Conductive porous materials having a high surface reactivity offer great promise for a broad range of applications. However, a general and scalable synthesis of such materials remains challenging. In this work, the facile synthesis of catalytic metal nanoparticles (NPs) embedded in 2D metal–organic frameworks (MOFs) is reported as highly active and conductive porous materials. After the assembly of 2D conductive MOFs (C-MOFs), i.e., Cu$_3$(hexahydroxytriphenylene)$_2$ [Cu$_3$(HHTP)$_2$], Pd or Pt NPs are functionalized within the cavities of C-MOFs by infiltration of metal ions and subsequent reduction. The unique structure of Cu$_3$(HHTP)$_2$ with a cavity size of 2 nm confines the bulk growth of metal NPs, resulting in ultra-small (=2 nm) and well-dispersed metal NPs loaded in 2D C-MOFs. The Pd or Pt NPs-loaded Cu$_3$(HHTP)$_2$ exhibits remarkably improved NO$_2$ sensing performance at room temperature due to the high reactivity of catalytic metal NPs and the high porosity of C-MOFs. The catalytic effect of Pd and Pt NPs on NO$_2$ sensing of Cu$_3$(HHTP)$_2$, in terms of reaction rate kinetics and activation energy, is demonstrated.

1. Introduction

Metal–organic frameworks (MOFs) have been extensively studied in various fields, such as gas separation,[1,2] gas storage,[3,4] catalysis,[5,6] energy storage system,[7,8] and sensors[9–11] due to their ultrahigh porosity, large surface area, and tunable structures.[12] In particular, MOFs are highly fascinating materials as gas-sensing layers because the signals of gas sensors rely on surface reactions of analytes. However, most MOFs have low electrical conductivity due to the lack of the orbital overlap between metal nodes and organic ligands,[13] impeding efficient signal transduction for gas sensing. Therefore, luminescence, localized surface plasmon resonance, interferometry, and electromechanical-based MOF sensors have been introduced to transduce gas-sensing signals,[9,14,15] which complicates the sensor system.

Recently, conductive MOFs (C-MOF) with high electrical conductivity and permanent porosity have been developed, exhibiting high feasibility for applications in supercapacitors,[16,17] electrocatalysts,[18] and field-effect transistors.[19,20] In addition, Dinca et al. first reported chemiresistive sensing properties of 2D C-MOFs.[21] They synthesized a conductive 2D Cu$_3$(hexaimnotriphenylene)$_2$, and demonstrated its impedance variations upon ammonia (NH$_3$) adsorption. In addition, they developed the chemiresistive sensor arrays consisted of Cu and Ni-based C-MOFs sensing layers for the detection of diverse volatile organic compounds.[22] Although C-MOF-based chemiresistors have been reported in a few articles, related with the detection of hydrogen sulfide (H$_2$S), nitrogen monoxide (NO), and NH$_3$ gases,[23–26] they still suffer from critical issues such as low sensitivity in air and poor cross-sensitivity (selectivity), which hinders the practical application of C-MOF-based gas sensors. Besides, studies on C-MOF-based chemiresistive sensors are in the early stage, thus further in-depth study is needed to address these limitations.

One of the noteworthy properties of MOFs is that their cavities can encapsulate noble metal nanoparticles (NPs), such as Au, Pt, and Pd.[27] The unique porous structures of MOFs allow the encapsulation of ultra-small and well-dispersed metal NPs in their cavities. Since the reactivity and selectivity of catalysts highly rely on their surface properties,[28] metal nanocatalysts embedded in highly porous MOFs are able to improve catalytic performance dramatically. For instance, Huo et al.[29] synthesized Au or Pt NPs-loaded zeolite imidazole frameworks (ZIF-8) by using polyvinylpyrrolidone as a surfactant, which exhibited active and selective catalytic properties for hydrogenation. They further demonstrated a general and versatile synthesis of metal NPs-loaded MOFs by extending the concept to various kinds of metal NPs.
of metals and MOFs.\textsuperscript{[30]} In addition, Yaghi et al.\textsuperscript{[31]} reported the site selective decoration of metal NPs in MOF and demonstrated their efficient catalytic performance in the conversion of methylcyclopentane. The functionalization of MOFs with metal NPs has been extensively studied to date.\textsuperscript{[32–34]} However, to the best of our knowledge, C-MOFs decorated with metal NPs have not been reported.

Here, we propose metal NPs embedded in C-MOFs, with integrated functionalities including moderate electrical conductivity and high porosity of C-MOFs, and the outstanding catalytic reactivity of metal NPs. The unique porous structure of C-MOFs inhibits the growth of metal NPs, thus ultra-small and well-dispersed metal NPs are embedded in the cavities of C-MOFs. C-MOFs provide numerous pores and high surface area, which are essential for the enhancement of the surface reaction, and their electrical conductivity realizes the direct transduction of signals from the surface reactions even at room temperature. The metal NPs in C-MOFs not only promote the surface reactions but also tune the electrical properties of C-MOFs, thereby improving the reactivity of C-MOFs. As a proof of concept, we synthesized Pd or Pt NPs-loaded 2D C-MOFs that assembled by Cu nodes and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) linkers, for developing C-MOFs-based chemiresistors. Pd or Pt NPs (\(\approx\) 2 nm) functionalized Cu\(_3\)(HHTP)\(_2\) (M@Cu\(_3\)(HHTP)\(_2\), M = Pd or Pt) exhibited dramatically enhanced NO\(_2\) response, superior cross-selectivity, and improved reaction kinetics (response speed). The important roles of metal NPs in C-MOFs for the improvement of sensing characteristics are discussed based on the interpretation of the reaction kinetics and activation energy for NO\(_2\) adsorption.

