



## Hydrogen-Storage Materials

# Intracell Hydrogen Adsorption–Transmission in a Co<sub>2</sub>P Solid Hydrogen-Storage Material

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**Abstract:**  $Co_2P$  nanoparticles, obtained by a simple mechanical ball-milling treatment, have been shown to undergo a new hydrogen adsorption-transmission process called intracell Kubas-enhanced adsorption, which results in an improved hydrogen-storage capacity. It is found that in this intracell Kubas-enhanced adsorption process hydrogen is firstly adsorbed by the Co atoms in  $Co_2P$  through a Co---H interaction and acti-

vated. It is then spilt over to the P atoms in  $Co_2P$  accompanied by the formation of a P–H bond, which has a lower bonding energy. This adsorption–transmission process is unambiguously proved by a detailed analysis of X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), cyclic voltammetry (CV), and quantum chemical calculation results.

#### Introduction

Hydrogen is a promising energy carrier because it has the highest energy density among fuels, but several difficulties are still faced in its applications for the automotive industry, such as its storage.<sup>[1,2]</sup> In order to store and release hydrogen under the desired temperature and pressure, a suitable binding energy between hydrogen and the host material is an important parameter. An overview of binding energies of hydrogen-storage mechanisms is provided in Figure 1. It can be seen that the binding energy of physisorption is low, indicating a weak interaction between hydrogen and the matrix, and the storage process often needs a very low temperature (-196 °C).<sup>[3]</sup> Therefore, many researches have turned their eyes to metal hydrides and chemical hydrides with higher binding energy, in which the dehydrogenation and rehydrogenation occur at higher temperatures.<sup>[4]</sup> Recently, it has been noted that the most favorable binding energy is located in the region of 10-50 kJ mol<sup>-1</sup>, because it is suitable for hydrogen storage at room temperature.<sup>[5]</sup> Through a large number of theoretical studies, a Kubas-enhanced adsorption mechanism with a 10-50 kJ mol<sup>-1</sup> binding

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201600345. energy has later been put on the table, which involves metal additives that act as an active catalytic center for the dissociation of molecular hydrogen and the following transmission of a hydrogen atom to nonmetal sites in the matrix.<sup>[6,7]</sup>



Figure 1. Overview of the binding energies of various solid hydrogen-storage materials  $^{\left[ 8,9\right] }$ 

Up to now, the Kubas-enhanced adsorption mechanism has only been described in host-guest systems, while an intracell process in a single compound has never been reported. In contrast with the process in host-guest mixtures, intracell Kubasenhanced adsorption occurs in a single metal-nonmetal compound, which simplifies the hydrogen-storage structure. Cobalt is a typical transition metal for hydrogen adsorption, and phosphorus is a nonmetal having a low P–H bonding energy. Our hypothesis was that a compound composed of these two elements might achieve an intracell Kubas-enhanced adsorption process. Fortunately, in this work we have demonstrated that this mechanism is realized by Co<sub>2</sub>P nanoparticles, which we obtained by a simple mechanical ball-milling treatment. The asobtained product shows a notable hydrogen-storage capacity

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of 2.60 wt.-% hydrogen at room temperature through a hydrotreating process. The intracell Kubas-enhanced adsorption mechanism is also proved by our detailed analysis of X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), cyclic voltammetry (CV), and quantum chemical calculation (DFT) results. Compared with other reported methods for preparing Co<sub>2</sub>P, this high-energy ball-milling method is safer, less expensive, more environment-friendly, and more practical; it does not require high temperatures and toxic reagents.<sup>[10–14]</sup>

#### **Results and Discussion**

Firstly, the phase, crystallinity, and purity of the raw materials were determined by XRD measurements. As shown in Figure S1, raw Co is pure face-centered-cubic (fcc) (JCPDS 89-4308), and raw P is pure monoclinic (JCPDS 44-0906). After ball-milling these two, various Co-P compounds such as Co<sub>2</sub>P, CoP, and CoP<sub>3</sub> appear, as shown in Figures 2, S2, and S3, and Table S1. At the same time, it was also observed that raw Co transforms from the fcc phase to the hcp (hexagonal close packing) phase during the ball-milling process and raw monoclinic P turns into an amorphous phase. Under suitable experimental conditions, a pure orthorhombic Co<sub>2</sub>P product is obtained with the lattice constants a = 5.5236 Å, b = 3.5127 Å, and c = 6.5847 Å, which agree well with the reported literature value (JCPDS 65-2380). The corresponding geometry optimization image of this product is shown in Figure S4. Furthermore, by changing the mol ratios of the reactants and adjusting the ball-milling speed, orthorhombic CoP (JCPDS 65-2593) and cubic CoP<sub>3</sub> (JCPDS 29-0496) are also obtained, as shown in Figures 2 and S3.



