OPEN

SUBJECT AREAS:

CATALYSIS

INORGANIC CHEMISTRY

Received
4 December 2013Accepted
13 January 2014Published
29 January 2014Correspondence and
requests for materials
should be addressed to
J.Z. (zhj@fjirsm.ac.cn)

Zeolitic BIF Crystal Directly Producing Noble-Metal Nanoparticles in Its Pores for Catalysis

Hai-Xia Zhang¹, Meng Liu¹, Xianhui Bu² & Jian Zhang¹¹State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China, ²Department of Chemistry and Biochemistry, California State University, Long Beach, 1250 Bellflower Boulevard, Long Beach, CA 90840, USA.

As an integral part of a porous framework and uniformly distributed throughout the internal pore space, the high density of the exposed B–H bond in zeolite-like porous BIF-20 (BIF = Boron Imidazolate Framework) is shown here to effectively produce nanoparticles within its confined pore space. Small noble-metal nanoparticles (Ag or Au) are directly synthesized into its pores without the need for any external reducing agent or photochemical reactions, and the resulting Ag@BIF-20 (or Au@BIF-20) samples show high catalytic activities for the reduction of 4-nitrophenol.

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) continue to attract much attention in new emerging areas, particularly those related to energy use and environmental conservation^{1–6}. With large internal surface areas and uniform pore and cavity sizes, MOFs share a number of structural and catalytical properties of inorganic zeolites^{7–9}. Typical zeolite-like MOF examples are zeolitic imidazolate frameworks (ZIFs) and boron imidazolate frameworks (BIFs)^{10–17}. Both ZIFs and BIFs adopt tunable zeolite-type topologies (e.g., SOD, RHO, LTA etc) and have promising applications for gas storage and separation^{11,16}. Among these, the ZIF-8 framework (Zn(mim)₂, mim = 2-methylimidazole) has become popular for use as support of select metal nanoparticles (M-NPs) for heterogeneous catalysis. However, loading of M-NPs into these zeolite-type MOF materials is typically achieved by the impregnation of a metal precursor via grinding or diffusion, followed by reduction of the metal precursor to metal(0) atoms via external reducing agents such as NaBH₄ or H₂ gas^{18–20}. Such multi-step procedure is also commonly used to incorporate metal or metal oxide NPs into other MOFs^{21–24}. This method has an intrinsic limitation for preparing M-NP@MOF with uniformly distributed M-NPs throughout the pore space, because the diffusion of external reducing agents through internal pore space of MOFs is complicated and sometimes impeded by many factors such as pore size and geometry and even the particle size and morphology of the host materials. External reducing agents can also enable the possible reduction of noble metal precursors on external surfaces of MOF particles, thus diminishing the important role of pore confinement effects and size selectivity of resulting catalysts.

Zeolitic BIFs are the most recent addition to the family of zeolite-like inorganic-organic hybrid materials. They contain tetrahedral cations (e.g., Li⁺, Cu⁺ or Zn²⁺) linked by various pre-synthesized boron imidazolate complexes^{12–15}. One distinct advantage of the BIFs system is that, both four-substituted B(mim)₄[–] ligand and three-substituted BH(mim)₃[–] ligand can be readily synthesized prior to solvothermal assembly. Of particular interest to the goal of this work is the unique BH(mim)₃[–] ligand that has been integrated into two BIFs (BIF-20 and BIF-21) with interrupted zeolite LTA and ATN topologies, respectively¹⁵. For these BH(mim)₃[–]-based BIFs, there exists a high density of B–H bonds on the framework BH(mim)₃[–] ligands. These B–H groups decorate the internal pore surface and their chemical functionality including the reducing property could clearly introduce novel functionality to these BIFs. Yet, prior to this work, such framework B–H functionality, with its potential for pore confinement effects and size control, has never been explored.

In this work, we report that BIF-20 crystal can directly produce small noble-metal nanoparticles (Ag or Au) in its pores without the need for any external reducing agent or photochemical reactions that are often employed for reduction of noble metal ions, and the resulting Ag@BIF-20 (or Au@BIF-20) samples exhibit high catalytic activities for the reduction of 4-nitrophenol (4-NP).