### 2. Results and Discussion

Figure 1 shows the synthetic process and conceptual design of metal NPs-loaded Cu\(_3\)(HHTP)\(_2\). First, Cu\(_3\)(HHTP)\(_2\) was prepared by a solvothermal reaction of copper(II) acetate and HHTP in methanol solution. Cu\(_3\)(HHTP)\(_2\) is an electrically conductive 2D extended framework (Figure 1a). After purification, Cu\(_3\)(HHTP)\(_2\) was dispersed in deionized (DI) water, and metal salts were added into the suspension. To synthesize Pd or Pt NPs, potassium tetrachloroplatinate(II) and potassium tetrachloropalladate(II) were used as precursors, respectively. The metal ions are bound to oxygen sites in Cu\(_3\)(HHTP)\(_2\).\textsuperscript{[35]} Then, the reduction by sodium borohydride (NaBH\(_4\)) solution results in Pd or Pt NPs embedded in Cu\(_3\)(HHTP)\(_2\) (Figure 1b). The porous structure of Cu\(_3\)(HHTP)\(_2\) that consisted of permanent pores with a diameter of 2 nm, limits the growth of Pd or Pt, thereby creating ultra-small and well-dispersed metal NPs throughout the structure of 2D Cu\(_3\)(HHTP)\(_2\). Then, we fabricated M@Cu\(_3\)(HHTP)\(_2\)-based sensors to take advantages of fascinating features of M@Cu\(_3\)(HHTP)\(_2\) (Figure 1c).

The scanning electron microscopy (SEM) image exhibited the particle-shaped pristine Cu\(_3\)(HHTP)\(_2\) with an average diameter of 40 nm (Figure 2a). The morphologies of Pd@Cu\(_3\)(HHTP)\(_2\) and Pt@Cu\(_3\)(HHTP)\(_2\) were similar with that of pristine Cu\(_3\)(HHTP)\(_2\) (Figure 2b,c). The transmission electron microscopy (TEM) image of Pd@Cu\(_3\)(HHTP)\(_2\) clearly showed that ultra-small Pd NPs were well-dispersed in Cu\(_3\)(HHTP)\(_2\) (Figure 2d). The high-resolution TEM (HRTEM) image of Cu\(_3\)(HHTP)\(_2\) revealed the lattice distance of 2.245 Å (Figure 2e), which is corresponded to the crystal plane of Pd (111).

![Figure 1](image_url)  
\textbf{Figure 1.} Schematic illustration of the synthesis of M@Cu\(_3\)(HHTP)\(_2\). a) Cu\(_3\)(HHTP)\(_2\) prepared by solvothermal synthesis and b) M@Cu\(_3\)(HHTP)\(_2\) synthesized by the infiltration of metal ions and subsequent reduction process. c) The conceptual design of the M@Cu\(_3\)(HHTP)\(_2\)-based gas sensors.
In addition, the size of Pd NPs was identified to be ≈2 nm, demonstrating the confined growth of Pd NPs in the cavities of Cu₃(HHTP)₂. The dark-field scanning TEM (STEM) analysis also confirmed that the nanoscale Pd was well-dispersed in Cu₃(HHTP)₂ (Figure 2f). The energy-dispersive X-ray spectroscopy (EDS) elemental mapping images of Pd@Cu₃(HHTP)₂ showed C, Cu, O, and Pd elements (Figure S1a, Supporting Information). However, the intensity of Pd was relatively low. In the case of Pt@Cu₃(HHTP)₂, the samples showed a similar microstructure with that of Pd@Cu₃(HHTP)₂. As shown in Figure 2g, the tiny-sized Cu₃(HHTP)₂ was decorated by Pt NPs with an average diameter of 2 nm, which were also well-dispersed in Cu₃(HHTP)₂. The lattice fringe of Pt (111) plane with the spacing of 2.265 Å was clearly observed in the HRTEM image (Figure 2h). In addition, the STEM image of Pt@Cu₃(HHTP)₂ revealed that Pt NPs are well dispersed throughout the structure of the Cu₃(HHTP)₂ (Figure 2i). The presence of C, Cu, O, and Pt elements in the samples was confirmed by EDS elemental mapping (Figure S1b, Supporting Information). These results demonstrated the versatile synthesis of the metal NPs-loaded C-MOFs. Therefore, the proposed synthesis can be easily extended to various types of metal NPs-loaded C-MOFs by varying the kind of metals and C-MOFs for the development of highly active and conductive porous materials.

