synthesis of Pt/DUT-5.** DUT-5 supported platinum was prepared by using a colloidal deposition method.<sup>7g</sup> The required amount of PVP (PVP monomer/Pt = 10:1, molar ratio) was added to an appropriate volume of H<sub>2</sub>PtCl<sub>6</sub> methanol solution (1×10<sup>-3</sup> M). The mixture was stirred for 1 h at 0 °C. Then, a freshly prepared methanol solution of NaBH<sub>4</sub> (0.1 M, NaBH<sub>4</sub>/Pt = 5:1, molar ratio) was rapidly added to the mixture under vigorous stirring. Subsequently, the activated DUT-5 was immediately added and the solution was further stirred for 8 h. Finally, the powder was washed thoroughly with methanol, dried under vacuum at 100 °C for 2 h to obtain the Pt/DUT-5.

### Catalyst characterization

Powder X-ray diffraction patterns of the samples were obtained on a Rigaku diffractometer (D/MAX-III A, 3 kW) using Cu K $\alpha$  radiation (40 kV, 30 mA, 0.1543 nm).

The nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 instrument. Before the analysis, the samples were evacuated at 120 °C for 12 h. The metal contents of the samples were determined quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD system with a base pressure of 10<sup>-9</sup> Torr. Binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. The UV-visible spectra were carried out using a Shimadzu UV-2450 spectrophotometer (Shimadzu, Japan). All spectra were background-corrected using a spectrum obtained from DMF.

The size and morphology of the samples were investigated by using a transmission electron microscope (TEM, JEOL, JEM-2010HR) with EDX analysis (Oxford INCA EDS) operated at 200 kV. Samples were suspended in ethanol and deposited straight away on a copper grid prior to analysis.

### Catalytic reactions

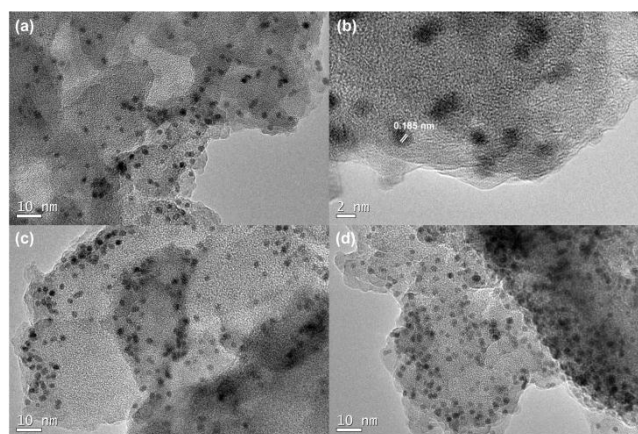
**Liquid-phase aerobic oxidation of alcohols.** Typically, alcohol (1 mmol) and catalyst (1 mol% Pt) were added to 10 mL of toluene. The reaction mixture was stirred at 80 °C under 1 atm of O<sub>2</sub>. Upon reaction completion, the catalyst particles were removed from the solution by filtration. The liquid phase was subsequently analyzed by GC/MS (Agilent 7890B/5977A equipped with a 0.25 mm × 30 m DB-WAX capillary column).

**Recycling of the Pt@DUT-5 catalyst.** For the recyclability tests, the reactions were performed under the same reaction conditions as described above, except using the recovered catalyst. Each time, the catalyst was separated from the reaction mixture by centrifugation at the end of catalytic reaction, thoroughly washed with toluene, and then heated at 150 °C under vacuum for the next run.

### Results and discussion

In this work, DUT-5 (Al(OH)(bpdc), bpdc = 4,4'-biphenyldicarboxylate),<sup>11c</sup> an aluminium based MOF with a large surface area and good chemical resistance, was first selected as an example for the incorporation of highly dispersed Pt NPs. Obviously different from previous two-step methods involving pre-synthesized MNPs stabilized by capping agents that were then used as seeds to induce the nucleation of MOF crystals, this one-step strategy was achieved by directly mixing the precursors of Pt (i.e., H<sub>2</sub>PtCl<sub>6</sub>) and MOFs (i.e., Al(NO<sub>3</sub>)<sub>3</sub> and 4,4'-biphenyldicarboxylic acid) in DMF without any additional protective agents and reductants.