Figure 1 | (a) The coordination mode of BH(mim)_3^- ligand. (b) the rich B-H bonds (H atoms bonded to B centers are highlighted as purple balls.) in the SOD cage of BIF-20. (c) the interrupted LTA-type framework of BIF-20, showing large cavities represented by the yellow and sky-blue balls. (d) a schematic representation of the loading of NPs into the cavities of BIF-20.

Results

BIF-20 ($\text{Zn}_2(\text{BH(mim)}_3)_2(\text{obb})$; obb = 4,4'-oxybis(benzoate)) possesses a neutral interrupted zeolite LTA structure with large cavities and permanent porosity¹⁵. Rich naked B-H bonds are present on the surface of porous space (Figure 1a–b). The as-synthesized BIF-20 crystals were used directly to produce Ag@BIF-20 and Au@BIF-20 materials (Figure 1c–d).

Ag@BIF-20 can be quickly prepared by immersing fresh BIF-20 crystals in a methanol or water solution of AgNO_3 at room temperature (Figure 2a–b). The amount of deposited Ag NPs and the rate of deposition increase with increasing AgNO_3 concentration, as shown by the color change of the BIF-20 crystals (Figure 2c). The color change of BIF-20 crystals from colorless to brown can be attributed

to the surface plasmons of spherical silver nanoparticles. After the loading, inductively coupled plasma atomic emission spectroscopy (ICP-AES) demonstrated that the weight percentage of Ag NPs in BIF-20 is 3.01%. The field-emission (FE) TEM image of the resulting dark-brown Ag@BIF-20 crystals prepared from methanol and water solutions, respectively, indicated the formation of ca. 3.0 nm Ag-NPs in the crystals (Figure 3a–b and S2). Moreover, the sizes of these particles are independent on the preparation conditions (e.g., concentration, solvent or time) (Figure S1), which suggests that the porous surface structure of BIF-20 may provide steric restriction to confine and limit the growth of Ag NPs although the particles are larger than the pore size of BIF-20, which is accordance with the reported metal NPs/MOF^{21–29}.

Figure 2 | (a) Optical image of BIF-20. (b) optical image of Ag@BIF-20. (c) optical images for BIF-20 crystals immersed in the methanol solution of AgNO_3 with different concentrations for 50 min.

The electron paramagnetic resonance (EPR) spectrum of the resulting solid shows a peak at $g = 2.046$ for metallic silver (Figure 3c). The X-ray photoelectron spectra (XPS) as well as the energy-dispersive X-ray spectroscopy (EDS) data indicate that Ag(0) and Zn(II) coexist in the solid (Figure S3). In the XPS, the $3d_{5/2}$ and $3d_{3/2}$ peaks for Ag(0) appear at 368.6 and 374.6 eV, respectively (Figure 3d)^{26,30}. The $2p_{3/2}$ and $2p_{1/2}$ peaks for Zn(II) appear at 1022.0 and 1045.0 eV, respectively (Figure S4). The powder X-ray diffraction (PXRD) patterns further reveal that the host framework of BIF-20 is retained after the loading of Ag NPs (Figure S5). The silver peaks are hardly seen in the PXRD pattern because the particle size is too small and the amount of silver is too little.

Similar procedure was employed to load Au NPs into BIF-20 crystals. However, the process is more complicated and slower compared to the loading of Ag NPs. As shown in Figure 4a, when BIF-20 crystals were immersed in the methanol solution of NaAuCl₄ at room temperature for 50 minutes, the color of BIF-20 crystals changed from colorless to yellow. The (FE)TEM image of the yellow solid indicated the formation of <2 nm Au NPs (Figure 4d). Once the soaking time increased to 6 hours and the resulting yellow crystals were further exposed in air for more than 24 hours, Au@BIF-20 crystal containing obvious pink Au-NP “core” was formed (Figure 4b). That means that the Au NPs are growing in BIF-20, which is also demonstrated by the (FE)TEM image of this pink solid. About 4.0 nm Au NPs were found in pink Au@BIF-20 (Figure 4e). If the concentration of Au(III) solution and soaking time further increased, the final red Au@BIF-20 crystals were obtained

(Figure 4c) and the size of the Au NPs increased to ca. 6.60 nm (Figure 4f). ICP-AES measurement indicated that the weight content of Au NPs in BIF-20 is 1.63%.

