

Redox-Active Porous Metal–Organic Framework Producing Silver Nanoparticles from Ag^I Ions at Room Temperature**

Hoi Ri Moon, Ji Hyun Kim, and Myunghyun Paik Suh*

Metal–organic framework (MOF) coordination polymers have been the focus of recent research interest because of their potential applications in molecular adsorption and separation processes,^[1] ion exchange,^[2] catalysis,^[3] sensor technology,^[4] and optoelectronics.^[5] They can be designed and assembled to generate cavities or channels of various sizes and shapes by the appropriate choice of building blocks.^[6] However, metal–organic open frameworks are often not robust, so they collapse when the guest molecules occupying the voids are removed, and thus applications are still very limited compared to those for zeolites.

The preparation of monodispersed silver nanoparticles has attracted great attention because they exhibit a strong surface plasmon resonance that depends on the particle size and shape.^[7] However, control of the size and shape of silver particles is much more difficult than that of gold or platinum particles.^[8] Metal nanoparticles are often prepared by accommodating micro- or mesoporous inorganic materials with metal compounds or metal nanocomposites, followed by reduction processes.^[8,9] The method requires a high temperature and long reaction time, and yet formation of small monodispersed (< 5 nm) silver particles is still very difficult. Calcination at higher than 450 °C and many subsequent washing steps are needed to obtain host-free nanoparticles from these matrixes. Silver nanoparticles can also be prepared by reduction of a solution of Ag^I ions with reducing agents such as borohydride in the presence of surfactant or polymers, but the method cannot prevent the formation of large aggregates of silver particles.^[10] Therefore, the preparation of monodispersed small silver nanoparticles under mild conditions without extra reduction processes would be very useful. However, it is extremely difficult to find an appropriate solid support that can reduce Ag^I ions to silver particles at ambient temperature.^[11] In particular, there has been no redox-active MOF for such a purpose.

Herein, we report the construction of the new MOF $[\text{Ni}(\text{C}_{10}\text{H}_{26}\text{N}_6)]_3(\text{bpdc})_3 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot 6\text{H}_2\text{O}$ (**1**; bpdc = 4,4'-biphenyldicarboxylate) with permanent porosity, as well as

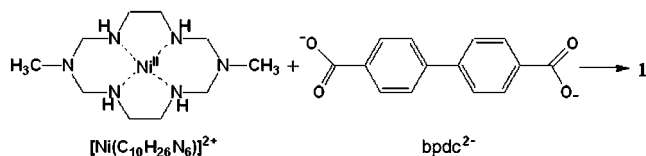
[*] H. R. Moon, J. H. Kim, Prof. Dr. M. P. Suh
School of Chemistry
Seoul National University
Seoul 151-747 (Republic of Korea)
Fax: (+82) 2-886-8516
E-mail: mpsuh@snu.ac.kr

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the room-temperature preparation of both silver nanoparticle/matrix composites and isolated silver nanoparticles (≈ 3 nm) by employing **1** as matrix. Compound **1** was constructed by packing of the linear coordination polymer chains formed from the nickel macrocyclic complex $[\text{Ni}(\text{C}_{10}\text{H}_{26}\text{N}_6)](\text{ClO}_4)_2$ and bpdc^{2-} ions in a water/pyridine mixture. Although various linear coordination polymers have



been prepared, those exhibiting permanent porosity are extremely rare.^[12,13] Previously, we reported a similar porous material, $[\text{Ni}(\text{cyclam})(\text{bpydc})] \cdot 5\text{H}_2\text{O}$ (**2**; cyclam = 1,4,8,11-tetraazacyclotetradecane; bpydc = 2,2'-bipyridyl-5,5'-dicarboxylate), which was assembled from $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$ and bpydc^{2-} ions in water.^[13] However, **2** dissociated in the AgNO_3 solution to liberate $[\text{Ni}(\text{cyclam})]^{2+}$ ions because of the strong affinity of bpydc^{2-} for Ag^+ ions, and no silver nanoparticles were produced. Therefore, we now employ bpdc^{2-} ligands as the organic building block. We also use a different macrocycle $\text{C}_{10}\text{H}_{26}\text{N}_6$, since it can stabilize the Ni^{III} state better than the cyclam ligand.^[14] To the best of our knowledge, **1** is the first MOF coordination polymer that produces metallic silver from Ag^+ ions.

