Materials Science inc. Nanomaterials & Polymers

Effect of Benzene Derivatives as Guest Molecules on Semiconductor Properties of MOF-199

Haleemathul Zahadiya,[a] Ruwan P. Wijesundera,[b] Champika V. Hettiarachchi,*[a] and Ishanie R. Perera*[a]

A metal organic framework, MOF-199, has been synthesized under solvothermal conditions. Powder X-ray diffraction (PXRD) pattern, Fourier-transform infrared spectra (FT-IR) and scanning electron microscopic images (SEM) confirmed the formation of the expected MOF-199 structure. The semiconductor properties of MOF-199 were then fine-tuned by introducing three benzene derivatives as guest molecules (aniline, *m*-amino-benzoic acid and *p*-benzoquinone). Modified MOF-199 samples were characterized using PXRD and FT-IR. Mott-Schottky analysis and solid-state UV-visible spectroscopy were used to investigate the semiconductor properties of these materials. Once MOF was modified with benzene derivatives, slight changes in *d* spacing values of PXRD patterns and appearance of new peaks in FT-IR spectra were observed. The Mott-Schottky analysis of modified MOF-199 demonstrated an enhancement in the carrier concentration up to 83% and a negative potential shift of the flat band potential compared to pure MOF-199, indicating a higher degree of band bending. According to the solid-state UV-visible spectra, doping with organic molecules reduced the bandgap in modified MOF-199. Thus, this study evidently showcases the potential of fine-tuning the semiconductor properties of a MOF according to the requirement that allows a single MOF to be utilized in a variety of applications with a simple modification.

Introduction

Metal organic frameworks (MOFs) also known as porous 3-dimensional coordination polymers (PCPs) are porous crystalline materials composed of metal centers/clusters coordinated with organic linker ligands via metal-ligand coordinate bonds.[1–3] The combination of organic, inorganic hybrid structure forms a 3D network that demonstrates high surface area ($>6000\ m^2g^{-1}$), large pore volume (up to 90% free volume), high thermal stability and high porosity.[4] By changing the metal center or the organic linker, the architecture and the chemical properties of a MOF could be easily fine-tuned and this enables MOFs to be utilized in a variety of applications. The modifications to the original MOF structure can be done at the synthesis stage or after the synthesis. As a result of the adjustable architecture, MOFs have been extensively investigated in research areas such as gas adsorption, separation, purification, catalysis, sensing, ion exchange and energy related technologies.[3–6]

MOFs with suitable bandgaps, higher conductivity, high porosity, and easy tunability of functionality and structural properties are potential candidates to be used as semiconductors in solar energy conversion industries.[1,7–10] The charge separation upon light irradiation is the fundamental principle of a semiconductor. In a typical semiconductor like TiO_2, empty *d* orbitals of Ti form the conduction band which accommodates the photo excited electrons. Similarly, in the 3D network of a MOF, since there are metal centers connected by the organic linkers, a proper mixing of empty *d* orbitals of the metal with the LUMOs of the organic linker is required to form the conduction band.[11] MOF-5 (3.4 eV), MIL-125 (2.6–3.6 eV), MFU-4 (3.1 eV), Zr-UiO-66 (2.2–3.1 eV) and Sr-MOF (2.3 eV) are a few of the MOFs with suitable bandgaps to be used as semiconductors.[12]

Inherent poor conductivity of MOFs is a main drawback that limits their utilization as semiconductors. *In-situ* and post synthetic doping has been recognized as one of the techniques to enhance the properties of MOFs including conductivity.[13–14] Improving conductivity has been achieved via strategies such as through-bond pathways, -space, -extended conjugation, redox hoping and guest-promoted transport. In guest-promoted transport method, porous MOFs were used since the loading of electroactive guest molecules were done in to pores of the framework.[15–17] Iodine and polyiodides,[18–20] organic and organometallic molecules,[21–23] and conductive polymers and oxides[24–27] have been used as guest molecules in this strategy. Even though the conductivity enhancement has been extensively demonstrated using the host-guest transport method, the formation of new charge transport pathways or a proper mechanism has not been clearly explained yet. It is reported that detailed compositional and crystallographic analysis

[a] *H. Zahadiya, Prof. C. V. Hettiarachchi, Dr. I. R. Perera*
Department of Chemistry
Faculty of Science
University of Peradeniya, Peradeniya, 20400, Sri Lanka
E-mial:
E-mail: ishanieperera@sci.pdn.ac.lk
champikav@sci.pdn.ac.lk
[b] *Prof. R. P. Wijesundera*
Department of Physics
Faculty of Science
University of Kelaniya, Kelaniya, 11600, Sri Lanka

Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.202004528