The crystal structures of pristine Cu₃(HHTP)₂, Pd@Cu₃(HHTP)₂, and Pt@Cu₃(HHTP)₂ were investigated by X-ray diffraction (XRD) analysis (Figure 3a). The pristine Cu₃(HHTP)₂ exhibited the crystal planes of (200), (210), and (004), which were similar to observations in previous literature. After the functionalization of Cu₃(HHTP)₂ with metal NPs, the peaks related to Pd and Pt were clearly observed in the XRD patterns of Pd@Cu₃(HHTP)₂ and Pt@Cu₃(HHTP)₂ (red dots for fcc Pd (JCPDS 65-2768)).
no. 46-1043) and blue dots for fcc Pt (JCPDS no. 04-0802) in Figure 3a), while the Cu3(HHTP)2 peaks were weak due to their low intensity. The chemical state of Pd and Pt in Cu3(HHTP)2 were verified by X-ray photoelectron spectrometer (XPS) analysis. The XPS survey spectra and the high-resolution spectra of Pd@Cu3(HHTP)2 and Pt@Cu3(HHTP)2 revealed the presence of Cu, O, and C elements (Figures S2 and S3, Supporting Information). In the case of Pd@Cu3(HHTP)2, the Pd 3d peaks in the XPS spectrum revealed the two characteristics peaks at 335.5 eV for Pd0 3d5/2 and 336.9 eV for Pd2+ 3d5/2 with an energy gap of 5.3 eV between 3d5/2 and 3d3/2 peaks (Figure 3b).[37] On the other hand, the high-resolution spectrum of Pt@Cu3(HHTP)2 in the vicinity of Pt 4f was deconvoluted into Pt0 at 71.2 eV and Pt2+ at 72.4 eV for 4f7/2, with background peaks related to Cu 3p, which correspond to metallic Pt and PtO, respectively (Figure 3c).[38,39] The XPS analysis of the samples confirmed that the metallic Pd and Pt NPs were embedded in the Cu3(HHTP)2 and that some of the metal NPs were partially oxidized to PdO and PtO.

The N2 adsorption and desorption isotherms at 77 K revealed the porous structure of the samples (Figure 3d). The N2 uptake of pristine Cu3(HHTP)2, Pd@Cu3(HHTP)2, and Pt@Cu3(HHTP)2 rapidly increased at low relative pressure (type I isotherms), revealing that the microporous structure of pristine Cu3(HHTP)2 was well preserved after the metal encapsulation. The increased N2 uptake of pristine Cu3(HHTP)2 at high relative pressure can be described by the pores between agglomerated Cu3(HHTP)2 particles, while this sharp increase did not appear after metal encapsulation. The specific surface areas calculated by Brunauer–Emmett–Teller (BET) method were 151.95 m2 g−1 for pristine Cu3(HHTP)2, 122.32 m2 g−1 for Pd@Cu3(HHTP)2, and 97.35 m2 g−1 for Pt@Cu3(HHTP)2, respectively. The decrease in the surface area was attributed to the mass contribution of nonporous metal NPs in M@Cu3(HHTP)2. To further investigate the structural stability of the samples, we carried out Fourier transform infrared (FT-IR) analysis. The FT-IR spectrum of pristine Cu3(HHTP)2 exhibited the major peaks at 1174 cm−1 for C–O stretching vibration and 1421 cm−1 for C–H scissoring vibration (Figure 3e).[40] The Pd@Cu3(HHTP)2 and Pt@Cu3(HHTP)2 showed FT-IR patterns similar to that of pristine Cu3(HHTP)2, indicating that the structure of Cu3(HHTP)2 was retained after the loading of Pd and Pt NPs. The new peaks at 1571 cm−1 for Pd@Cu3(HHTP)2 and at 1558 cm−1 for Pt@Cu3(HHTP)2 were associated with the vibration of adsorbed H2O on metal NPs,[41] revealing the presence of metal NPs in the M@Cu3(HHTP)2. The loading amounts of Pd and Pt in Cu3(HHTP)2 were analyzed by using inductively coupled plasma optical emission spectrometry. The relative weight ratio of Pd and Pt was verified to be 3.3 wt% in Pd@Cu3(HHTP)2 and 5.6 wt% in Pt@Cu3(HHTP)2, respectively. The thermal gravimetric analysis (TGA) further confirmed the loading amounts of Pd and Pt (about 4 wt% in both samples), which remained as residues upon decomposition of organic matter at high temperature (Figure 3f). In addition, we observed that the thermal stability of Cu3(HHTP)2 was slightly improved after the loading of metal NPs, which perhaps resulted from the interaction of Pd and Pt with Cu3(HHTP)2.

To verify the high reactivity of metal NPs in C-MOFs, we conducted gas-sensing measurements against nitrogen dioxide (NO2) molecules by using Cu3(HHTP)2, Pd@Cu3(HHTP)2, and Pt@Cu3(HHTP)2. NO2 is one of the toxic gases, and can be emitted from industrial sources such as vehicles and power plants, raising serious concerns on environment and human

