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SERS-Active Metal−Organic Frameworks Embedding Gold Nanorods

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Supporting Information

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Metal−organic frameworks (MOFs), consisting of metal ions or metal ion clusters and bridging organic ligands, have recently emerged as a promising material for applications in storage,[1−3] separation,[4−6] catalysis,[7−10] and molecular recognition.[11−13] For further functionalization of MOFs, the MOF composite materials with nanomaterials such as metal nanoparticles[9,10,14] and carbon nanotubes[15,16] have been prepared, and their heterogeneous catalysis and gas adsorption ability have been investigated. Moreover, understanding their noble abilities for inclusion or adsorption of gases and guest molecules, mass transport phenomena, insertion, exchange, and release of guest molecules in the nanopores of MOFs have been of growing interest. In particular, monitoring of guest diffusion in a piece of MOF crystal by computational[17,18] and experimental approaches,[19,20] including diffusion of dye molecules monitored by confocal laser scanning microscope (CLSM),[6] have been reported.

Surface-enhanced Raman scattering (SERS), dramatic enhancement of the intensity of the analyte located adjacent to metal nanostructures in particular gold nanorods (AuNRs),[21−23] has emerged as a powerful analytical technique for monitoring trace amounts of chemical and biological analytes because of its high sensitivity and rapid response.[24−27] Some attempts have already been made to incorporate AuNRs to microporous materials such as alumina[22] and silicon.[28] However, to the best of our knowledge, no trials for constructing the composites of AuNRs and nanoporous materials have been ever reported. Herein, we demonstrate the fabrication of composite crystals of MOFs embedding AuNRs (AuNR-MOFs) for monitoring in situ diffusion of guest molecules from a piece of MOF crystals by SERS as schematically shown in Figure 1. AuNR-MOFs were prepared by the direct growth of $Zn_4O(bpdc)_3$, bpdc = 4,4′-biphenyldicarboxilate, on the surface of 11-mercaptoundecanoic acid (MUA) self-assembled monolayer-coated AuNRs. In this study, we used AuNRs having a high-aspect ratio of ∼5 in order to prevent their aggregation in the reaction mixture.

AuNRs were synthesized by a reported method using a seed-mediated growth in the presence of cetyltrimethylammonium bromide (CTAB) as a shape-directing surfactant.[29,30] Replacement of CTAB with MUA was carried out by treatment with a MUA/ethanol solution under ultrasonication. Obtained MUA-capped AuNRs showed a blue shift by 25 nm of the longitudinal surface plasmon band (Figure 2), which is due to the change of local refractive index produced by MUA capping.[31] In a

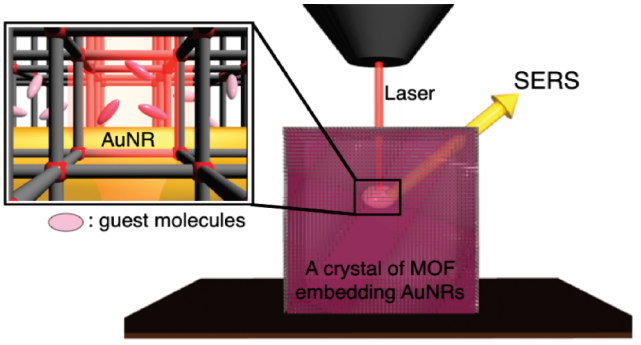

Figure 1. Schematic illustration of SERS-active MOFs embedding AuNRs.

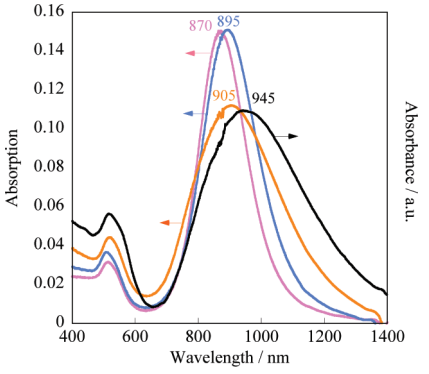

Figure 2. Vis−NIR spectra of AuNRs capped with CTAB in water (blue), MUA in water (pink), and in DEF (orange), and solid-state absorption spectrum of AuNR-MOFs (black).

zeta-potential measurement, MUA-capped AuNRs showed a positive value (19 mV) in acidic pH and a negative value (−20 ∼ −25 mV) in basic pH (Figure S1 of the Supporting Information), clearly showing the introduction of carboxyl groups onto the surface of AuNRs.[32]

MUA-capped AuNRs redispersed in *N,N*-diethylformamide (DEF) was mixed with DEF containing predissolved bpdc and $Zn(NO_3)_2•6H_2O$ at 80 °C. After 12 h incubation of the mixture

