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Ultrafine Gold Clusters Incorporated into a Metal–Organic Framework

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The preparation of small Au nanoparticles (NPs) is scientifically important and has attracted increased attention. Gold clusters smaller than 2 nm in diameter and less than 300 atoms appear to be critical because of dramatic changes in catalytic and physicochemical properties.[1] However, controlling the size of Au clusters is very difficult because aggregation readily occurs due to high cohesive energy and low melting points.[1b] Currently, most synthetic methods for Au clusters are based on protection by surfactants,[2] immobilization through the strong junction between gold and support, or confinement of small Au NPs/clusters in nanopores of mesoporous materials and zeolite supports.[3] Meanwhile, metal–organic frameworks (MOFs) are becoming a focus of great interest owing to intriguing structural topologies and potential applications as functional materials.[4,5] Similar to zeolites, the structures of MOFs are usually microporous. In addition, there are advantages in the easily tunable sizes, shapes, and surrounding environments of the pores in MOFs; these endow MOFs with broader properties and applications. Therefore, it is reasonable to apply porous MOFs as supports and/or hard templates for preparation of small Au NPs. The porous structures in MOFs are expected to limit the migration and aggregation of Au NPs. However, to date, all reported Au NPs are larger than 1.5 nm because of the poor understanding of the ruling factors of the size of Au particles.[6] Herein, we report the preparation of the first 3D fluorous MOF with an unprecedented hexagonal (4,8)-connected topology. By employing the predesigned MOF as a novel host, we have successfully incorporated ultrafine Au_2 and Au_3 clusters into the porous structures by a facile "solid-grinding" method. To the best of our knowledge, this is the first report of stabilizing ultrafine Au clusters, of this size, by a surfactant-free method.

The solvothermal reaction of $Cd(NO_3)_2\cdot 6H_2O$ with a fluorous multicarboxylic acid ligand, 4,4′-(hexafluoroisopropylidene)diphthalate (L), in $EtOH/H_2O$ yielded $[Cd_2(L)(H_2O)]\cdot 0.5H_2O$ (**1**). The asymmetric unit of **1** contains two crystallographically unique cadmium(II) ions and one independent L. The interconnection of Cd^{II} by eight carboxylic groups from four L in bridging and chelating modes (denoted as L_{bri} and L_{che}, respectively) leads to a planar tetranuclear Cd cluster, and the other four L are further attached to the Cd_4 clusters by bridging oxygen atoms (Figure 1 a). Each ligand also connects four Cd_4 clusters (Figure 1 b). The interconnection of the Cd_4 clusters through L results in a complicated 3D network with two types of channels along the *c* axis (Figure 1 c). The larger hexagonal channel with a diameter of 7.830(1) Å is composed of six Cd(1) atoms and six L, in which the diagonal distance between the Cd(1) atoms is 21.167(2) Å and the fluorine atoms are located inside the channel. The smaller type of channel with dimensions of $6.285(1)\times 6.285(1)$ Å^2 is formed by three Cd(2) atoms and three L, in which the distances between the Cd(2) atom and the opposite C(9) atom are 12.635(2) or 13.171(1) Å, respectively. The discrete and coordinated aqua molecules are located in the small channels (see the Supporting Information).

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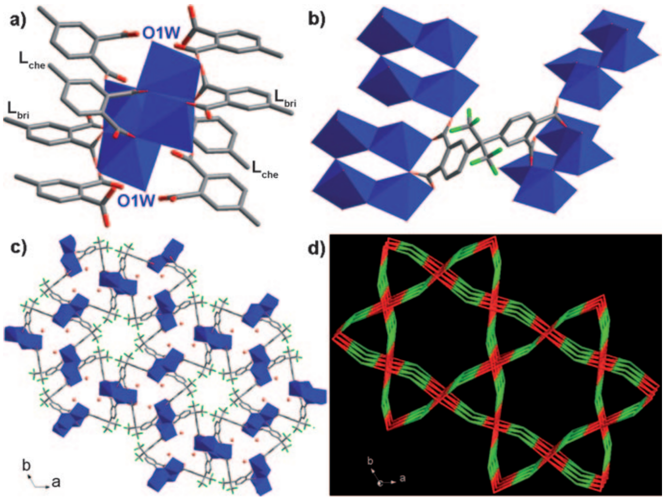

Figure 1. View of the coordination environments of **1**: a) the Cd_4 cluster connected by eight L and b) L connected by four metal clusters. c, d) View and topological view of the 3D network of **1** (blue Cd, red O, green F, gray C).