Figure 3. a) XRD analysis of Cu3(HHTP)2, Pd@Cu3(HHTP)2, and Pt@Cu3(HHTP)2. XPS spectra of b) Pd@Cu3(HHTP)2 for Pd 3d and c) Pt@Cu3(HHTP)2 for Pt 4f. d) N2 adsorption and desorption isotherms of the samples at 77 K. e) FT-IR spectra of Cu3(HHTP)2, Pd@Cu3(HHTP)2, and Pt@Cu3(HHTP)2. f) TGA of the samples under air atmosphere.
health.\cite{42,43} Thus, it is important to develop highly sensitive sensors capable of detecting NO\textsubscript{2} in the order of sub-part per million (ppm) levels. The sensors were fabricated by the drop-coating of the samples on an alumina (Al\textsubscript{2}O\textsubscript{3}) substrate patterned with two parallel Au electrodes. The sensing characteristics were evaluated at room temperature in dry air (relative humidity: \textapprox5\%). It was noted that the baseline resistance of the sensors in humid atmospheres (relative humidity: \textapprox95\%) continuously increased to the measurement limit (100 M\textOmega) of our sensing system. This is because H\textsubscript{2}O molecules (hundreds to tens of thousands of ppm levels) in air can be easily adsorbed on the open Cu sites in Cu\textsubscript{3}(HHTP)\textsubscript{2}.\cite{44} The baseline resistances of the samples in dry air were 13 M\textOmega for pristine Cu\textsubscript{3}(HHTP)\textsubscript{2}, 25 M\textOmega for Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2}, and 63 M\textOmega for Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2} (Figure S4, Supporting Information). The increase in baseline resistances was attributed to the creation of multiple junctions between materials of different work functions (5.99 eV for Cu\textsubscript{3}(HHTP)\textsubscript{2}, 5.12 eV for Pd, and 5.65 eV for Pt).\cite{26,45} Because the majority current carriers in Cu\textsubscript{3}(HHTP)\textsubscript{2} are holes,\cite{26} the resistance of Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2} was much higher than that of Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} (Table S1, Supporting Information). The slight increase of lattice spacing to z-axis can reduce the hopping current between C-MOF layers.\cite{44} Moreover, the partially oxidized Pd and Pt (PdO and PtO as confirmed with XPS analysis) can further affect the baseline resistance by creating additional junctions. Since the work functions of PdO and PtO are 7.90 and 5.65 eV, respectively,\cite{46,47} PtO donates electrons to Cu\textsubscript{3}(HHTP)\textsubscript{2}, whereas PdO deprives Cu\textsubscript{3}(HHTP)\textsubscript{2} of electrons (Figure S5, Supporting Information). Therefore, from these reasons, the baseline resistance of Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2} was much higher than that of Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2}.

The variations in the sensor resistances upon exposure to 5 ppm of NO\textsubscript{2} were monitored in real time at room temperature in air (Figure S4, Supporting Information). The dynamic resistance variations were normalized to dynamic response transitions. The response is defined by the ratio of the resistance change to the baseline resistance ($\Delta R/R_0$) (Figure 4a). The sensors showed slow recovery speed, due to the difficulty in desorption of NO\textsubscript{2} molecules at room temperature. Because NO\textsubscript{2} is a strong electron acceptor, the resistance of the Cu\textsubscript{3}(HHTP)\textsubscript{2}, which exhibits a p-type semiconducting behavior,\cite{26} decreased by the adsorption of NO\textsubscript{2}. When Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} and Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2} were exposed to NO\textsubscript{2}, their resistances drastically decreased compared with that of pristine Cu\textsubscript{3}(HHTP)\textsubscript{2}. The Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} and Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2} showed much improved response to 5 ppm of NO\textsubscript{2} (–62.11% for Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} and –57.38% for Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2}) than pristine Cu\textsubscript{3}(HHTP)\textsubscript{2} (–29.95%). In addition, Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} and Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2} exhibited higher response to 1 ppm of NO\textsubscript{2} (–13.5% for Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} and –12.1% for Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2}) than pristine Cu\textsubscript{3}(HHTP)\textsubscript{2} (–5.0%) (Figure 4b and Figure S6, Supporting Information). Response time of Cu\textsubscript{3}(HHTP)\textsubscript{2} was also hugely improved by embedding Pd or Pt NPs in Cu\textsubscript{3}(HHTP)\textsubscript{2} (Figure S7, Supporting Information). In particular, the response time to 1 ppm of NO\textsubscript{2} was 13.8 min for Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2}, 14 min for Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2}, and 18 min for Cu\textsubscript{3}(HHTP)\textsubscript{2}. This result indicates that the M@Cu\textsubscript{3}(HHTP)\textsubscript{2}-based sensors can detect 1 ppm of NO\textsubscript{2} molecules within 15 min, which is the short-term permissible exposure limit designated by the Occupational Safety and Health Administration (OSHA) in the United States.\cite{48} These results confirm that the sensing properties are significantly improved after the decoration Pd or Pt NPs on Cu\textsubscript{3}(HHTP)\textsubscript{2}.

Moreover, we examined the selectivity of Cu\textsubscript{3}(HHTP)\textsubscript{2}, Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2}, and Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2} sensing layers. The Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} and Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2} exhibited high resistance changes when they were exposed to NO\textsubscript{2}, and negligible resistance changes upon exposure to nitrogen monoxide (NO), ammonia (NH\textsubscript{3}), hydrogen (H\textsubscript{2}), toluene (C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}), ethanol (C\textsubscript{2}H\textsubscript{5}OH), and acetone (CH\textsubscript{3}COCH\textsubscript{3}) (Figure 4c). The normalized response values of Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} (62.11%) and Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2} (57.38%) toward NO\textsubscript{2} molecules were tenfold higher than those (lower than 5.90% for Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} and lower than 5.03% for Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2}) toward interfering gases (Figure 4d), demonstrating the high NO\textsubscript{2} selectivity of the catalyst-loaded C-MOFs sensors. In terms of repeatability, the resistance of pristine Cu\textsubscript{3}(HHTP)\textsubscript{2} did not recover to the baseline value during 14 cyclic sensing tests toward 1 ppm of NO\textsubscript{2}. However, the Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} and Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2} showed stable response and recovery dynamics during the cyclic tests (Figure 4e), demonstrating that the response and recovery kinetics of the sensors to low levels of NO\textsubscript{2} were improved by the addition of Pd and Pt NPs. Note that the response of Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} and Pt@Cu\textsubscript{3}(HHTP)\textsubscript{2} slightly decreased as the cycling number increased, which was originated from the residual adsorbed NO\textsubscript{2} that gives rise to the change of NO\textsubscript{2} adsorption equilibrium.