It is common that a framework with different topology results when any building block or solvent system is changed in self-assembly systems.^[6a,b] However, although we employed different metal and organic building blocks as well as a different solvent system in the present study from those used to prepare **2**,^[13] we obtained **1** with a similar structure to that of **2**. In the X-ray structure of **1** (Figure 1), linear polymer chains are formed by the coordination of bpdc^{2-} ligands to the Ni^{II} macrocycle in a bimonodentate fashion, and they extend in three different directions ([010], [001], and [101]) to construct a double network of threefold braids.^[15] The flat bpdc^{2-} ligand creates grooves between the macrocycles in a chain such that the macrocycles in the other chain fit into the

grooves, thus providing robustness of the framework. There are interchain $\text{CH} \cdots \pi$ interactions^[16] between the CH of the macrocycle and the phenyl rings of the bpdc^{2-} ligand ($\text{C} \cdots \text{H}$ distance, 3.442–3.662 Å; dihedral angles, 32.8–40.0°; see Supporting Information). The structure generates 1D channels with honeycomb-like windows of diameter 9.7 Å (effective size, 7.3 Å), which are filled with water and pyridine guest molecules.

Compound **1** is insoluble in water or organic solvents. The thermogravimetric analysis trace of **1** indicates that all guest molecules can be removed at 138°C and the apohost is stable up to 250°C. The X-ray powder diffraction (XRPD) pattern of the desolvated solid is the same as that of as-prepared **1** (Figure 2a and b), which indicates that the open structure is

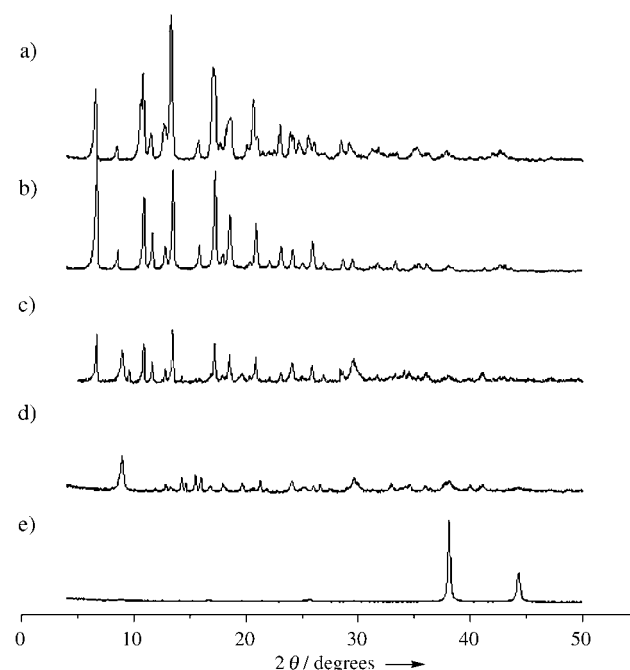


Figure 2. XRPD patterns for a) original host framework **1**, b) desolvated host framework prepared by drying **1** at 130°C for 1 h, c) desolvated host solid after immersion in a methanolic solution of AgNO_3 for 10 min, d) after immersion for 18 h, and e) host-free silver nanoparticles.

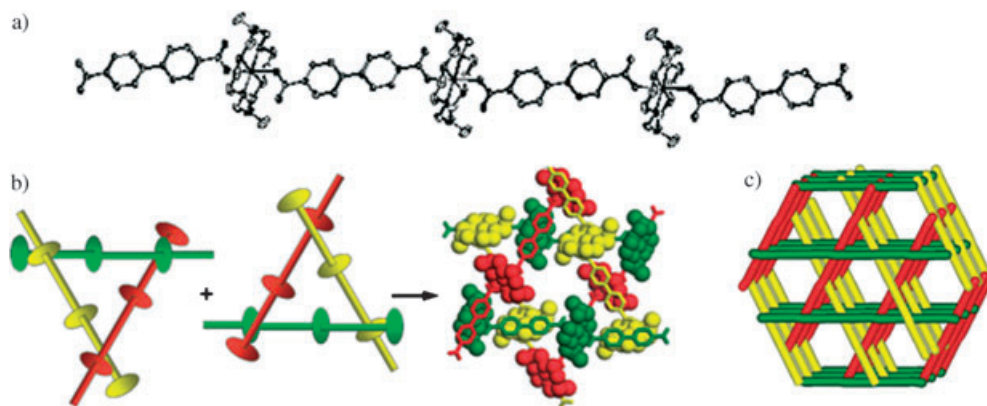


Figure 1. X-ray structure of **1**. a) Structure of the linear coordination polymer. b) Double network of threefold braids where macrocycles fit into the grooves created by bpdc^{2-} ligands. c) View showing the stacking of the linear chains to generate 1D channels.