The EPR spectrum of the yellow solid shows a peak at $g = 2.052$ for Au(0) and a peak at $g = 2.376$ for Au(III), respectively (Figure S7a). These values are consistent with the results of the XPS and EDS data of pink Au@BIF-20 solids (Figures S3–4 and S7), which indicate that Au(0), Au(III) and Zn(II) coexist in the solid. In the XPS traces, the $4f_{7/2}$ and $4f_{5/2}$ peaks of Au(0) appear at 84.35 and 88.00 eV and those of Au(III) appear at 87.05 and 90.65 eV (Figure S7)^{31,32}. The existence of Au(III) may be attributed to the unreacted AuCl₄[−] that is mixed with the Au(0) nanocomposite. The PXRD patterns of the pink and red Au@BIF-20 solids show that the host framework are still retained and the gold peaks are also hardly seen in the PXRD patterns (Figure S6).

Discussion

Based on above (FE)TEM, EPR and XPS data, the color change of the crystals from colorless to yellow may be attributed to the migration of AuCl₄[−] ions into the pores of BIF-20. At this first stage, the special color of Au NPs is hardly seen because the amount of Au NPs is too little. As for the pink Au@BIF-20 crystals, the NPs are found predominantly in the core of the crystal surrounded by a clear, NP-free shell (Figure 4b). This result illustrated that the redox reaction to produce Au NPs might slowly progress from the core towards the outside. Finally, the deposition of Au NPs became uniform throughout the BIF-20 crystal (Figure 4c). Since the reduction of Au(III)

Figure 3 | (FE)TEM images for the solid BIF-20 was immersed in (a) methanol solution of AgNO₃ (80 mmol/L) and (b) H₂O solution of AgNO₃ (2.5 mmol/L) at room temperature. (c) EPR spectrum of Ag@BIF-20. (d) XPS spectrum of Ag@BIF-20.

Figure 4 | Optical images (top) for Au@BIF-20 crystals prepared under different conditions and their related (FE)TEM images (bottom). (a, d) yellow crystals prepared from BIF-20 in CH₃OH solution of NaAuCl₄ (5 mmol/L) for 50 min; (b, e) pink crystals obtained after BIF-20 immersed in CH₃OH solution of NaAuCl₄ (5 mmol/L) for 6 h, and the resulting solid exposed in air for more than 24 h; (c, f) red crystals after BIF-20 immersed in CH₃OH solution of NaAuCl₄ (10 mmol/L) for 9 h, and the resulting solid exposed in air for more than 24 h.

needs multiple electrons, this Au@BIF-20 formation process is thus slow, but its formation mechanism becomes easy to understand.

Considering the structural feature of BIF-20, the presence of potentially active B–H bonds from the coordinated BH(mim)₃[−] ligands may act as the reducing agent and contribute to the direct

formation of M-NPs in BIF-20 crystals. To demonstrate the vital role of these B–H bonds, further experiments have been performed. Another BIF-25 (Co₂[B(im)₄]₄, im = imidazolate) without any B–H bond was employed to run the similar NPs-loading experiments as BIF-20. However, no M-NPs can be formed in the BIF-25 samples

Figure 5 | (a) UV-vis spectra showing gradual reduction of 4-NP over Ag@BIF-20; (b) the relationship between $\ln(C_t/C_0)$ and reaction time (t); (c) (FE)TEM image of Ag@BIF-20 after catalytic reaction; (d) (FE)TEM image of Au@BIF-20 after catalytic reaction.

