Remarkably enhanced hydrogen-storage capacity and speed in Pd nanocrystals covered with a metal-organic framework

Hydrogen is an essential component in many industrial processes. Due to the recent shale gas revolution and the need to use hydrogen more effectively, hydrogen production through steam reforming reaction of methane has received increased attention. Palladium has been intensively researched for hydrogen storage and hydrogen-related catalytic reactions because hydrogen easily dissociates on the surface of Pd, and hydrogen atoms can permeate into the metal lattice. To date, attempts to improve the hydrogen storage properties of Pd have typically involved the creation of Pd alloys [1]. Metal-organic frameworks (MOFs), which are assembled from metal ions and organic bridging ligands, are promising as coatings on Pd for more effective hydrogen storage due to their high surface area, porosity, and the condensation effect. Here, we introduce the remarkably enhanced capacity and speed of hydrogen storage in Pd nanocrystals as a result of coating with a MOF, copper(II) 1,3,5-benzenetricarboxylate ($Cu_3(BTC)_2$, [2] HKUST-1).

We synthesized Pd nanocrystals coated with HKUST-1 (Pd@HKUST-1) by a facile reactive seeding method, where the Pd nanocrystals act as seeding sites for MOF growth [3]. The powder X-ray diffraction (XRD) pattern of the composite consists of diffracted peaks from both the Pd and HKUST-1 lattices, indicating that the composite includes both Pd and HKUST-1. From the transmission electron microscopy (TEM) images of the Pd nanocubes and the composite (Figs. 1(a) and 1(b)), the MOF film was observed around the Pd nanocubes after hybridization. The scanning TEM-energy-dispersive X-ray maps demonstrated that the obtained material forms Pd nanocrystals covered with HKUST-1 [3].

The hydrogen storage properties of Pd@HKUST-1 were investigated by hydrogen pressure-composition isotherm measurements at 303 K, as shown in Fig. 1(c). The hydrogen concentration in Pd increases with increasing hydrogen pressure for both materials, but the total amount of hydrogen absorption at 101.3 kPa was enhanced from 0.5 H/Pd in bare Pd nanocubes to 0.87 H/Pd for the Pd@HKUST-1. Considering that pure HKUST-1 does not adsorb H_2 at all, the absorption of 74% more hydrogen is attributed to the Pd nanocubes within the Pd@HKUST-1.

We elucidated the structural change during the hydrogen absorption/desorption process by *in situ* XRD measurements every 10 min for each hydrogen pressure at **BL02B2** beamline (Figs. 2(a) and 2(b)).

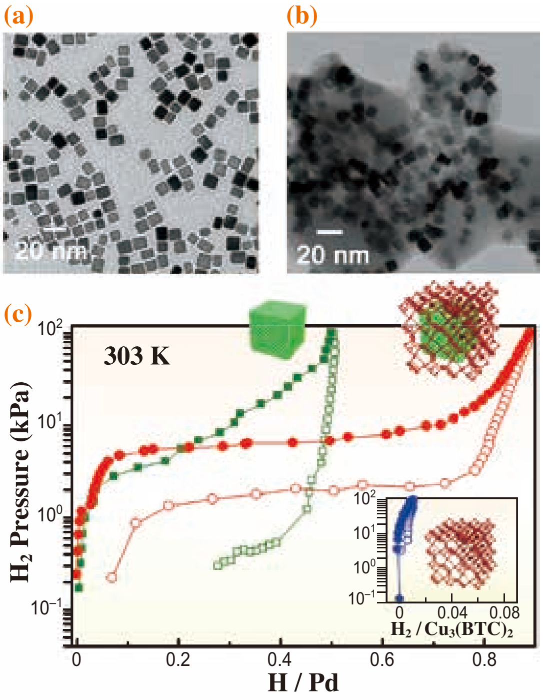

Fig. 1. TEM images of **(a)** Pd nanocubes and **(b)** Pd@HKUST-1. **(c)** Pressure-composition isotherms of Pd nanocubes (green) and Pd@HKUST-1 (red) at 303 K.

In addition to the unchanged diffraction from the α phase solid solution Pd lattice, the diffraction peaks for the bare Pd nanocubes from the face-centered-cubic (fcc) hydride β phase lattice began to appear at the lower-angle side during hydrogen absorption. Upon further increasing the hydrogen pressure, these two fcc components remained, even in the hydrogen desorption process at 0 kPa. On the other hand, in Pd@HKUST-1, the diffraction peaks completely shifted to the lower-angle side with hydrogen pressure and then returned to the same positions as the pristine sample upon the desorption process. The reversible hydrogen absorption/desorption behavior of Pd@HKUST-1 suggests that the absorption/desorption response of Pd nanocrystals is enhanced by the HKUST-1 coating. To obtain direct evidence of the enhanced hydrogen storage speed for the Pd nanocubes coated with HKUST-1, the kinetics of the hydrogenation of Pd nanocubes and Pd@HKUST-1 were investigated using the isothermal hydrogenation profiles at 303 K after introducing a hydrogen pressure of 101.3 kPa, as shown in Fig. 2(c). Within 10 min the Pd nanocubes absorbed only 0.11 H/Pd (ca. 22% of total capacity), while Pd@HKUST-1 absorbed a significant amount of hydrogen, 0.33 H/Pd (ca. 38% of the total capacity). These results indicate that Pd@HKUST-1 can absorb hydrogen about twice as fast as the Pd nanocubes within the first 10 min.