robust even after removal of the guest molecules. The N_2 gas sorption data revealed a reversible type I isotherm as a consequence of the permanent porosity. The Langmuir surface area and pore volume estimated from the data are $691 \text{ m}^2 \text{ g}^{-1}$ and $0.390 \text{ cm}^3 \text{ g}^{-1}$ ($0.45 \text{ cm}^3 \text{ cm}^{-3}$), respectively, which compare favorably with those of zeolites (pore volume: $0.18\text{--}0.47 \text{ cm}^3 \text{ cm}^{-3}$).^[17]

A pink-colored desolvated framework was prepared by heating **1** at 130°C and 10^{-5} Torr for 1 h. Immersion of this product in a methanolic solution of AgNO_3 ($8.0 \times 10^{-2} \text{ M}$) at room temperature afforded a dark-brown host solid containing silver nanoparticles ($\approx 3 \text{ nm}$ diameter; Figure 3) as a result of the redox reaction between Ag^{I} ions and the Ni^{II} macrocycles of the host. Aqueous solvent should not be used for this reaction because the host framework dissociates in the AgNO_3 solution. The electron paramagnetic resonance (EPR) spectrum (Figure 4) of the resulting solid shows peaks at $g_{\perp} = 2.183$ and $g_{\parallel} = 2.024$, indicative of the tetragonally distorted Ni^{III} species,^[14,18] and a peak at $g = 2.005$ for metallic silver.^[19] X-ray photoelectron spectroscopy ($3d_{5/2}$ and $3d_{3/2}$ peaks for Ag, 368.0 and 374.1 eV, respectively; $2p_{3/2}$ and $2p_{1/2}$ peaks for Ni^{III} , 855.4 and 872.8 eV, respectively)^[20] and energy-dispersive X-ray spectroscopy data also indicate that Ag^0 and Ni^{III} coexist in the solid (see Supporting Information). The color change of the host solid from pink to dark brown must be attributed to the formation of Ni^{III} ions^[14] and the surface plasmons of spherical silver nanoparticles.^[21,22] The Ni^{III} species is in an uncommon oxidation state, but it can be stabilized by azamacrocyclic as a pseudooctahedral species.^[14] The Ag^{I} ions interact with the aromatic rings of the bpdc^{2-} ligands that form the channel surface of **1**,^[23] and the redox reaction between the Ag^{I} ions and the Ni^{II} ions incorporated in the host leads to the silver nanoparticles. To see if the silver nanoparticles can be formed only by the nonporous insoluble solid of the Ni^{II} macrocyclic complex, crystals of $[\text{Ni}(\text{C}_{10}\text{H}_{26}\text{N}_6)](\text{ClO}_4)_2$ (0.078 g, 0.16 mmol) were immersed in a methanolic solution of AgNO_3 (20 mL, $8.0 \times 10^{-2} \text{ M}$, 1.6 mmol) for several hours. The reaction did not produce silver nanoparticles, which indicates that both the redox-active Ni^{II} -macrocyclic component and the porous structure are necessary to obtain the nanoparticles.

In general, the size, shape, and crystallinity of the nanoparticles depend on the concentration of the metal ions, the temperature, and the type of solvent.^[24] However, these properties were not significantly affected by the range

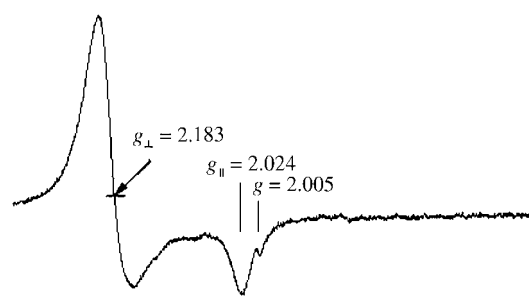


Figure 4. EPR spectrum measured at room temperature for the powder sample isolated after immersion of the desolvated solid of **1** in a MeOH solution of AgNO_3 ($8.0 \times 10^{-2} \text{ M}$).

of experimental conditions used in this study (metal ion concentration: $4.0 \times 10^{-3}\text{--}2.0 \times 10^{-1} \text{ M}$; solvent: MeCN, EtOH, or toluene), except that the lattice fringe of the silver nanoparticles became more distinct when the composites were prepared in a boiling methanolic solution of AgNO_3 (see Supporting Information).