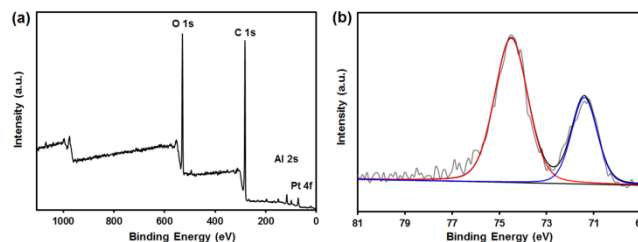
By varying the amount of H<sub>2</sub>PtCl<sub>6</sub> added, the content of Pt doped on DUT-5 could be adjusted effectively. Accordingly, a series of Pt@DUT-5 with Pt loadings in the range of 0.5 to 1.5 wt% were obtained. As revealed by powder X-ray diffraction (XRD) patterns (Figure S1 in the Supporting Information, SI), the characteristic diffraction peaks of Pt@DUT-5 matched well with the parent DUT-5, indicating that the incorporation of Pt did not affect the MOF formation. The absence of Pt diffraction peaks could presumably be associated with the low Pt concentration and the small particle size. This was further confirmed by the TEM images (Figure 2). The representative TEM micrographs showed that the materials had mostly a monomodal distribution of Pt NPs, with particle sizes typically between 1.5 and 2.0 nm (Figure S2 in the SI). In any case, the observed nanoparticles were homogeneously dispersed in the samples and no significant formation of aggregates was observed regardless of the Pt content. This could be related to the mild reducibility and stabilizing metal capability of DMF. The high-resolution TEM images of 0.5 wt% Pt@DUT-5 (Figure 2b) showed that the inter planar spacing of the particle lattice was 0.185 nm, in good agreement with the spacing of (200) planes of fcc Pt.



**Figure 2.** TEM images of Pt@DUT-5 with Pt loading of 0.5 wt% (a, b), 0.8 wt% (c), and 1.5 wt% (d), respectively.

The specific surface areas and porosities of the samples were determined by N<sub>2</sub> physisorption (Figure S3). All the Pt@DUT-5 samples displayed similar type I isotherms, suggesting a microporous structure. Compared with the parent DUT-5, the surface areas of Pt@DUT-5 were slightly decreased as expected, due to the contributions of non-porous Pt NPs to the masses of the composites. Considering the fact that the introduced Pt NPs (1.5–2.0 nm for Pt@DUT-5) were obviously larger than the cavity size (ca. 7 Å) of the MOF, it is plausible that the Pt NPs were encapsulated in the networks of DUT-5 instead of in the cavities.

In order to further investigate the surface compositions and chemical states of Pt, we performed X-ray photoelectron spectroscopy (XPS) analysis on 0.8 wt% Pt@DUT-5. As displayed in Figure 3, the Pt 4f, C 1s, O 1s, and Al 2s were observed from the complete spectral survey of Pt@DUT-5. The binding energies of the Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> peaks were 70.9 and 74.5 eV respectively, typical of the metallic Pt, suggesting that the Pt species was mostly in reduction state on the Pt@DUT-5.



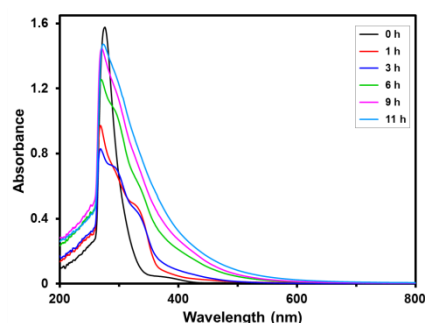
**Figure 3.** XPS spectra of Pt@DUT-5 with Pt loading of 0.8 wt%: (a) survey spectra of Pt@DUT-5; and (b) Pt 4f.