(Figure S9). It is notable that the $\text{BH}(\text{mim})_3^-$ ligand itself can reduce $\text{Ag}(\text{I})$ or $\text{Au}(\text{III})$ to metal(0). When the $\text{KBH}(\text{mim})_3$ salt was dissolved in the methanol solution of NaAuCl_4 or the water solution of AgNO_3 , respectively, Au or Ag particles were produced. Specifically, two oxidation products in the mother liquid, $\text{B}(\text{mim})_3(\text{OCH}_3)^-$ ($M_w = 285.14$) and $\text{B}(\text{mim})_3(\text{OH})^-$ ($M_w = 271.11$) were also identified by the mass spectrum, respectively (Figure S13). These results reveal that the B–H bonds in BIF-20 do play a dominant role on producing M-NPs. It is also widely recognized that the B–H bonds are traditional reducing groups. However, as part of a porous framework structure, such a reducing function of the B–H bond, to the best of our knowledge, is first realized in BIF-20 material.

The reduction of 4-nitrophenol (4-NP) by KBH_4 was chosen as a model reaction for studying the catalytic performance of Ag@BIF-20 and Au@BIF-20 , respectively. The reduction kinetics was monitored by UV-vis absorption spectroscopy of the reaction mixture after the addition of the catalyst. Only tiny change (from 1.901 to 1.490 at 400 nm) in the absorption was determined even after standing for 24 h with BIF-20, indicating that BIF-20 has no catalytic activity for the reduction. After addition of a small amount (5.0 mg) of Ag@BIF-20 or Au@BIF-20 , the absorption of 4-NP at 400 nm significantly decreases along with a concomitant increase of the ~ 300 nm peak of 4-aminophenol (4-AP) (Figure 5a and S10). The UV-vis spectra show an isosbestic point (around 318 nm), suggesting that the catalytic reduction of 4-nitrophenol gives 4-aminophenol only without byproduct^{33,34}. Considering the concentration of BH_4^- is much higher than that of 4-NP ($C_{\text{KBH}_4}/C_{4\text{-NP}} = 1000$), the reaction should be of pseudo-first-order with regard to the reactant. As expected, linear relationships between $\ln(C_t/C_0)$ and reaction time are obtained in the reduction catalyzed by Ag@BIF-20 or Au@BIF-20 (Figure 5b). The rate constant k was calculated to be 0.37 and 0.22 for the reactions using catalysts Ag@BIF-20 and Au@BIF-20 , respectively. Ag@BIF-20 has much higher activity than Au@BIF-20 , which is also superior to that of most Au- and Ag-based catalysts under ambient conditions^{33,34}.

To investigate the reusability, four recycles of the activity were examined for Ag@BIF-20 and Au@BIF-20 , respectively. The catalyst exhibits similar catalytic performance without significant reduction in the conversion for the same reaction time (8 min for Ag@BIF-20 , and 14 min for Au@BIF-20) (Table S1), revealing the stability of the catalysts. (FE)TEM measurements of the catalysts indicate the size of the Ag and Au NPs almost remained the same after reaction, further suggesting an excellent stability and long life (Figure 5c–d).

In summary, the zeolitic BIF-20 crystal with rich naked B–H bonds in its porous structure successfully used the reducing function of these B–H bonds to produce small noble-metal (Ag or Au) NPs directly, leading to the formation of NPs-embedding crystalline materials, Ag@BIF-20 and Au@BIF-20 . Both resulting materials have high catalytic activities for the reduction of 4-nitrophenol. The results not only demonstrated the potential activity of the B–H bonds in a BIF structure for post-synthetic chemical modification, but also opened a new approach toward the fabrication of NPs in zeolitic MOF crystals.

Methods

Materials and instrumentation. All reagents were purchased commercially and used without further purification. All Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056$ Å) with a step size of 0.05° . TEM measurements were performed by using a JEOL-2010 TEM equipped with the energy dispersive X-ray spectrum operated at 200 kV. ICP analysis was conducted by using Inductively Coupled Plasma OES spectrometer (Ultima2, JobinYvon). X-ray photoelectron spectra (XPS) were acquired with a PHI Quantum 2000 XPS system with a monochromatic Al $\text{K}\alpha$ source and a charge neutralizer. The binding energies (BE) were referred to the C1s peak at 284.6 eV. The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker E 500. The UV-VIS absorption spectra were measured at room temperature with a Perkin-Elmer Lambda 950 UV/vis spectrophotometer.