Figure 2. XRD patterns of the Co-P products obtained with different mol ratios of reactants at a ball-milling speed of 600 rpm.

In order to investigate the morphology and microstructure of the as-obtained  $Co_2P$  nanoparticles, SEM and HRTEM measurements were carried out. As shown in Figure 3(a), the asprepared product has many tiny nanoparticles. The statistical results for the size distribution of the  $Co_2P$  nanoparticles, obtained by dynamic light scattering (DLS), are exhibited in the inset of Figure 3(a). The columns represent the statistical count ratio corresponding to the diameter and the fitted line is calculated by using the Gauss function. It can be seen that the diameters are in the range 5–8 nm, and the average size of the  $Co_2P$ nanocrystals according to the Gauss distribution model is about 6.0 nm. The HRTEM image of the Co<sub>2</sub>P nanoparticles [Figure 3(b)] contains many dark/light stripes and reveals a lattice spacing of 0.221 nm corresponding to the (112) plane of the orthorhombic-phase Co<sub>2</sub>P. Moreover, the crystallinity of the sample is further confirmed by the SAED results, as shown in Figure 3(c). Reflection from a typical Co<sub>2</sub>P nanoparticle is observed, and the diffraction rings are attributed to the (201), (121), (103), (131), and (320) crystal planes of orthorhombic Co<sub>2</sub>P, which further confirm the phase composition of the product. In addition, the porosity was analyzed by a Brunauer–Emmett–Teller (BET) measurement. The specific surface area of the as-obtained product is 35.16 m<sup>2</sup> g<sup>-1</sup> (Figure S5).



Figure 3. (a) SEM, (b) HRTEM, and (c) SAED images of the as-obtained  $Co_2P$  nanoparticles; the inset in (a) is the size distribution determined by dynamic light scattering (DLS). (d) XRD patterns of the  $Co_2P$  products obtained with various ball-milling times (600 rpm, mol ratio Co/P = 1:0.5).

To investigate the crystallization process of  $Co_2P$  nanoparticles during the ball-milling process, the corresponding products (ball-milling speed 600 rpm, mol ratio Co/P = 1:0.5) have also been characterized by XRD measurements after various reaction times. As shown in Figure 3(d), the diffraction peaks of  $Co_2P$  are sharpened and strengthened obviously with the extension of the ball-milling duration up to 8 h, and the crystal grain size ranges from 9.2 to 6.0 nm as calculated by the Scherrer formula, indicating that  $Co_2P$  grains of different sizes can be selectively obtained by controlling the ball-milling time.

The composition of Co<sub>2</sub>P nanoparticles was further analyzed by XPS measurements. The wide-scan surface spectrum (Figure S6) displays only the signals arising from the elements Co, P, C, and O. The presence of a slight amount of oxygen is attributed to the water adsorbed on the surface of the sample.<sup>[15]</sup> Before hydrotreating, as shown in Figures 4(a) and (b), peaks for P 2p<sub>1/2</sub> (130.2 eV) and P 2p<sub>3/2</sub> (129.6 eV), with an electron binding energy ( $\Delta$ BE) of 0.6 eV, and the characteristic peaks for Co 2p [BE (Co 2p<sub>1/2</sub>) = 778.2 eV; BE (Co 2p<sub>3/2</sub>) = 793.8 eV] are





observed; these values are very similar to those reported for Co<sub>2</sub>P.<sup>[15]</sup> Interestingly, after the hydrotreating process, a new peak at 129.3 eV in the spectrum of P 2p [Figure 4(c)] is observed, which is assigned to P-H bonding, again very close to the value reported in the literature (129.1 eV).<sup>[16,17]</sup> So it can be concluded that P-H bonds form after hydrotreating. Furthermore, as shown in the Co 2p spectrum [Figure 4(d)], in addition to the initial peaks, one pair of new characteristic Co peaks is found at 780.3 (Co 2p<sub>3/2</sub>) and 796.3 eV (Co 2p<sub>1/2</sub>), which can be attributed to Co---H interactions.[18] On the basis of the above XPS analysis, a possible hydrogen adsorption-transmission process is depicted as follows: Firstly, when H<sub>2</sub> approaches the Co<sub>2</sub>P nanoparticles, it is weakly adsorbed on the Co surface due to a Kubas adsorption effect. Secondly, the adsorbed H<sub>2</sub> is decomposed through Co---H interactions owing to activation by Co. At last, due to the lower bonding energy of P-H, the activated H is spilt over to P, with which it forms a more stable P-H bond.