To better understand the formation process of Pt NPs in DMF, UV-vis spectrometer was employed to gain insights into the interactions of metal ions with DMF as well as the time evolution. The H<sub>2</sub>PtCl<sub>6</sub>/DMF solution was heated at 130 °C for different times and the UV-vis absorbance was recorded. As illustrated in Figure 4, the as-prepared H<sub>2</sub>PtCl<sub>6</sub>/DMF solution (0 min) showed no appreciable absorption from visible to ultraviolet region except for a sharp absorbance maximum at



275 nm due to the  $[\text{PtCl}_6]^{2-}$  ions. During the time range of 0–6 h, two new shoulder peaks at approximate 300 and 340 nm appeared, while the strong peak at 275 nm also changed in intensity and symmetry, which may be assigned to ligand-to-metal electron-transition  $n \rightarrow d^*$  from N to Pt cations in mono- and multinuclear Pt(II) complexes stabilized by DMF. This was consistent with the previous reports that  $(\text{Pt}^{\delta+})_n$  cluster has characteristic absorption bands at around 290–300 nm and 347–375 nm.<sup>14</sup> Meanwhile, the absorbance in visible region continued to increase gradually with time, which suggested the partial formation of metal nanoparticles due to the reducing ability of DMF.<sup>15</sup> It should be mentioned that the Pt(II) complexes were obtained through the reduction of  $\text{Pt}^{4+}$  to  $\text{Pt}^{2+}$  by DMF, which was a fast process compared with the further reduction of  $\text{Pt}^{2+}$  to  $\text{Pt}^0$ . As expected, increasing the mixing time to 9 h, the two shoulder peaks at approximate 300 and 340 nm almost completely decayed. Moreover, hardly any increase in absorption intensity of the region between 400 and 600 nm was observed at a longer time of 11 h, indicating the complete generation of metallic Pt species.

The selective oxidation of alcohols to corresponding aldehydes or ketones is a fundamentally important transformation in both laboratory and industrial syntheses.<sup>16</sup> Accordingly, a remarkable number of supported transition-metal catalysts have been explored in this regard.<sup>17</sup> Although some catalysts have been shown to be effective for the aerobic oxidation reactions, a large excess of base additives or expensive oxidizing agents have been usually used in conjunction with harsh reaction conditions. Thus, the development of highly active and selective catalysts which exhibit a wide range of substrates tolerance under mild and base-free conditions is still highly desirable.



**Figure 4.** Time-resolved UV-Vis absorbance spectra of  $\text{H}_2\text{PtCl}_6$  in DMF solution at 130 °C.

The benefit of MOFs encapsulated naked Pt NPs was first demonstrated by carrying out the liquid-phase aerobic oxidation of cinnamyl alcohol under base-free conditions. As shown in Table 1, the use of the pristine DUT-5 gave essentially no conversion in this reaction system (Table 1, entry 1). The incorporation of Pt nanoparticles significantly promoted the reaction (Table 1, entries 2–4). Results of the aerobic oxidation pointed to an optimized performance of 0.5% Pt@DUT-5 (Table 1, entry 3), which provided a complete conversion of

cinnamyl alcohol to cinnamyl aldehyde within 15 h at 80 °C. It is worth noting that all the Pt@DUT-5 displayed >99% selectivity to cinnamyl aldehyde, leaving the C=C bond untouched, even at a complete conversion of the starting material. For comparison, we also prepared Pt nanoparticles supported on DUT-5 by a previously reported colloidal deposition method with PVP as protecting agent.<sup>7g</sup> Only 38% conversion of cinnamyl alcohol was obtained over the Pt/DUT-5 under the same reaction conditions (Table 1, entry 5). As expected, the catalytic activity of Pt/DUT-5 could be enhanced by thermal treatment at a high temperature (Table S1 in the SI), possibly due to the movement or partial decomposition of PVP molecules from the Pt surface.<sup>18</sup>