The response values (AR/R\textsubscript{0}) of NO\textsubscript{2} sensors reported in recent literatures are illustrated in Figure 4f, and the detailed sensing properties are summarized in Table S2 in the Supporting Information.\cite{49–56} Although the response of Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} was slightly lower than those of other materials, a significant improvement in MOF-based sensors has been achieved in this work by combining the metal NPs with C-MOFs. The Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} exhibited the highest NO\textsubscript{2} response among MOF-based sensors reported to date, including MOFs, C-MOFs, and MOF derivatives. The response of Pd@Cu\textsubscript{3}(HHTP)\textsubscript{2} increased by more than 12 times with improved reaction kinetics even at room temperature, compared with the response of reported MOFs-based sensors. These outstanding results confirmed the superiority of metal NPs-loaded C-MOFs, as a highly active material with electrical conductivity, for applications in NO\textsubscript{2} sensors operated at room temperature. Although the stability of M@Cu\textsubscript{3}(HHTP)\textsubscript{2} against humidity was not demonstrated here due to easy adsorption of H\textsubscript{2}O on Cu\textsubscript{3}(HHTP)\textsubscript{2} at high humidity, we suppose that the introduction of additional catalysts or humidity screening membranes, as previously demonstrated,\cite{57,58} can improve the sensing properties even in humid atmospheres.

In general, the adsorption of NO\textsubscript{2} deprived sensing materials of electrons, thereby changing the resistance of the sensors.\cite{59,60} In the case of C-MOFs, the chemiresistive sensing behaviors originate from the charge transfer between C-MOFs and adsorbed gas molecules.\cite{26} Analytes are preferentially adsorbed...
on open metal sites that are coordinatively unsaturated metal centers in MOFs, changing their electrical resistance.[44] Since NO₂ is an electron acceptor at room temperature, the resistance of Cu₃(HHTP)₂, a p-type sensing material, decreases when C-MOFs were exposed to NO₂. The highly porous Cu₃(HHTP)₂ with MΩ-level resistance and high surface area not only facilitate gas diffusion into sensing layers through a number of pores but also transduce electrical signals from the surface reaction. In addition, the metal NPs embedded in the cavities of C-MOFs can activate the surface reaction, enabling effective modulation of resistance upon exposure to target analytes. To investigate the catalytic effect of Pd and Pt NPs on the NO₂ sensing behavior of Cu₃(HHTP)₂, we calculated NO₂ response and recovery kinetics of the sensors based on i) the mass action law of NO₂ adsorption reaction on sensing materials (Cu₃(HHTP)₂ or M@Cu₃(HHTP)₂) (Reactions 1 and 2) and ii) the assumption that response is proportional to the amounts of gas adsorbed.[60] The adsorption rate constant ($k_{ads}$), desorption rate constant ($k_{des}$), and equilibrium constant ($K = k_{ads}/k_{des}$) were obtained from the first reaction of the sensors to 5 ppm of NO₂ by the exponential fitting of the response versus time curves ($R(t)$) (Figure S8, Supporting Information) as shown in the equations below:

\[
\begin{align*}
\text{NO}_2 \text{(gas)} + \text{Cu}_3 \text{(HHTP)}_2 \text{(s)} &\leftrightarrow \text{NO}_2 - \text{Cu}_3 \text{(HHTP)}_2 \text{(s)} \\
\text{NO}_2 \text{(gas)} + \text{M@Cu}_3 \text{(HHTP)}_2 \text{(s)} &\leftrightarrow \text{NO}_2 - \text{M@Cu}_3 \text{(HHTP)}_2 \text{(s)}
\end{align*}
\]

(1) \hspace{1cm} (2)

\[ R(t) \text{ for NO}_2 \text{ adsorption} = R_{max} \cdot \frac{C_i \cdot K}{1 + C_i \cdot K} \cdot \left(1 - \exp \left[ - \frac{1 + C_i \cdot K}{K} \cdot k_{ads} \cdot t \right] \right) \]

(3)

\[ R(t) \text{ for NO}_2 \text{ desorption} = R_0 \exp \left[ - k_{des} \cdot t \right] \]

(4)
where \( R_{\text{max}} \) is the maximum response of the sensors, \( C_a \) is the concentration of analytes (NO\(_2\)), and \( R_0 \) is the response of the sensors before refreshing with air. The calculated adsorption and desorption rate constants are described in Figure 5a. The Pt@Cu\(_3\)(HHTP)\(_2\) exhibited higher NO\(_2\) adsorption and desorption kinetics (5.54 \times 10^{-2} \text{ ppm}^{-1} \text{ s}^{-1} \) for adsorption and 7.30 \times 10^{-5} \text{ s}^{-1} \) for desorption) than pristine Cu\(_3\)(HHTP)\(_2\) (2.43 \times 10^{-2} \text{ ppm}^{-1} \text{ s}^{-1} \) for adsorption and 5.03 \times 10^{-5} \text{ s}^{-1} \) for desorption), demonstrating the activation of NO\(_2\) reaction by Pt NPs. On the other hand, Pd@Cu\(_3\)(HHTP)\(_2\) showed a slightly improved NO\(_2\) reaction kinetics (2.51 \times 10^{-2} \text{ ppm}^{-1} \text{ s}^{-1} \) for adsorption and 5.10 \times 10^{-5} \text{ s}^{-1} \) for desorption) compared with pristine Cu\(_3\)(HHTP)\(_2\). To further understand the catalytic effect of Pd and Pt NPs, we investigated the activation energy (\( E_a \)) of the sensors for NO\(_2\) adsorption and desorption by using Arrhenius equation

