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A room-temperature growth of gold nanoparticles on MOF-199 and its transformation into the $[Cu_2(OH)(BTC)(H_2O)]_n$ phase

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ABSTRACT

We report a two-step room temperature protocol for functionalization of copper-based metal–organic framework MOF-199, also known as HKUST-1, with gold nanoparticles. The resulted material is characterized with XRD, TEM, BET, UV–Vis and FTIR techniques building up a complete picture of its structural, electronic and vibrational properties. We also found, that the presence of gold induces a partial phase transformation of MOF under microwave heating, leading to formation of $[Cu_2(OH)(BTC)(H_2O)]_n$ material with one-dimensional channels.

1. Introduction

Metal–organic frameworks (MOFs) are new materials representing the next generation of porous materials characterized by a high surface area and huge variety of structures. Their crystal lattice can be described as periodical repetition of interconnected organic and inorganic units. Organic units act as linker binding the inorganic parts into a uniform framework. Inorganic cluster entities, called secondary building units (SBUs), are capable to coordinate polytopic linkers into an organized 3D network [1]. Such modular structures allow the synthesis of purpose-designed MOFs with a pore size varying from 0.1 to 10 nm [2], with a specific surface area up to 10 000 m^2/g [3] and with a huge topological variety [4–6]. These tunable properties ensured multiple applications [7–11], more precisely, MOFs are used for gas storage and separation [12–15], catalysis [16–22], biomedical targeting [23], sensing [24], luminescence [14,25–32], magnetic properties [33], and host–guest chemistry [34].

Together with MOF-5 [35], HKUST-1 (synthesized in the Hong Kong University of Science and Technology and successively also named MOF-199) [36], has been one of the very first MOFs showing a stable structure after desolvation. MOF-199, $[Cu_3(BTC)_2(H_2O)_3]_n$ (BTC = benzene-1,3,5-tricarboxylate), has a framework characterized by internal pores of ~14 Å [36,37] and exhibiting Cu^{2+} metal centers with a coordinative unsaturation [38] that can be used for molecular adsorption [39–41]. As a consequence of the interest generated by MOF-199 and its possible applications, its synthesis has already been commercialized on an industrial scale by BASF Corp. under the Basolite™ C300 name and by MOF Technologies™ under the MTA4 name. Indeed, this MOF has already been employed in a large number of consumer goods. The most evident examples comes from the field of gas capture and storage where MOF-199 has been used as: (i) an adsorbent in natural gas fuel tanks (allowing to increase their capacity by 30%, as was demonstrated during the EcoFuel Asia Tour across 14 countries in 2007), (ii) an additive to textile tissues improving their protective properties (capable to trap toxic gases such as hydrogen sulfide, ammonia and cyclohexane when introduced into protective liners of respirators), (iii) an adsorbent for the capture of toxic gases and unpleasant odors [42], already covered by patents [43,44].

The MOF-199 structure is shown in Fig. 1a, Fig. S1a,b. Each SBU contains two Cu^{2+} ions, each being surrounded by six neighboring atoms: four of them (in the equatorial plane) are bridging oxygens from carboxylate groups of the BTC linker, other two (in the axial plane) are the neighboring copper ion and the oxygen from an adsorbed water molecule. The axial water molecules can be removed by activation (heating under reduced pressure), thus, forming the coordinative vacancies, whose presence determines the catalytic activity of MOF [38]. MOF-199 has a structural isomer, $[Cu_2(OH)(BTC)(H_2O)]_n$ [45,46], whose structure is depicted in Fig. 1

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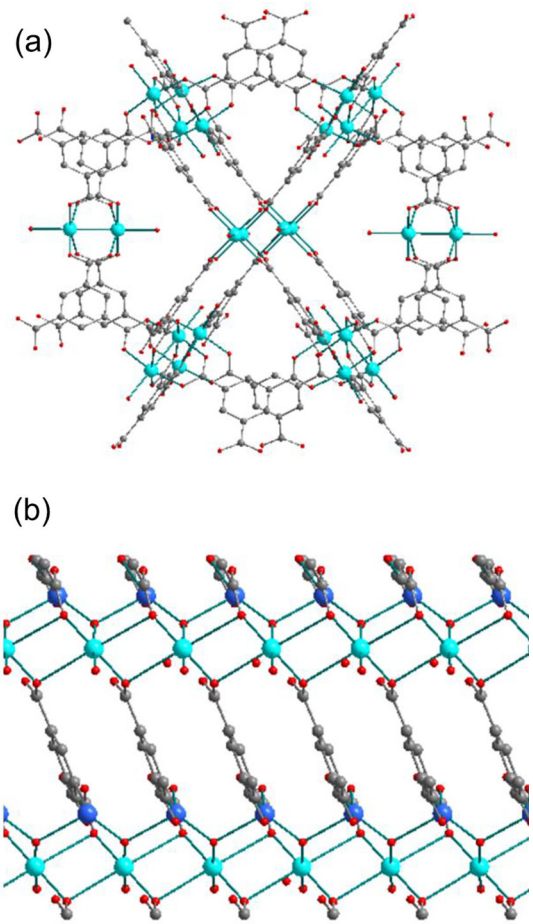

Fig. 1. Schematic illustration for MOF-199 (a) and $[Cu_2(OH)(BTC)(H_2O)]_n$ (b) structures, viewed along (0 0 1) and (0 1 0) directions, respectively. Color legend: cyan (blue) – Cu^{2+}, red – O, and gray – C. Hydrogens are not shown for simplicity. (Color online.)