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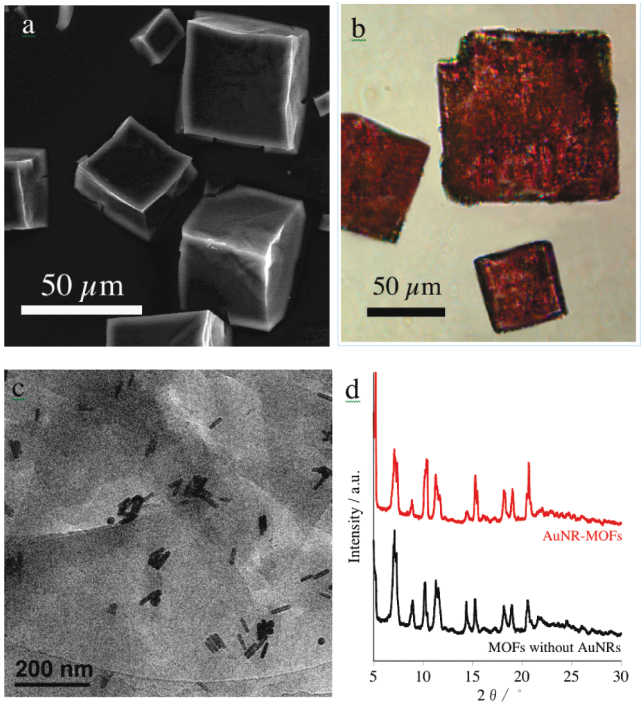

Figure 3. (a) SEM image and (b) optical micrograph of AuNR-MOFs crystals. (c) TEM image of AuNR-MOFs on cupper grid. (d) XRPD patterns of AuNR-MOFs and MOFs without AuNRs.

at 80 °C, the supernatant turned its color from purple to light yellow, and purple cubic crystals were deposited on a glass wall. Panels (a) and (b) of Figure 3 show scanning electron microscopic (SEM) images and optical micrographs of the crystals, respectively. The crystal morphology is characterized by well-defined cubic crystals 20−120 μm in width. The smooth crystal surface (Figure S2a of the Supporting Information) and the purple color (Figure 3b) indicate that AuNRs were incoporated inside MOFs because virgin MOF is intrinsically transparent (Figure S2b of the Supporting Information). Transmission electron microscopic (TEM) observation for AuNR-MOFs showed that the partially aggregated AuNRs were embedded homogeneously in the MOF crystals (Figure 3c). This partial aggregation of AuNRs promised promotion of SERS activity.[33−35] These results agreed with the result of thermogravimetric (TG) analysis (Figure S5 of the Supporting Information) showing that 1.6 wt % of AuNRs was embedded in AuNR-MOFs. Their solid-state vis−NIR absorption spectrum in dried state illustrated that the characteristic peak assignable to AuNRs was clearly observed at 945 nm (Figure 2, black solid line). This suggested that AuNRs embedded in MOF crystals maintained surface plasmon effect and SERS activity. IR spectra showed the C−O stretching band at 1400 cm^{-1} characteristic to zinc carboxylate (Figure S3 of the Supporting Information),[36] and the X-ray powder diffraction (XRPD) pattern of AuNR-MOFs was found to be in agreement with that of MOFs without AuNRs (Figure 3d). A characteristic AuNR peak was hidden by strong-intensity MOF peaks. Furthermore, the inclusion ability of AuNR-MOFs was estimated by ^{1}H NMR measurment and TG analysis (Figure S4 of the Supporting Information). ^{1}H NMR measurement revealed that AuNR-MOFs could include 17.6 DEF molecules per unit, which was similar to that of MOFs without AuNRs (19.2 DEF molecules per unit). This result was

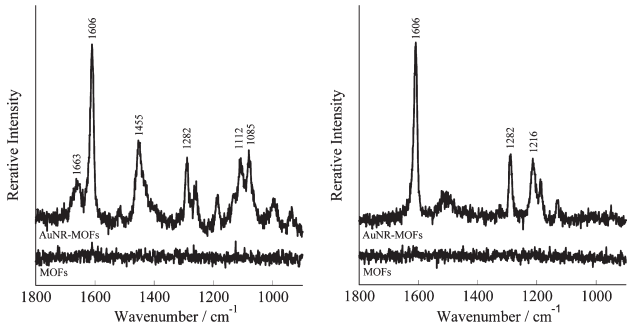

Figure 4. SERS spectra of (a) DEF and (b) $CHCl_3$ in MOFs and AuNR-MOFs. Experimental conditions are as follows: λ_{ex} = 785 nm, power = 2 mW, integration time = 2 s.