**Table 1.** Results of the oxidation of cinnamyl alcohol.<sup>a</sup>

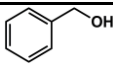
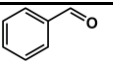
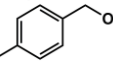
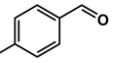
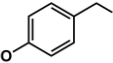
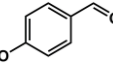
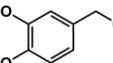
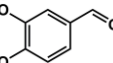
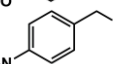
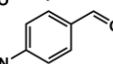
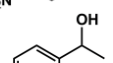
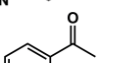
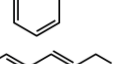
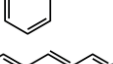
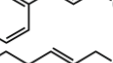
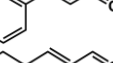
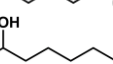
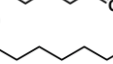
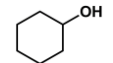
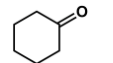
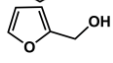
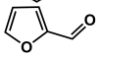
Entry	Catalyst	Conversion (%)	Selectivity (%)
1	DUT-5	—	—
2	0.5 % Pt@DUT-5	>99	>99
3	0.8 % Pt@DUT-5	91	>99
4	1.5 % Pt@DUT-5	75	>99
5	0.5 % Pt/DUT-5	38	>99
6	1.0 % Pt/C	18	86
7 <sup>b</sup>	Reused 0.5 % Pt@DUT-5	>99	>99

<sup>a</sup> Reaction conditions: cinnamyl alcohol (1 mmol), catalyst (Pt 1 mol%), toluene (10 mL), 80 °C, 15 h, 1 atm  $\text{O}_2$ . <sup>b</sup> Result of the sixth use.

Commercial Pt/C has been widely demonstrated as superior catalyst for a series of oxidation reactions.<sup>19</sup> In this study, a commercial 1% Pt/C (Alfa Aesar) catalyst was also tested in the oxidation of cinnamyl alcohol under identical reaction conditions for comparative purpose. The observed conversion of cinnamyl alcohol for Pt/C was remarkably inferior (below 20%) as compared to the Pt@DUT-5 material (Table 1, entry 6).

The scope of the present catalyst system was subsequently extended to the aerobic oxidation of a series of alcohols under base-free conditions using the 0.5 wt% Pt@DUT-5 catalyst. The results summarized in Table 2 proved that the catalyst was highly active and extremely selective for the oxidation of all the substrates studied, indicating a high versatility of the MOF encapsulated Pt catalyst. Benzyl alcohols, either primary or secondary, were smoothly converted to the corresponding benzyl aldehydes or ketones in quantitative yields (Table 2, entries 1–6). The presence of substituents on the aromatic ring such as  $-\text{CH}_3$ ,  $-\text{OCH}_3$  or  $-\text{NO}_2$  influenced the reaction rate, but did not affect the selectivity of the process. Benzyl alcohols substituted with electron-donating groups such as  $-\text{CH}_3$ ,  $-\text{OCH}_3$  (Table 2, entries 2 and 3) were more easily oxidized than those containing electron-withdrawing groups (entry 5). In the case of  $\alpha$ ,  $\beta$ -unsaturated alcohols, the presence of an allylic C=C double

**Table 2.** Aerobic oxidation of various alcohols catalyzed by 0.5 wt% Pt@DUT-5.<sup>a</sup>

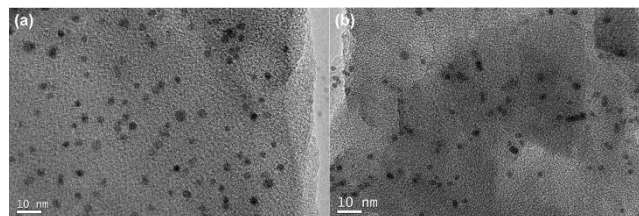
Entry	Substrate	Product	Time (h)	Yield (%)
1			20	>99
2			15	>99
3			15	>99
4			24	>99
5			40	>99
6			20	>99
7			15	>99
8			25	>99
9 <sup>b</sup>			30	93
10 <sup>b</sup>			40	96
11 <sup>b</sup>			35	96

<sup>a</sup> Reaction conditions: alcohol (1 mmol), catalyst (Pt 1 mol%), toluene (10 mL), 80 °C, 1 atm O<sub>2</sub>. <sup>b</sup> 2 mol% Pt, 100 °C.