\[
\text{Reaction rate constant (} k_{\text{ads}} \text{ or } k_{\text{des}} \text{) } = A_0 \exp\left(\frac{-E_a}{RT}\right)
\]

where \( A_0 \) is a pre-exponential factor, \( E_a \) is the activation energy for the reaction, and \( R \) is the universal gas constant. Considering that Cu\(_3\)(HHTP)\(_2\) is not stable over 100 °C in air (Figure 3f), we conducted additional sensing measurements using 5 ppm of NO\(_2\) at 50 and 75 °C to investigate the variation of reaction rate constants at different operating temperatures. Then, we calculated the NO\(_2\) adsorption and desorption rate constants of the samples by using Equations (1) and (2) (Figures S9 and S10, Supporting Information). As the operating temperature increased, the adsorption and desorption rate constants also increased due to the high thermal energy of analytes (Table S3, Supporting Information). The activation energy of the samples was calculated from the slope (\(-E_a/R\)) of the natural logarithm of the reaction rate constants (\(k_{\text{ads}}\) or \(k_{\text{des}}\)) versus
the inverse of the operating temperature (1/T) (Figure 5b,c). The calculated activation energy for NO₂ adsorption was 511.5 cal mol⁻¹ for pristine Cu₃(HHTP)₂, 1351.5 cal mol⁻¹ for Pd@Cu₃(HHTP)₂, and 83.4 cal mol⁻¹ for Pt@Cu₃(HHTP)₂, whereas for NO₂ desorption was 3644.8 cal mol⁻¹ for pristine Cu₃(HHTP)₂, 4015.7 cal mol⁻¹ for Pd@Cu₃(HHTP)₂, and 3822.7 cal mol⁻¹ for Pt@Cu₃(HHTP)₂ (Figure 5d). The activation energy of NO₂ adsorption dramatically decreased with loading of Pt NPs, indicating the chemical catalytic effect of Pt NPs that facilitate NO₂ adsorption on Cu₃(HHTP)₂ (Figure 5e). The NO₂ spill-over was also observed in the system of Pt NPs with supporting materials (NO₂ adsorbents).[61] On the other hand, the decoration of Pd NPs increased the activation energy of NO₂ adsorption and desorption compared with pristine Cu₃(HHTP)₂, revealing that the resistance change of Pd@Cu₃(HHTP)₂ during NO₂ adsorption is not solely related to the charge transfers between NO₂ and Cu₃(HHTP)₂. It is reported that NO₂ molecules are adsorbed on Pd NPs in the form of nitroso geometry.[62] The NO₂ adsorption on Pd NPs withdrew electrons from Pd, lowering the potential barriers of Schottky junctions between Pd NPs and Cu₃(HHTP)₂. Therefore, the resistance of the sensors was decreased by the electronic catalytic effect of Pd NPs upon exposure to NO₂. This mechanism of the electronic sensitization is also worked for the Pt catalysts on Cu₃(HHTP)₂, because NO₂ can be adsorbed on Pt NPs. Although the minor phases of oxidized metal NPs (PdO and PtO NPs) can differently affect the sensing properties, the calculation from the sensing results included the effect of both the major phases of metallic Pd and Pt and the minor phases of PdO and PtO in Cu₃(HHTP)₂-based NO₂ sensors. Therefore, it is apparent that the sensing properties of Cu₃(HHTP)₂ were dramatically enhanced by the catalytic effect of Pd and Pt NPs in Cu₃(HHTP)₂.

3. Conclusion

In conclusion, we confirmed the facile synthesis of Pd and Pt NPs-loaded Cu₃(HHTP)₂ and their potential applications in NO₂ sensors. The porous structure of C-MOFs effectively limits the growth of Pd and Pt NPs, thereby creating ultrasmall (~2 nm) and well-dispersed catalyst NPs in their cavities. The chemical and electronic catalytic effect of Pd and Pt NPs dramatically improved the NO₂ sensing properties of Cu₃(HHTP)₂-based sensors in terms of response, selectivity, and enhanced response and recovery speed. These results demonstrated the high feasibility of Pd@Cu₃(HHTP)₂ and Pt@Cu₃(HHTP)₂ as gas-sensing layers for room temperature NO₂ detection. To the best of our knowledge, this is the first report on metal NPs embedded in C-MOFs as highly active and conductive porous sensing materials. Considering that the synthetic versatility of C-MOFs has been established, various combinations of metal NPs and C-MOFs can be easily explored, providing new materials platform for diverse applications.