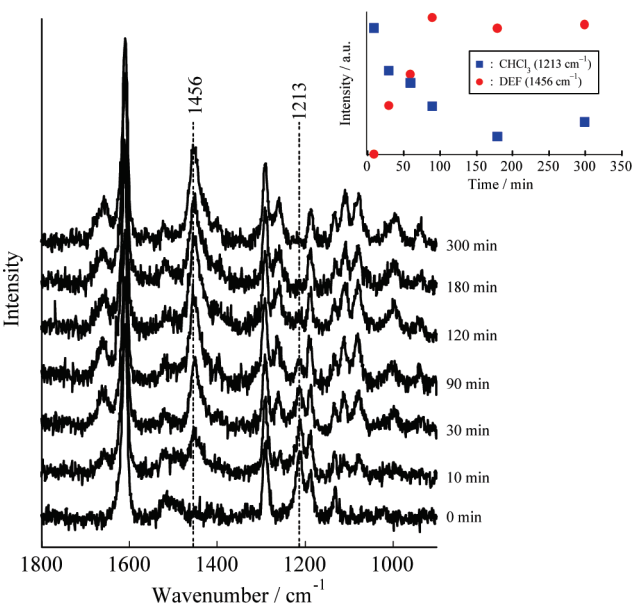

Figure 5. Time-dependent SERS spectra of AuNR-MOF/$CHCl_3$ sealed into a glass capillary with DEF. Inset: Changes of the intensity of SERS signals at 1456 cm^{-1} from DEF and 1213 cm^{-1} from $CHCl_3$ against time. Experimental conditions are as follows: λ_{ex} = 785 nm, power = 2 mW, integration time = 2 s.

supported by TG analysis; the numbers of included DEF molecules per unit were 20.2 and 22.5 for MOFs with and without AuNRs, respectively. These results clearly confirmed that embedding AuNRs neither destroyed nanopores nor disturbed transfer of guest molecules into the nanopore.

The obtained AuNR-MOFs were immersed in DEF or $CHCl_3$ for more than 12 h. Raman spectra from AuNR-MOFs, including DEF (AuNR-MOFs/DEF) and $CHCl_3$ (AuNR-MOFs/$CHCl_3$), were measured. In AuNR-MOFs/DEF, several bands at 1663, 1455, 1112, and 1085 cm^{-1} assignable to DEF were confirmed, in addition to the bands of MOFs (1606 and 1282 cm^{-1}; Figure 4a).[37] The bands assignable to DEF were slightly shifted by comparing to those in bulk, implying incorporation of DEF in nanopores of AuNR-MOFs. Furthermore, AuNR-MOFs/$CHCl_3$ showed the characteristic band at 1216 cm^{-1} assignable to $CHCl_3$ (Figure 4b). Under the same conditions, the intensity of these bands obtained from MOFs without AuNRs was very weak, suggesting that AuNR-MOFs have SERS activity and the

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guest molecules can be monitored directly and easily from a piece of MOF crystal.

For in situ monitoring of guest molecule diffusion, a piece of AuNR-MOF/$CHCl_3$ with about 80 μm in width was fixed and sealed into a glass capillary with DEF, which was set into Raman spectrometer immediately (Figure 1). Laser (785 nm) with about 5 μm diameter was irradiated to the center of the crystal. The SERS spectra from the fixed crystal were monitored at constant intervals to monitor exchange of the guest molecules from $CHCl_3$ to DEF. Time-dependent SERS spectra are shown in Figure 5. In the initial state, only the $CHCl_3$ band at 1216 cm^{-1} was observed. As the incubated time increased, the characteristic band for $CHCl_3$ at 1216 cm^{-1} gradually decreased and new bands at 1663, 1455, 1112, and 1085 cm^{-1} increased. These new bands could be assigned to DEF as compared with the authentic AuNR-MOFs, including DEF (Figure 4a). The intensity of the bands of DEF (1456 cm^{-1}) and $CHCl_3$ (1213 cm^{-1}) was saturated simultaneously in 100−150 min as shown in the inset of Figure 5 . This time-dependent phenomenon clearly demonstrated that incorporation of AuNRs into MOF crystals did not lead to further resistance for guest molecules to transfer in nanopores and comes close to AuNR, which enabled us to detect guest molecules efficiently by SERS.

In summary, SERS-active MOFs have been successfully fabricated by direct growth of MOFs [$Zn_4O(bpdc)_3$] in the presence of 11-mercaptoundecanoic acid-capped AuNRs. The embedded AuNRs were aggregated partially and did not disturb or destroy the inherent open frameworks and inclusion abilities. They enabled in situ monitoring of guest diffusion. The present system should be suitable for studying transport phenomenon in the nanopores of MOFs, which make a major contribution to the design function of MOFs. Moreover, the infinite variety of MOFs having nanopores with various sizes, shapes, and functionality would enable us to design chemical sensors for specific molecules. Finally, composites of MOFs with functional nanomaterials would provide wide applications.[9,14,15]

■ ASSOCIATED CONTENT

Supporting Information. Experimental details and results of zeta-potential and ATR-IR measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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