The change in the electronic structure due to the HKUST-1 coating on the surface of Pd was also investigated by X-ray photoelectron spectroscopy (XPS) measurements. The XPS spectra of Pd@HKUST-1 suggested that the electronic states of Pd@HKUST-1 differ from those of bare Pd nanocubes and pure HKUST-1, and that the electrons in the Pd nanocubes are slightly transferred to the HKUST-1 (Fig. 3). It has been reported for Pd alloys that the hydrogen concentration in Pd increases with the number of 4d-band holes and that there is a relationship between band filling and the hydrogen concentration [4]. This electron transfer may be responsible for the increased number of holes in the 4*d* band of Pd nanocubes with the HKUST-1 coating and the origin of the enhanced hydrogen storage capacity.

Our present work suggests that the presence of a MOF coating significantly altered the surface/bulk reactivity of the nanocrystals, allowing for a more facile reactivity with hydrogen. Although Pd is relatively scarce and expensive, this method of enhancement may be utilized to bolster the hydrogen storage properties using less expensive metals. This enhanced reactivity may also be applicable to other metal@MOF systems, possibly providing a general method to improve the reactivity of nanocrystals.

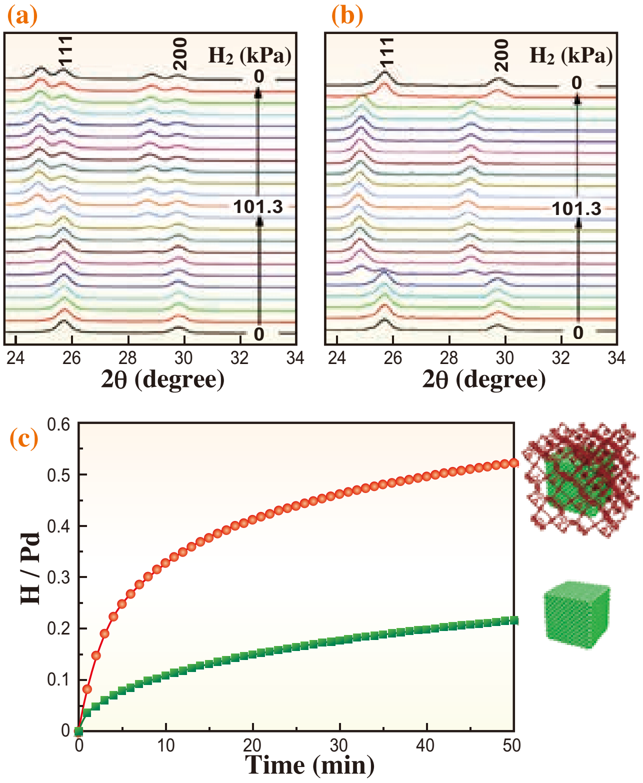

Fig. 2. *In situ* powder XRD patterns of **(a)** Pd nanocubes and **(b)** Pd@HKUST-1 upon the process of hydrogen absorption/desorption at 303 K. **(c)** Isothermal hydrogenation profiles of Pd nanocubes (green) and Pd@HKUST-1 (red) at 303 K after introducing a hydrogen pressure of 101.3 kPa.

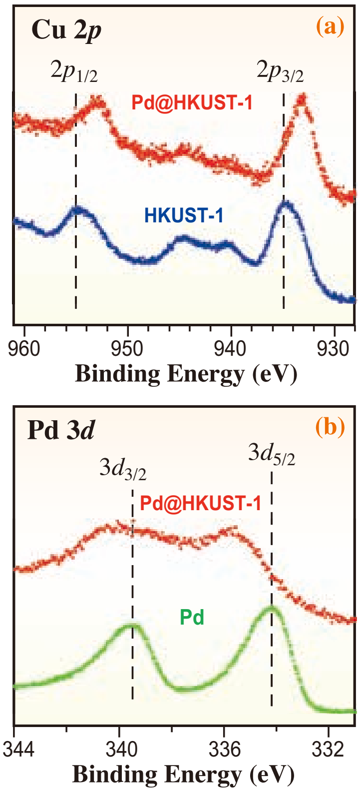

Fig. 3. XPS spectra of **(a)** Cu 2*p* and **(b)** Pd 3*d* (green : Pd nanocubes; blue : HKUST-1; red : Pd@HKUST-1).

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