b (and in Fig. S1cd). Its SBU consists of two independent four-coordinate and five-coordinate Cu^{2+} connected through BTC by μ_2-bonding and one μ_3-hydroxy group. The latter binds the adjacent molecular sheet to generate a 3D network with distinct 1D channels (ca. 5 × 7 Å). $[Cu_2(OH)(BTC)(H_2O)]_n$ is still much less studied in respect to MOF-199, although it is compositionally stable up to 280 °C, as shown in the TGA study of Chen et al. [46]. This is probably because it has been always obtained as a side product in the synthesis purposely designed for HKUST-1 [45,46]. Some representative examples of the synthetic methods used to obtain these two phases are listed in Table S1. The $[Cu_2(OH)(BTC)(H_2O)]_n$ phase is preferentially formed under a solvothermal or microwave- (MW)-assisted solvothermal process in water-containing medium at higher temperature than for MOF-199. The conversion of MOF-199 into $[Cu_2(OH)(BTC)(H_2O)]_n$ was observed to occur in the temperature range from 110 to 120 °C [45].

Periodical structure of MOFs makes them attractive candidates for synthesis of hybrid materials and encapsulation of active nanoparticles (NPs) [47–51] such as Cu [52,53], Ag [54,55], Ru [56], Pt [57–60], Pd [61–67] and Au [68–75]. There are some advantages in the encapsulation of metal NPs inside MOFs frameworks, among them, a higher control in the NPs dimension distribution (driven by the well-defined size of MOFs cavities), an enhancement of NPs stability and an inhibition of the aggregation phenomenon. In the same time, NPs remain accessible for volatile reagents due to high porosity of MOFs. During the last years, many synthesis techniques and application fields for hybrid materials combining MOFs and metal NPs were reported [47–75]. In particular, MOFs with gold NPs demonstrate catalytic activity in: oxidation of alcohols [68,69], oxidation of carbon monoxide [70], N-alkylation reaction [71], reduction of 4-nitrophenol [72] and electrocatalytic oxidation of hydrazine [73], while bimetallic PdAu NPs inside MIL-101(Fe) catalyze tandem reactions between amines and alcohols for efficient N-alkyl amines syntheses under visible light [75].

Basically, metal precursors can be delivered inside the MOF pores by different methods: MW irradiation [76], chemical vapor deposition or chemical vapor infiltration [77], solid grinding [68], encapsulation of pre-synthesized metal NPs [78,79] or by the use of functionalized, metal-containing, ligands and successive H_2-reduction [57,58,67,80–82]. Syntheses can follow either one-pot [80,83], or more time-consuming and difficult multi-pot [80,84,85] approaches. Moreover, in order to avoid aggregation of NPs and to promote crystallization of MOF on the surface of NPs some additional surfactants or capping agents are required.

As far as gold NPs are concerned, Au@MOF-199 can be synthesized by growing Au NPs inside the MOF-199 pores or by covering preformed Au NPs with MOF. Zhu et al. [86] succeeded in the preparation of Au/UiO-66 MOF via a two stages protocol: (i) Au^{3+}/UiO-66 MOF encapsulation of $NaAuCl_4$ Au^{3+} precursor using a double solvent (hexane-water) method; (ii) reduction of Au^{3+} via $NaBH_4$. This method was applied with success on UiO-66 [87] because of its very high stability to chemical agents [88], but we found that MOF-199 cannot resist the reduction step in $NaBH_4$ being decomposed into copper oxide (see Fig. S2). Consequently, we were forced to modify the procedure using the less aggressive reduction agent; $Na_3C_6H_5O_7$ (sodium citrate) allowed us to form Au NPs in MOF-199 at a room temperature.

In this study, we observed for the first time that the presence of gold NPs was found influential on further phase transformation of MOF-199 into $[Cu_2(OH)(BTC)(H_2O)]_n$ under a MW heating. Stimulated by this observation we decided to perform a systematic study to follow such phase transition along the MOF solvothermal synthesis, extracting portions of reaction mixture through a special valve into an ice-cooled beaker at different steps of the synthesis for phase analysis. The properties of resulted materials were probed by different structural and spectroscopic techniques, including Cu K-edge X-ray absorption near edge structure (XANES) spectroscopy.

2. Experimental details

2.1. Reagents and characterization methods

Reagents $NaAuCl_4$, $Na_3C_6H_5O_7$, $Cu(Ac)_2{\cdot}H_2O$ (copper acetate monohydrate), benzene-1,3,5-tricarboxylic acid ($C_9H_6O_6$ or trimesic acid) and hexane were purchased from Sigma-Aldrich. Basolite™ C300, a commercial analogue of MOF-199 (HKUST-1), was purchased from BASF Corp. Ultra-pure water (18 MΩ·cm) was produced by SimplicityUV (Millipore) system from distilled water.

Laboratory MW system Discovery SP (CEM) was employed for the synthesis. Powder X-ray diffraction (PXRD) were collected using D2 Phaser (Bruker) X-ray diffractometer with Cu Kα radiation. Diffuse reflectance (DR) UV–Vis spectra were collected on UV-2600 (Shimadzu) spectrophotometer with 2 nm step by using integrating sphere accessory; the spectra were obtained using powdered $BaSO_4$ as blank. The measured %R values were converted into absorbance. Transmission electron microscopy (TEM) was performed on FEI Tecnai G2 Spirit TWIN transmission electron microscope operated at an accelerating voltage of 80 kV. Particle size distribution histogram was build based on graphical analysis of 150 NPs in ImageJ software. Ultra-high-resolution Scanning