- Horcajada, P. *et al.* Metal-organic frameworks in biomedicine. *Chem. Rev.* **112**, 1232–1268 (2012).

- Vaidhyanathan, R. *et al.* Direct observation and quantification of CO_2 binding within an amine-functionalized nanoporous solid. *Science* **330**, 650–653 (2010).
- Herm, Z. R. *et al.* Separation of hexane isomers in a metal-organic framework with triangular channels. *Science* **340**, 960–964 (2013).
- Zhang, J.-P., Zhang, Y.-B., Lin, J.-B. & Chen, X.-M. Metal azolate frameworks: from crystal engineering to functional materials. *Chem. Rev.* **112**, 1001–1033 (2012).
- Nugent, P. *et al.* Porous materials with optimal adsorption thermodynamics and kinetics for CO_2 separation. *Nature* **495**, 80–84 (2013).
- Yoon, M., Srirambalaji, R. & Kim, K. Homochiral metal-organic frameworks for asymmetric heterogeneous catalysis. *Chem. Rev.* **112**, 1196–1231 (2012).
- Cooper, E. R. *et al.* Ionic liquids and eutectic mixtures as solvent and template in synthesis of zeolite analogues. *Nature* **430**, 1012–1016 (2004).
- Lin, H.-Y. *et al.* Crystalline Inorganic Frameworks with 56-Ring, 64-Ring, and 72-Ring Channels. *Science* **339**, 811–813 (2013).
- Kang, Y., Wang, F., Zhang, J. & Bu, X. Luminescent MTN-type cluster–organic framework with 2.6 nm cages. *J. Am. Chem. Soc.* **134**, 17881–17884 (2012).
- Banerjee, R. *et al.* High-throughput synthesis of zeolitic imidazolate frameworks and application to CO_2 capture. *Science* **319**, 939–943 (2008).
- Phan, A. *et al.* Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks. *Acc. Chem. Res.* **43**, 58–67 (2009).
- Zhang, J. *et al.* Zeolitic boron imidazolate frameworks. *Angew. Chem. Int. Ed.* **48**, 2542–2545 (2009).
- Wu, T. *et al.* Zeolite RHO-type net with the lightest elements. *J. Am. Chem. Soc.* **131**, 6111–6113 (2009).
- Zheng, S. *et al.* Porous metal carboxylate boron imidazolate frameworks. *Angew. Chem., Int. Ed.* **49**, 5362–5366 (2010).
- Zhang, H.-X. *et al.* Interrupted Zeolite LTA and ATN-Type Boron Imidazolate Frameworks. *J. Am. Chem. Soc.* **133**, 11884–11887 (2011).
- Tan, J.-C., Bennett, T. D. & Cheetham, A. K. Chemical structure, network topology, and porosity effects on the mechanical properties of zeolitic imidazolate frameworks. *Proc. Nat. Acad. Sci. USA* **1107**, 9938–9943 (2010).
- Zhang, J.-P., Zhu, A.-X., Lin, R.-B., Qi, X.-L. & Chen, X.-M. Pore surface tailored SOD-type metal-organic zeolites. *Adv. Mater.* **23**, 1268–1271 (2011).
- Jiang, H.-L. *et al.* Au@ZIF-8: CO oxidation over gold nanoparticles deposited to metal-organic framework. *J. Am. Chem. Soc.* **131**, 11302–11303 (2009).
- Jiang, H.-L. *et al.* Synergistic catalysis of Au@Ag core-shell nanoparticles stabilized on metal-organic framework. *J. Am. Chem. Soc.* **133**, 1304–1306 (2011).
- Esken, D. *et al.* GaN@ZIF-8: Selective formation of gallium nitride quantum dots inside a zinc methylimidazolate framework. *J. Am. Chem. Soc.* **133**, 16370–16373 (2011).
- Hermes, S. *et al.* Metal@MOF: Loading of highly porous coordination polymers host lattices by metal organic chemical vapor deposition. *Angew. Chem. Int. Ed.* **44**, 6237–6241 (2005).