The XRPD pattern (Figure 2) does not show formation of silver nanomaterials distinctly, even though the high-resolution (HR) TEM (Figure 3) images clearly showed incorporation of silver lattices in the matrix: when the desolvated solid of **1** was immersed in the Ag^{I} solution for 10 minutes, the isolated solid showed the same XRPD pattern as that of **1**, which indicates that the open framework structure was maintained. However, the XRPD pattern (Figure 2d) changed completely and became much weaker and broader after immersion of the host solid in the Ag^{I} solution for 18 hours. This observation suggests that the original host structure was destroyed. The silver peaks in these XRPD patterns are extremely weak, probably because the silver particles are too small (3 nm)^[25] and the number of silver crystals is too small compared with that of the host solid. Elemental analysis data (see Experimental Section) for the framework solid isolated after immersion in the AgNO_3 solution for 10 minutes indicate that the reaction stoichiometry of the Ni^{II} ion of the host and AgNO_3 is 1:1. Since the host framework becomes positively charged, it includes free NO_3^- ions as shown by the unsplit 1382 cm^{-1} peak in the IR spectra. The NO_3^- ions in the nanocomposite were partially exchanged with ClO_4^- ions when the solid was immersed in a methanolic solution of LiClO_4 for 48 hours (see Supporting Information).

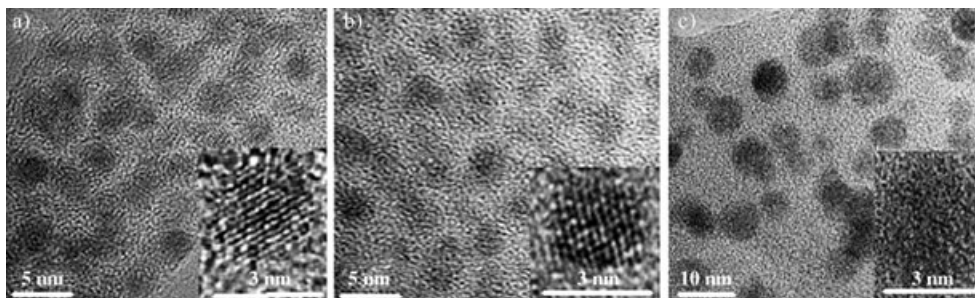


Figure 3. HRTEM images of the solid isolated after immersion of the desolvated **1** in a methanolic solution of AgNO_3 ($8.0 \times 10^{-2} \text{ M}$) at room temperature: a) for 10 min, b) for 18 h, and c) after removal of the host framework by heating the solid of (b) in dioctyl ether in the presence of oleic acid.

We cannot yet explain clearly how silver nanoparticles larger than the window size of the host framework channels formed or how they grew. However, on the basis of the present XRPD results and elemental analysis data, as well as the fact that the nonporous insoluble Ni^{II} -macrocyclic complex $[\text{Ni}(\text{C}_{10}\text{H}_{26}\text{N}_6)](\text{ClO}_4)_2$ did not produce silver nanoparticles, we suggest that the Ag^0 atoms initially collect in the channels, then diffuse into the surface of the host solid where they aggregate to form nanoparticles,^[21] which are stabilized by the bpdc^{2-} ligands as the immersion time progresses, until the framework structure is destroyed.^[26]

Host-free silver nanoparticles about 3 nm in diameter (Figure 3c), which might be capped with long-chain carboxylic acids, were isolated by treating the nanocomposite in boiling diethyl ether (at $\approx 290^\circ\text{C}$) in the presence of oleic acid. The XRPD pattern (Figure 2e) of the host-free silver nanoparticles exhibits intense peaks characteristic of crystalline silver at $2\theta = 38^\circ$ and 44° .^[25,27] When the host framework of the silver nanocomposite was destroyed with acid or heat without capping agents, the particles were significantly aggregated (see Supporting Information).