Figure 4. XPS spectra of P 2p and Co 2p of the  $Co_2P$  samples before [(a), (b)] and after [(c), (d)] the hydrotreating process, the peak at 129.3 eV in (c) is assigned to P–H bonding, the peaks marked with # at 796.3 and 780.3 eV in (d) are assigned to Co-+H adsorption.

To further reveal the hydrogen-storage mechanism, DFT is used to analyze the hydrotreating process. The basic features of the electronic structure and bonding states have also been established, and the optimized geometry is presented in Figures 5 and S7. It has been pointed out that Co can exothermically adsorb a considerable amount of hydrogen by Co---H interactions,<sup>[19]</sup> which is also proved by our DFT results. As shown in Figure 5, as a H atom is injected into the  $Co_2P$  lattice (2  $\times$  2), it is firstly adsorbed around the Co atom. Interestingly, when three H atoms are added, it is found that H atoms start to interact with P atoms to form P-H bonds. When hydrogen is adsorbed into the Co<sub>2</sub>P matrix, it is found that Co<sub>2</sub>P undergoes a transition from ferrimagnetic to paramagnetic, which is demonstrated by the calculation results presented in Table S2. After that, the hydrogen on the metal sites will be activated, and it then spills over onto the nearby nonmetallic atoms, such as carbon atoms.<sup>[8,20,21]</sup> Herein, the P-H bonding energy is lower than that of  $C-H_{1}^{[22-24]}$  and the P atoms can form stable P-H

bonds.<sup>[10,25]</sup> As shown in Figure S7, the length of the P-H bond is 1.222 Å, which is even shorter than that of PH<sub>3</sub> (1.420 Å),<sup>[26]</sup> hence the P-H bonding in this system is a strong interaction. In addition, it is also found that after three H atoms are added, the bond (ca. 1.607 Å) between Co atoms and H atoms becomes longer (one H atom: 1.141 Å and 1.329 Å). These results mean that H atoms are transferred from Co atoms to P atoms, which indicates a so-called "intracell Kubas-enhanced adsorption process". In addition, the shortest H-H distance is 2.068 Å, which is much larger than that in free  $H_2$  (0.74 Å),<sup>[6]</sup> implying that the strong H-H force is weakened. At the same time, it is also found that the peaks belonging to Co<sub>2</sub>P are shifted slightly to the left after hydrotreating, as shown in Figure S8, which further confirms that hydrogen has diffused into the Co<sub>2</sub>P crystal lattice and has induced a change in the lattice spacing. A similar change in the lattice spacing has also been found in previous reports.<sup>[28]</sup> In contrast to the conventional Kubas-enhanced adsorption mechanism occurring in host-guest systems such as metal-graphene or metal-carbon nanotubes,<sup>[8,9,27]</sup> the intracell Kubas-enhanced adsorption mechanism proposed in this work is realized in a single compound.



Figure 5. Hydrotreating of  $Co_2P$  by the intracell Kubas-enhanced adsorption effect [four unit cells, model (2 × 2), are simulated in the calculation].

To further investigate the hydrogen-storage ability and mechanism of the  $Co_2P$  nanoparticles, their hydrotreating cycles at a charging/discharging rate of 0.1 C are recorded, as shown in Figure 6(a). A long and stable charging/discharging



Figure 6. (a) Hydrogen charging/discharging curves of the as-obtained  $Co_2P$  products. (b) Cyclic voltammogram of the as-obtained  $Co_2P$  vs. Hg/Hg<sub>2</sub>Cl<sub>2</sub> in 6 M KOH solution. (c) Hydrogen-storage capacity retention ratios of electrodes made of  $Co_2P$  obtained by ball-milling at 600 rpm for 2, 4, 6, and 8 h at various discharging rates. (d) Cycle performances of  $Co_2P$  products obtained at 600 rpm for 2, 4, 6, and 8 h.





plateau appeared at about 0.7/1.4 V, which indicates a balanced hydrogen discharging/charging process.<sup>[29-31]</sup> In the cyclic voltammogram shown in Figure 6(b), cathodic peaks at -1.10 and -1.00 V are due to the P-H bonding and Co-H interaction, respectively. Accordingly, anodic peaks at -0.92 and -0.70 V belong to the breaking of P-H bonds and the desorption of the hydrogen from the Co surface, respectively.<sup>[31,32]</sup> These redox peaks also provide evidence for the intracell Kubas-enhanced hydrogen adsorption process in Co<sub>2</sub>P. In addition, it is found that the hydrogen-storage capacity decreases at high rates of hydrogen charging/discharging, because the fast injection/extraction of hydrogen is disadvantageous to its spilling-over process, as shown in Figure 6(c) and Table S3. In addition, the as-prepared Co<sub>2</sub>P nanoparticles display recommendable cycling stability as hydrogen-storage materials. As displayed in Figure 6(d), the Co<sub>2</sub>P samples achieve a maximum hydrogen discharging capacity of 710 mA h g<sup>-1</sup> (2.60 wt.-% hydrogen), which is 1.65 times of that of Co nanoparticles.<sup>[33,34]</sup> And, even after 50 cycles, the hydrogen discharging capacity is still 451 mA h g<sup>-1</sup> (1.65 wt.-% hydrogen).

