3B01

Significantly Enhanced Hydrogen-storage Capacity and Speed in Pd Nanocrystals Coating with $Cu_3(BTC)_2$, BTC = 1,3,5-benzenetricarboxylate)

(Grad. Sch. Sci. of Kyoto Univ. [1], JST-CREST[2], Grad. Sch. Sci. of Osaka Pref. Univ. [3], HVEM of Kyushu Univ. [4]) ○ Guanggin LI[1]; Hirokazu KOBAYASHI[1,2]; Hiroshi KITAGAWA[1,2]; Yoshiki KUBOTA[3]; Shoichi TOH[4]; Tomokazu YAMAMOTO[4]; Syo MATSUMURA[4]

[Introduction] Efficient hydrogen storage methods are necessary in order to store the gas more safely, while obtaining a sufficient energy density for power generation from next generation devices such as fuel cells. Palladium (Pd) nanocrystals[1] are one candidate as a hydrogen-storage material because of a high hydrogen-storage capacity, and the ability to form a stable hydride under ambient pressure and temperature. On the other hand, metal-organic frameworks (MOFs) are porous, organic–inorganic hybrid solids with zeolite-like structures and properties.

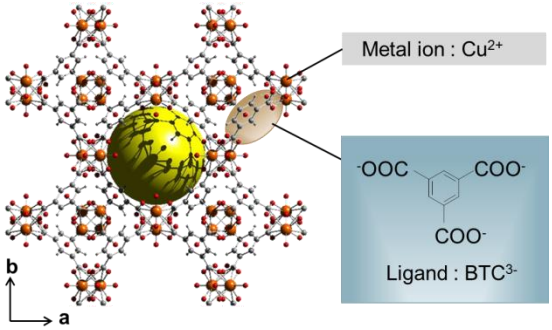

Fig.1 The structure of HKUST-1

MOFs are promising materials for applications in gas storage[2], catalyst[3] and separation[4]. However, MOFs adsorb an insignificant amount of hydrogen at room temperature. Due to their extraordinarily high surface area and well defined pore structure, MOFs can be used for the stabilization of metal nanoparticles with adjustable size. For example, HKUST-1[5] is composed of copper(II) as the metal ion and 1,3,5-benzenetricarboxylate as the ligand (structure shown in Figure 1). HKUST-1 can store large amount of hydrogen at 77 K. It is expected to be a coating material for hydrogen storage.

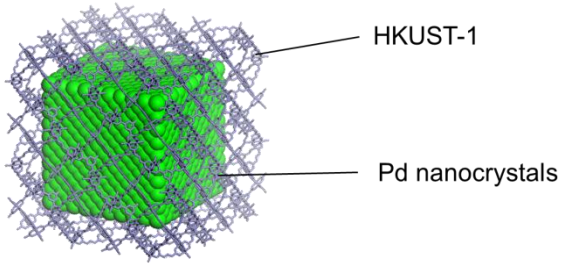

Fig.2 Pd@HKUST-1 coating material for hydrogen storage

In this study, we have synthesized and characterized Pd nanocrystals coating with HKUST-1 (Pd@HKUST-1). The structure of

Pd@HKUST-1 was shown in Figure 2. Its hydrogen storage properties have been investigated. Pd@HKUST-1 shows high capacity and rapid speed of hydrogen-storage property.

[Experiment] Pd@HKUST-1 was synthesized by a liquid-phase method. At first, Pd nanocrystals were prepared by a reduction of Na_2PdCl_4 using ascorbic acid. The mixture of $Cu(NO_3)_2 \cdot 3H_2O$ and benzene 1,3,5-tricarboxylic acid in ethanol solution was stirred at ambient temperature in the presence of the obtained Pd nanocrystals.

[Results and discussion] The powder X-ray diffraction (XRD) pattern of Pd@HKUST-1 consisted of two kinds of Pd and HKUST-1 patterns (Fig. 3). Figure 4 shows TEM image of Pd@HKUST-1. From the TEM image, it was found that the nanofilms were observed around the surface of Pd nanocrystals with mean diameter of ca. 10 nm. STEM-EDS maps demonstrated that the nanofilms include Cu element derived from HKUST-1. The differences of hydrogen-storage properties between Pd and Pd@HKUST-1 have been investigated by hydrogen pressure composition isotherms (PCT). From the PCT result, Pd@HKUST-1 showed rapid and high-capacity hydrogen storage in Pd nanocrystals covered with metal-organic framework.

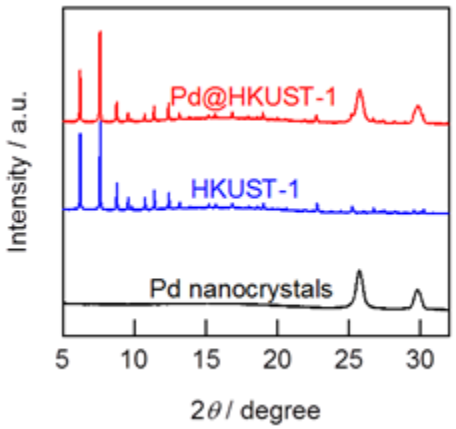

Fig. 3 XRPD patterns of samples

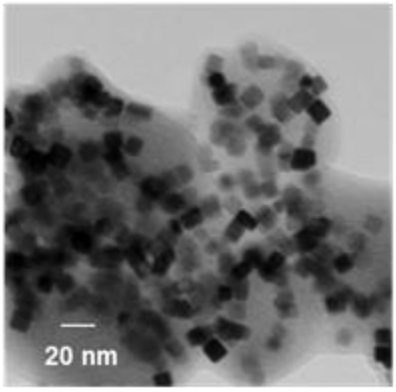

Fig. 4 TEM image of Pd@HKUST-1

Reference：

(1) M. Yamauchi et al. *J. Phys. Chem. C*, 2008, 112, 3294. (2) L. J. Murray et al. *Chem. Soc. Rev.* 2009, 38, 1294–1314. (3) J. Lee et al. *Chem. Soc. Rev.* 2009, 38, 1450–1459. (4) E. D. Bloch et al. *Science 2012*, 30, 1606–1610. (5) S. S. Y. Chui et al. *Science* 1999, 283, 1148-1150.