Topological analysis presents a better insight into the nature of the involved framework. As described above, the Cd_4 cluster and L can be regarded as eight- and four-connected building units, thus the whole network can be extended to an unusual 3D (4,8)-connected net with the Schläfli symbol $(4^{16}{\cdot}6^{12})(4^4{\cdot}6^2)_2$ (Figure 1 d and the Supporting Information).[7] So far, many uninodal and low binodal network topologies have been reported,[8] whereas coordination networks with locally high or mixed-high connectivities are still rare.[9] It is very difficult to obtain (4,8)-connected frameworks and the limited reports are all concerned with fluorite analogues.[10] To the best of our knowledge, compound **1** represents the first hexagonal (4,8)-connected network.

Thermal gravimetric analysis (TGA) shows that **1** evacuates isolated and coordinated water molecules up to around 150 °C (exptl 3.9 %; calcd 3.7 %). The framework remains crystalline upon desolvation at 255 °C over 2 h and is stable to around 300 °C in a He stream. The permanent porosity of **1** is confirmed by N_2 adsorption at 77 K. After activation at 250 °C, compound **1** exhibits a BET surface area of $170.4\,m^2g^{-1}$. The effective free volume is 23.4 % by PLATON calculations.[11]

The pursuit of applications of MOFs prompted us to employ obtained **1** as a host/template for preparing small Au NPs. Desolvated **1** and 1 wt % Au of a slightly volatile organogold complex with a vapor pressure of 1.1 Pa at room temperature, $[Au(acac)(CH_3)_2]$ (acac = acetylacetonate), were ground uniformly for approximately 30 min in an agate mortar at room temperature, followed by reduction in a stream of 10 vol % H_2 in He at around 170 °C for 2 h to yield **1** loaded with 1 wt % Au, denoted here as Au-**1**. No diffractions from Au species were detected for Au-**1** by powder XRD, suggesting that the Au loading was too low and/or Au NPs were too small. The latter was proven by further TEM observations. Unexpectedly, compound **1** shows unusual electron-beam stability with observable fringes (Figure 2 b),[5e] whereas the Au clusters in Au-**1** cannot be observed by TEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Figure 2 and the Supporting Information). No Au clusters larger than 1 nm could be found even after storage of the sample in air for six months (see the Supporting Information). We believe that the Au clusters are well embedded into the crystalline porous structures in **1** and the migration and/or aggregation of Au clusters is prevented.[6] Accordingly, tiny particles remained even after reduction at a relatively high temperature (≈170 °C). Although the Au clusters were invisible, the energy dispersive X-ray spectroscopy (EDS) signals were unambiguous from either a whole image or a point analysis (see the Supporting Information); this strongly supports the existence of highly dispersed Au clusters. Moreover, an appreciable decrease in the specific surface area (BET, $74.6\,m^2g^{-1}$) of Au-**1** also supports the fact that cavities of the host framework are occupied/blocked by highly dispersed Au clusters. We assume that the hydrophobic fluoro-coated channels could embody the Au clusters based on the following considerations: 1) Fluorinated channels have been reported to exhibit remarkable enclathration ability and encapsulate guest molecules because fluorinated ligands favor “heterorecognition”, whereas poor enclathration abilities were confirmed for nonfluorinated counterparts, that is, nonfluorinated ligands prefer “self-recognition”.[12] 2) There are many CF_3 groups inside the large channels of **1**. Because of the hydrophobicity of these groups, the channel is bare, which could be favorable for the loading of Au clusters. In contrast, water or other solvent molecules, which could be barriers for loading metal NPs and result in aggregation of particles on the surface of MOFs, are commonly reported for hydrophilic channels in other MOFs. 3) N_2 adsorption and micropore size distribution analyses indicated that the larger fluoro-coated channels could be occupied after Au loading (see the Supporting Information).

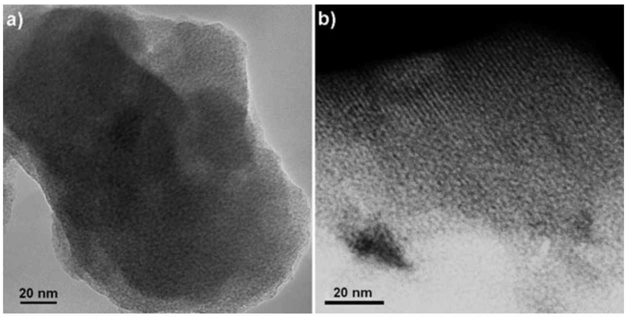

Figure 2. a) TEM and b) HAADF-STEM images for Au-**1**. No NPs can be identified in either of the images.

To precisely determine the size, coordination environment, and chemical form of the Au clusters, Au L_{III}-edge X-ray absorption near-edge structure (XANES) and extended

X-ray absorption fine structure (EXAFS) spectra for Au-**1** were measured. The data analyses revealed the presence of Au^0 and ultrafine Au clusters with the average atom number of 2.5 (Table 1 and the Supporting Information). The Au···Au distances are comparable to those in previously reported Au_2 and Au_3 clusters.[13] Moreover, in addition to Au–Au, Au–F or Au–O interactions could also exist in Au-**1**, as suggested by the Fourier transform magnitude of the EXAFS (FT-EXAFS) spectrum (Figure 3).