In conclusion, we have demonstrated that the present MOF is multifunctional: it acts as a porous material and also as a redox catalyst for the synthesis of silver nanoparticles (≈ 3 nm in diameter) at ambient temperature. We cannot yet explain clearly how silver nanoparticles larger than the window size of the framework channels form or how they grow, but further studies on the mechanistic aspects and the reduction of other metal ions will be performed.

Experimental Section

1: $[\text{Ni}(\text{C}_{10}\text{H}_{26}\text{N}_6)](\text{ClO}_4)_2$ ^[28] (0.098 g, 0.20 mmol) was dissolved in water/pyridine (6 mL, 2:1 v/v), and an aqueous solution (2 mL) of Na_2bpdc (0.07 g, 0.24 mmol) was added dropwise. The yellow solution was allowed to stand at room temperature until pale purple crystals formed which were isolated by filtration, washed with methanol, and dried in air. Yield: 95%. FTIR (Nujol mull): $\nu = 3370$ (m, br), 3169 (m), 1606 (w), 1586 (s), 1541 (m), 1018 (m), 833 (s), 771 (s) cm^{-1} ; UV/Vis (diffuse reflectance spectrum, λ_{max}): 509 nm. Elemental analysis: calcd for $\text{Ni}_3\text{C}_{82}\text{H}_{124}\text{N}_{20}\text{O}_{18}$ (%): C 53.12, H 6.74, N 15.11; found: C 51.66, H 7.01, N 15.01.

X-ray crystallography: Crystal data for **1**: $\text{Ni}_3\text{C}_{82}\text{H}_{124}\text{N}_{20}\text{O}_{18}$, $M_r = 1854.08$, triclinic, space group $P\bar{1}$, $a = 11.530$, $b = 15.663$, $c = 15.634$ Å, $V = 2295.4$ Å³, $Z = 1$, $T = 293$ K, $R_1 = 0.0618$ ($I > 2\sigma(I)$), $wR_2(F^2) = 0.1851$ ($I > 2\sigma(I)$), GOF = 1.017. CCDC 242970 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Preparation of silver nanocomposites: Framework **1** was desolvated at 130°C under vacuum (10^{-5} Torr) for 1 h, which resulted in a pink color. The desolvated solid (0.100 g, 0.16 mmol) was immersed in a methanolic solution (20 mL) of AgNO_3 (8.0×10^{-2} M, 1.6 mmol) at room temperature for 10 min, which resulted in a dark-brown solid, and kept immersed for an additional 18 h. The resulting dark-brown powder was isolated by filtration, washed with MeOH, and dried in air. Elemental analysis for the solid immersed in the AgNO_3 solution for 10 min: calcd for $[\text{Ni}(\text{C}_{10}\text{H}_{26}\text{N}_6)]_3(\text{bpdc})_3 \cdot 6\text{H}_2\text{O} \cdot 3\text{AgNO}_3$ ($\text{Ni}_3\text{C}_{72}\text{H}_{114}\text{N}_{21}\text{O}_{27}\text{Ag}_3$) (%): C 39.21, H 5.21, N 13.34; found: C 38.42, H 4.69, N 11.71; UV/Vis (diffuse reflectance spectrum, λ_{max}): 378, 449 nm; elemental analysis (%) for the solid

immersed for 18 h: found: C 25.50, H 2.79, N 9.95. The desolvated framework **1** (0.100 g, 0.16 mmol) was also immersed in 4.0×10^{-3} M (0.080 mmol) and 4.0×10^{-2} M (0.80 mmol) methanolic AgNO_3 solutions (20 mL) at room temperature for 10 min. The same experiments were carried out in boiling MeOH as well as in toluene, ethanol, and acetonitrile.

Isolation of host-free silver nanoparticles: The solid sample (0.11 g, 0.17 mmol based on Ni^{II}) isolated after immersion of the dried framework compound **1** in the AgNO_3 solution for 18 h was refluxed for 4 h in diethyl ether (10 mL) in the presence of oleic acid (0.18 g, 0.65 mmol). The solution became yellow as the host framework dissociated into the building blocks. The dark-brown powder was filtered off, washed with MeOH, and dried in air.

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