bond did not affect the catalytic efficiency of Pt@DUT-5 significantly (Table 2, entries 7 and 8). Moreover, the corresponding unsaturated aldehydes were successfully obtained without observing intermolecular hydrogen transfer, epoxidation, or polymerization of the C=C bond. Aliphatic alcohols have been reported to be more reluctant to undergo oxidation, presumably due to the stronger C<sub>α</sub>-H bond strength compared with those in benzyl and allylic alcohols.<sup>17c</sup> The Pt@DUT-5 was also capable of catalyzing the oxidation of these alcohols, furnishing the corresponding ketones in 93-96% yields, although a higher Pt quantity (2 mol% Pt) and temperature (100 °C) were required (entries 9 and 10). Furthermore, heterocyclic alcohols could also be smoothly oxidized to the corresponding aldehydes in excellent yields (entry 11).

The reusability of Pt@DUT-5 was demonstrated from the recycling experiments of cinnamyl alcohol oxidation that showed no appreciable reduction of reactivity even after six runs (Table 1, entry 7). PXRD patterns for the reused catalyst suggested that the MOF structure was completely preserved after reactions (Figure S1 in the SI). Furthermore, the metal dispersion and chemical composition were very similar to that of the fresh catalyst based on N<sub>2</sub> adsorption, TEM, and AAS measurements (Figures S3 and S4). These results indicated that the Pt@DUT-5 was highly stable under the investigated conditions. The excellent stability and recyclability are believed

to be related to the role of the MOF framework on preventing the encapsulated platinum NPs from aggregation during the reaction.

**Figure 5.** TEM images of Pt@UiO-66 (a) and Pt@MOF-253 (b).

Finally, in order to demonstrate the general applicability of the proposed methodology, we attempted to extend this approach to other types of MOF matrices, e.g., UiO-66, and MOF-253. UiO-66 (Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BDC)<sub>12</sub>, BDC = terephthalate)<sup>11a</sup> is another representative carboxylate-based MOF without any potential protecting groups. MOF-253 (Al(OH)(bpydc), bpydc = 2,2'-bipyridine-5,5'-dicarboxylate),<sup>11b</sup> features open 2,2'-bipyridine moieties, possessing the abilities as stabilizing agent for incorporation of metal NPs. Interestingly, regardless of the different structures of the MOFs, it was evident that Pt NPs with tiny and uniform size were all successfully encapsulated in the two MOFs (Figure 5). Furthermore, the Pt@UiO-66 and Pt@MOF-253 also exhibited excellent catalytic activities in the aerobic oxidation of cinnamyl alcohol under base-free conditions (Table S1 in the SI). It should be noted that the Pt@MOF-253 exhibited a slightly higher activity as compared to the Pt@UiO-66 and Pt@DUT-5, which might be attributed to the promoting effects of the alkalic 2,2'-bipyridine moieties in the MOF-253 host.

## Conclusions

In conclusion, we have demonstrated a general and effective one-step strategy to encapsulate tiny MNPs in various kinds of MOFs without any additional protecting agents and reducing agents. The key to successful formation of such nanocomposites is closely correlative with the use of DMF as solvent, which serves as both mild reductant for metal ions and stabilizer during the formation of Pt NPs. Moreover, DMF is also capable of adsorbing hard metal cations (i.e., the metal precursors for MOFs) during the MOFs formation, affording preferential self-assembly of MOFs around the in-situ formed Pt NPs. The resultant Pt@MOFs materials are stable, readily reusable, and exhibit high catalytic activity in liquid-phase aerobic oxidation of a variety of alcohols under mild and base-free conditions. The in situ one-step strategy adopted in this work is envisioned to open up a new avenue for fabricating 'unprotected' MNPs within MOFs with excellent catalytic properties.

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## Notes and references

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Electronic Supplementary Information (ESI) available: [XRD data; particle size distribution histograms; N<sub>2</sub> physisorption; TEM images; and additional oxidation reaction results.]. See DOI: 10.1039/b000000x/

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## Graphical Abstract

A general and effective one-step strategy is developed to encapsulate tiny metal nanoparticles in various kinds of MOFs without any additional protecting agents and reducing agents.