- Zlotea, C. *et al.* Pd Nanoparticles embedded into a metal-organic framework: synthesis, structural characteristics, and hydrogen sorption properties. *J. Am. Chem. Soc.* **132**, 2991–2997 (2010).
- Lim, D.-W., Yoon, J., Ryu, K. Y. & Suh, M. P. Magnesium nanocrystals embedded in a metal-organic framework: hybrid hydrogen storage with synergistic effect on physis- and chemisorption. *Angew. Chem. Int. Ed.* **51**, 9814–9817 (2012).
- Zhu, Q.-L., Li, J. & Xu, Q. Immobilizing metal nanoparticles to metal-organic frameworks with size and location control for optimizing catalytic performance. *J. Am. Chem. Soc.* **135**, 10210–10213 (2013).
- Moon, H. R., Kim, J. H. & Suh, M. P. Redox-active porous metal-organic framework producing silver nanoparticles from Ag^+ ions at room temperature. *Angew. Chem. Int. Ed.* **44**, 1261–1265 (2005).
- Suh, M. P., Moon, H. R., Lee, E. Y. & Jang, S. Y. A redox-active two-dimensional coordination polymer: preparation of silver and gold nanoparticles and crystal dynamics on guest removal. *J. Am. Chem. Soc.* **128**, 4710–4718 (2006).
- Cheon, Y. E. & Suh, M. P. Enhanced hydrogen storage by palladium nanoparticles fabricated in a redox-active metal-organic framework. *Angew. Chem. Int. Ed.* **48**, 2899–2903 (2009).
- Wei, Y., Han, S., Walker, D. A., Fuller, P. E. & Grzybowski, B. A. Nanoparticle core/shell architectures within MOF crystals synthesized by reaction diffusion. *Angew. Chem. Int. Ed.* **51**, 7435–7439 (2012).
- Moon, H. R., Limb, D.-W. & Suh, M. P. Fabrication of metal nanoparticles in metal-organic frameworks. *Chem. Soc. Rev.* **42**, 1807–1824 (2013).
- Yang, H., Wang, Y. & Zheng, N. Stabilizing subnanometer $\text{Ag}(0)$ nanoclusters by thiolate and diphosphine ligands and their crystal structures. *Nanoscale* **5**, 2674–2677 (2013).
- Yang, H. *et al.* Ligand-stabilized $\text{Au}_{13}\text{Cu}_x$ ($x = 2, 4, 8$) bimetallic nanoclusters: ligand engineering to control the exposure of metal sites. *J. Am. Chem. Soc.* **135**, 9568–9571 (2013).
- Casaleto, M. P. *et al.* XPS study of supported gold catalysts: the role of Au^0 and Au^{+6} species as active sites. *Surf. Interface Anal.* **38**, 215–218 (2006).
- Deng, Y. *et al.* Multifunctional mesoporous composite microspheres with well-designed nanostructure: a highly integrated catalyst system. *J. Am. Chem. Soc.* **132**, 8466–8473 (2010).

34. Lee, J., Park, J. C. & Song, H. A nanoreactor framework of a Au@SiO₂ yolk/shell structure for catalytic reduction of p-nitrophenol. *Adv. Mater.* **20**, 1523–1528 (2008).

Acknowledgments

This work is supported by 973 program (2012CB821705 and 2011CB932504), NSFC (91222105, 21203196, 21221001), NSF of Fujian Province (2011J06005), CAS (XDA07070200) and NSF (X.B. DMR-0846958).

Author contributions

H.Z., J.Z. and M.L. designed and carried out the experiments. H.Z., J.Z. and X.B. analyzed the results and wrote the manuscript. All authors reviewed the manuscript.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Zhang, H.-X., Liu, M., Bu, X.H. & Zhang, J. Zeolitic BIF Crystal Directly Producing Noble-Metal Nanoparticles in Its Pores for Catalysis. *Sci. Rep.* **4**, 3923; DOI:10.1038/srep03923 (2014).

This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 Unported license. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc-sa/3.0>