4. Experimental Section

Materials: 2,3,6,7,10,11-hexahydroxytriphenylene hydrate (HHTP, C₃₃H₃₂O₈·H₂O, 95.0%) was purchased from Tokyo Chemical Industry. Copper(II) acetate monohydrate (Cu(C₂O₄·H₂O), 99.9%), methanol (CH₃OH, 99.9%), ethanol (C₂H₅OH 99.5%), and acetone (CH₃COCH₃, 99.5%) were purchased from Sigma-Aldrich. Potassium tetrachloroplatinate(II) (K₂PtCl₄), potassium tetrachloropalladate(II) (K₂PdCl₄), and sodium borohydride (NaBH₄, 96%) were purchased from Aldrich. All materials were used as received.

Synthesis of Cu₃(HHTP)₂: Cu₃(HHTP)₂ was prepared by solvothermal synthesis. 0.320 g of copper(II) acetate monohydrate was dissolved in 100 mL of methanol, whereas 0.260 g of HHTP was separately dissolved in 125 mL of methanol. Two solutions were mixed in a 500 mL capped bottle, and vigorously stirred by using a magnetic bar at room temperature for 10 min. Then, the mixture was heated in a box furnace at 65 °C for 24 h, resulting in dark solutions. The solution was naturally cooled to room temperature, and the upper transparent solvent was removed. The samples were washed with fresh methanol (three times) and acetone (two times) by centrifugation, and dried at 50 °C for 12 h in air and at 100 °C for 12 h in vacuum.

Synthesis of M@Cu₃(HHTP)₂ (M = Pd or Pt): M@Cu₃(HHTP)₂ was prepared by the infiltration of metal ions followed by a reduction process. 40 mg of Cu₃(HHTP)₂ was homogeneously dispersed in 5 mL of DI water, 5 mg of potassium tetrachloroplatinate(II) or potassium tetrachloropalladate(II) was added into the suspension, and the mixture was stirred for 30 min. To reduce metal ions in the cavities of Cu₃(HHTP)₂, NaBH₄ solution (1 mg mL⁻¹) was added to the mixture. After 30 min, the samples were purified by centrifugation and washing with DI water (three times) and acetone (two times). Lastly, for activation, the samples were dried at 50 °C for 6 h in air and at 100 °C for 12 h in vacuum.

Material Characterization: SEM (XL30, Philips) and TEM (Technai G2 F30 S-Twin, FEI) were used to investigate the morphology and microstructure of the samples. The crystal structure was investigated by XRD (SmartLab, Rigaku) with Cu Kα radiation (λ = 1.5418 Å). The composition and chemical binding states of the samples were investigated by XPS (Sigma Probe, Thermo VG Scientific). N₂ adsorption/desorption isotherms at 77 K (Tristar 3020, Micromeritics) were carried out to investigate the porous structure of the samples. The surface area was calculated from the N₂ isotherms of the samples by using BET method.

Gas-Sensing Measurement: 6 mg of Cu₃(HHTP)₂, Pd@Cu₃(HHTP)₂, and Pt@Cu₃(HHTP)₂ were independently dispersed in 300 mL of ethanol, and sonicated for 10 min. Then, the dispersion solution of each sensing material was drop-coated on the alumina (Al₂O₃) substrate (dimension: 2.5 mm × 2.5 mm and thickness: 0.2 mm). The alumina substrate was patterned with two parallel Au electrodes (width: 25 µm, distance: 70 µm) on the top side and a Pt microheater on its back side. 5 µL of the suspension was drop-coated on the sensing substrate three times. The sensing measurements were carried out in a sealed chamber at room temperature and dry condition (relative humidity = 5%). To control the operating temperature (50 and 75 °C), a voltage was applied to the Pt microheater using a DC power supply (E3647A, Agilent). The sensors were stabilized in air for 3 h before each sensing test. Then, the sensors were exposed to target gas, and subsequently recovered by air injection. To investigate the sensing properties of the sensors, nitrogen dioxide (NO₂), ammonia (NH₃), hydrogen (H₂), tolune (C₆H₅CH₃), ethanol (C₂H₅OH), and acetone (C₂H₅COCH₃) were injected into the chamber, in turn. The dynamic resistance of the sensors was obtained in real time by using a data acquisition system (34972, Agilent). The response was calculated as the ratio of the sensor resistance before and after exposure to analytes (ΔR/R₀) × 100 (%), where ΔR is the resistance variation of the sensors when exposed to gas and R₀ is the baseline resistance of the sensors when exposed to air. The error bars were added by multiple sensing tests of three independent sensors for each sensing material.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
Acknowledgements
This work was supported by the Ministry of Trade, Industry & Energy (Korea) under Industrial Technology Innovation Program (no. 10070075). This work was also supported by Wearable Platform Materials Technology Center (WMC) funded by National Research Foundation of Korea (NRF) Grant of the Korean Government (MSIT) (no. 2016R1A5A1099926). This work was supported by Nano-Convergence Foundation(www.nanotech2020.org) funded by the Ministry of Science and ICT(MSIT, Korea) & the Ministry of Trade, Industry and Energy(MOTIE, Korea) (no. 200000230).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
catalysts, conductive, metal nanoparticles, metal–organic frameworks, sensors

Received: January 31, 2019
Revised: April 9, 2019
Published online: September 12, 2019

