

# In-depth understanding of atomic and electronic structure properties of Ni-NP/MOF composites by synchrotron X-ray total scattering and high-resolution X-ray photoelectron spectroscopy

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Metal-organic frameworks (MOFs) are porous crystalline materials that are synthesized by assembling metal salts with organic ligands usually in appropriate solvents [1]. MOFs are currently having much attraction as potential candidate for gas storage, separation, catalytic, optical and ion conduction [2]. Among the various MOFs, M-MOF-74 (M= Mg, Mn, Fe, Co, Ni, Zn) has relatively large surface area and high density of unsaturated M<sup>2+</sup> cation sites that can selectively interact with gases.

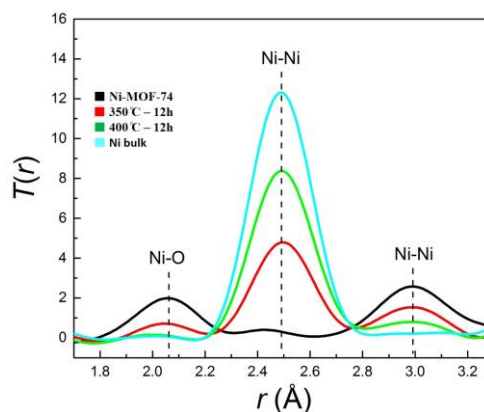
Highly active Ni nanoparticles (NPs) in MOF were synthesized using novel hybridization method by partial thermal decomposition of a Ni-MOF-74, without any additional protecting agents or surfactants [3]. The high energy X-ray diffraction (HEXRD) and hard X-ray photoelectron spectroscopy (HAXPES) of Ni-NP/MOFs were performed at BL04B2 and BL15XU at SPring-8, respectively.

The pair distribution function (PDF) analysis uses HEXRD data to calculate local and long-range atomic structure via Fourier transform of total structure factors. The total correlation functions,  $T(r)$ , for Ni-MOF-74 with and without heat treatment are shown in Fig. 1 together with fcc-type Ni bulk. The absence of the Ni-O contribution and the presence of Ni-Ni contribution for the Ni-MOF-74 at 400°C are consistent with the reduction of Ni<sup>2+</sup> to metallic Ni. In order to study the electronic structure, Ni

2p<sub>3/2</sub> core-level spectra indicated the formation of Ni<sup>0</sup> (852.7 eV), Ni<sup>2+</sup> (853.9 eV) and Ni<sup>3+</sup> (856.6 eV) for Ni-NP/MOFs, which suggested that Ni species was metallic Ni over Ni-NP/MOF composite. The atomic and electronic structural characterization of the Ni-NP/MOF provide useful information of the interaction of metal atom in this hybrid materials.

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- (1). O. Yaghi *et al.* Nature **423** (2003)705.
- (2). G. Lu. *et al.* Nature. Chem. **4** (2012) 310.
- (3). M. Mukoyoshi *et al.* Chem. Commun. 51 (2015) 12463.



**Fig. 1** Total correlation function  $T(r)$  of Ni-MOF-74, 350-12h, 400-12h and Ni bulk.