Table 1. EXAFS fit parameters for Au-**1** (k^3: k range is 2.5–12.5, and r range is 1.4–3.5). Intrinsic loss factor $S_0^2=0.895$ (Au–Au, from Au foil data), $S_0^2=1$ (Au–F or Au–O, fixed).

Shells	CN[a]	R [Å][b]	σ^2 [$Å^2$][c]	E^0 [eV][d]	R_{factor} [%][e]
Au–Au	1.5 ± 0.7	2.62 ± 0.02	0.0062	−5.63	1.01
Au–F	0.42 ± 0.21	2.04 ± 0.03	0.0014	4.37	
Au–Au	1.6 ± 0.7	2.62 ± 0.02	0.0066	−5.86	1.00
Au–O	0.48 ± 0.26	2.04 ± 0.03	0.0011	3.34	

[a] The first shell coordination number. [b] Bond length. [c] Debye–Waller factor. [d] E^0 parameter. [e] The goodness-of-fit index.

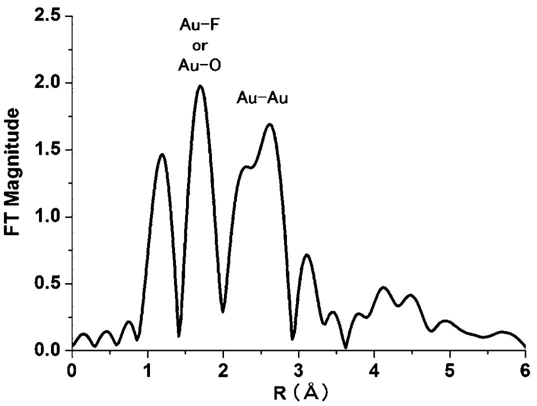

Figure 3. Au L_{III}-edge FT-EXAFS spectrum for Au-**1**. The signal at approximately 1.2 Å is due to an experimental artifact.

In summary, the first hexagonal (4,8)-connected MOF has been assembled and characterized. For the first time, we have succeeded in incorporating ultrafine Au clusters in the pores of a MOF. The existence of Au clusters was supported by EDS analyses, whereas they were too small to be observed by both TEM and HAADF-STEM. The ultrafine Au clusters with an average atom number of 2.5, corresponding to a mixture of Au_2 and Au_3 clusters, were demonstrated by further EXAFS investigations. The fluoro-coated channels are proposed to be helpful/responsible for the formation of these ultrafine Au clusters. We anticipate that the current method will be applicable for the preparation of other highly monodisperse clusters/NPs of inorganic materials, which could exhibit new properties and potential applications.

Experimental Section

Preparation of 1: $Cd(NO_3)_2\cdot 6H_2O$ (185 mg, 0.6 mmol) and L (133 mg, 0.3 mmol) in EtOH (5 mL) and distilled water (5 mL) were sealed in a Parr Teflon-lined autoclave (23 mL) and heated at 140 °C for 4 days to give colorless crystals of **1** (257 mg, based on Cd 59 %). IR (KBr): 3469 (b), 2360 (s), 2341 (s), 1544 (vs), 1418 (vs), 1388 (vs), 1248 (s), 1218 (s), 1188 (s), 1140 (m), 1087 (m), 991 (m), 964 (m), 915 (m), 842 (m), 797 (m), 728 (m), 668 (w), 597 (w), 496 cm^{-1} (w); elemental analysis calcd (%) for **1**: C 31.34, H 1.25; found: C 31.59, H 1.48.

Single-crystal X-ray crystallography: The crystal data were collected on an R-AXIS RAPID II diffractometer at room temperature with $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å).[14a] The structure was solved by direct methods with the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.[14b] Metal atoms were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses, which were refined with anisotropic thermal parameters on F^2. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The hydrogen atoms of the water molecules were located with the difference Fourier method and refined freely.

Crystallographic data for **1**: $Cd_4(C_{19}H_6F_6O_8)_2(H_2O)_2\cdot H_2O$; $M_r=1456.12$; hexagonal; $R\bar{3}$; $a=40.024(6)$, $b=40.024(6)$, $c=7.7200(15)$ Å; $V=10{,}710(3)$ $Å^3$; $Z=9$; $\rho_{calcd}=2.032$ $g\,cm^{-3}$; μ ($Mo_{K\alpha}$) = 1.883 mm^{-1}; $2\theta_{max}=54.91°$; 5388 reflections measured ($R_{int}=0.0874$); $R_1=0.0687$ and $wR_2=0.0937$ (all data); GOF = 1.069. CCDC-725964 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: cluster compounds · gold · metal–organic frameworks · microporous materials · topochemistry

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