[1] J.-R. Li, R. J. Kuppler, H.-C. Zhou, Chem. Soc. Rev. 2009, 38, 1477.
[2] G. Liu, V. Chernikova, Y. Liu, K. Zhang, Y. Belmakhbout, O. Shekhah, C. Zhang, S. Yi, M. Eddaoudi, W. J. Koros, Nat. Mater. 2018, 17, 283.
[3] Y. Lin, C. Kong, Q. Zhang, L. Chen, Adv. Energy Mater. 2017, 7, 1601296.
[4] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, H.-C. Zhou, Coord. Chem. Rev. 2011, 255, 1791.
[5] J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, Chem. Soc. Rev. 2009, 38, 1450.
[6] J. Liang, Z. Liang, R. Zou, Y. Zhao, Adv. Mater. 2017, 29, 1701139.
[7] W. Xia, A. Mahmood, R. Zou, Q. Xu, Energy Environ. Sci. 2015, 8, 1837.
[8] H. Wang, Q.-L. Zhu, R. Zou, Q. Xu, Chem. Soc. Rev. 2017, 2, 52.
[9] L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, Chem. Rev. 2012, 112, 1105.
[10] W.-T. Koo, S. Qiao, A. F. Ogata, G. Jha, J.-S. Jang, V. T. Chen, I.-D. Kim, R. M. Penner, Angew. Chem. Int. Ed. 2011, 17, 9276.
[11] W.-T. Koo, S.-J. Choi, S.-J. Kim, J.-S. Jang, H. L. Tuller, I.-D. Kim, J. Am. Chem. Soc. 2016, 138, 13431.
[12] H. Furukawa, K. E. Cordova, M. O’Keeffe, O. M. Yaghi, Science 2013, 343, 1230444.
[13] L. Sun, M. G. Campbell, M. Dinca, Angew. Chem., Int. Ed. 2016, 55, 3566.
[14] S. Achmann, G. Hagen, J. Kita, I. M. Malkowsky, C. Kien, R. Moos, Sensors 2009, 9, 1574.
[15] Z. Hu, B. J. Deibert, J. Li, Chem. Soc. Rev. 2014, 43, 5815.
[16] D. Feng, T. Lei, M. R. Lukatskaya, J. Park, Z. Huang, M. Lee, L. Shaw, S. Chen, A. Yakovenko, A. Kulkarni, J. Xiao, K. Fredrickson, J. B. Tok, X. Zou, Y. Cui, Z. Bao, Nat. Energy 2018, 3, 30.
[17] D. Sheberla, J. C. Bachman, J. S. Elias, C.-J. Sun, Y. Shao-Horn, M. Dinca, Nat. Mater. 2016, 15, 220.
[18] E. M. Miner, T. Fukushima, D. Sheberla, L. Sun, Y. Surendranath, M. Dinca, Nat. Commun. 2016, 7, 10942.
[19] A. A. Talin, A. Centrone, A. C. Ford, M. E. Foster, V. Stavila, P. Haney, R. A. Kinney, V. Szalai, F. El Gabaly, H. P. Yoon, F. Leonard, M. D. Allendorf, Science 2013, 343, 66.
[20] G. Wu, J. Huang, Y. Zang, J. He, G. Xu, J. Am. Chem. Soc. 2017, 139, 1360.
[52] Z. Chen, J. Wang, D. Pan, Y. Wang, R. Noetzel, H. Li, P. Xie, W. Pei, A. Umar, L. Jiang, N. Li, N. F. Rooij, G. Zhou, ACS Nano 2018, 12, 2521.
[53] W. Yang, P. Wan, X. Zhou, J. Hu, Y. Guan, L. Feng, ACS Appl. Mater. Interfaces 2014, 6, 21093.
[54] B. Cho, M. G. Hahm, M. Choi, J. Yoon, A. R. Kim, Y.-J. Lee, S.-G. Park, J.-D. Kwon, C. S. Kim, M. Song, Y. Jeong, K.-S. Nam, S. Lee, T. J. You, C. G. Kang, B. H. Lee, H. C. Ko, P. M. Ajayan, D.-H. Kim, Sci. Rep. 2015, 5, 8052.
[55] K. Y. Ko, J.-G. Song, Y. Kim, T. Choi, S. Shin, C. W. Lee, K. Lee, J. Koo, H. Lee, J. Kim, T. Lee, J. Park, H. Kim, ACS Nano 2016, 10, 9287.
[56] T. Xu, Y. Liu, Y. Pei, Y. Chen, Z. Jiang, Z. Shi, J. Xu, D. Wu, Y. Tian, X. Li, Sens. Actuators, B 2018, 259, 789.
[57] J.-W. Yoon, J.-S. Kim, T.-H. Kim, Y. J. Hong, Y. C. Kang, J.-H. Lee, Small 2016, 12, 4229.
[58] W. Liu, K. Sheng, X. Zhou, B. Dong, G. Lu, H. Song, NPG Asia Mater. 2018, 10, 293.
[59] J. Z. Ou, W. Ge, B. Carey, T. Daeneke, A. Rotbart, W. Shan, Y. Wang, Z. Fu, A. F. Chrimes, W. Wlodarski, S. P. Russo, Y. X. Li, K. Kalantar-Zadeh, ACS Nano 2015, 9, 10313.
[60] C. Y. Lee, M. S. Strano, Langmuir 2005, 21, 5192.
[61] S. Roy, A. Baiker, Chem. Rev. 2009, 109, 4054.
[62] D. T. Wickham, B. A. Banse, B. E. Koel, Surf. Sci. 1991, 243, 83.