#### Conclusions

In summary, Co<sub>2</sub>P nanoparticles have been prepared by a simple ball-milling method. XPS, XRD, and electrochemical analyses and DFT calculations prove that hydrotreating this product leads to an intracell hydrogen desorption-transmission process by an intracell Kubas-enhanced adsorption mechanism. This results in an improvement of the hydrogen-storage capacity (reversible hydrogen-storage capacity: 2.6 wt.-%). This new hydrogen-storage mechanism may open a window for the exploration of phosphides for hydrogen storage in future.

### **Experimental Section**

Preparation of Co<sub>2</sub>P Products: High-purity cobalt (99.99 %) and red phosphorus (99.99 %) powders were mixed with zirconium dioxide balls and then added into a zirconium dioxide vial. The raw materials were weighed in a P/Co mol ratio of 1:2. The vial was then moved into a glovebox, leaving the raw materials inside the vial exposed to the Ar gas in the glovebox. Afterwards, the vial was sealed and moved out of the glovebox. The ball-milling of the powder mixture was carried out with a planetary micromill (pulverizette 7 plus, FRITSCH), using a ball-to-powder mass ratio of 10:1 at a ballmilling speed of 600 rpm for 6 h under an atmosphere of Ar gas. After the ball-milling treatment, the P remaining in the samples was removed by heat treatment at 500 °C under an atmosphere of Ar gas (subliming point of red phosphorus: 427 °C). After cooling to room temperature, the as-obtained powders were washed with distilled water and absolute ethanol for several times and air-dried to prepare them for characterization.

#### Characterization

The crystallographic structures of the materials were determined by using a powder XRD system (TTR-III, Japan) equipped with Cu- $K_{\alpha}$  radiation ( $\lambda = 0.15406$  nm). A scan rate of 10 ° min<sup>-1</sup> was used to record the patterns in the range 10–70°. The products were observed with a SU8000 cold emission field scanning electron micro-analyzer (Hitachi, Japan) operated at 10 kV to detect microstruc-

tures. Transmission electron microscope (TEM) images and highresolution transmission electron microscopic (HRTEM) images of the nanostructures were taken with a JEOL HRTEM (JEM2010 electron microscope) at 200 kV accelerating voltage. Dynamic light scattering (DLS) measurements were performed with a Malvern Zetasizer NS90, provided with a He/Ne laser of 633 nm wavelength. Furthermore, N<sub>2</sub> adsorption/desorption measurements were measured at liquid nitrogen temperature (77 K) with a Micromeritics ASAP 3020 instrument. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The XPS measurements were performed by using a PHI 5700 ESCA system with a monochromatic Al- $K_{\alpha}$  (1486.6 eV) radiation source and a hemisphere detector, the XPS spectra were calibrated to the binding energy of C1s photoelectrons at 284.8 eV.

The hydrogen charging and discharging curves were measured in a two-electrode test cell by a LAND battery test instrument (CT2001A), which contains one piece of positive electrode and one piece of negative electrode, and the electrolyte was 6 m KOH aqueous solution. The negative electrode was made from 85 wt.-% of the as-obtained powder, 10 wt.-% acetylene black. The positive electrode material consisted of 80 wt.-% nickel hydroxide, 15 wt.-% Co. Each of the positive and negative electrode material was mixed with 5 wt.-% PTFE and coated on a 1 cm<sup>2</sup> Ni-foam. The electrode plates were pressed at a pressure of 50 kg cm<sup>-2</sup> for 30 s.

The CV measurement was performed by using an electrochemical workstation (CHI660E) consisting of a three-electrode test cell. The Co–P compounds were used as the working electrode, a metal platinum gauze was the counter electrode, and a Hg/Hg<sub>2</sub>Cl<sub>2</sub> electrode was the reference electrode; the electrolyte was 6 m KOH. The scan range was between -1.2 V and 0 V vs. Hg/Hg<sub>2</sub>Cl<sub>2</sub>, and the scan started from the open circuit potential and then along the negative direction at a scan rate of 10 mV s<sup>-1</sup>. All the experiments were performed at room temperature.

Calculation Details: The CATEP code was used to study the atomic structure, and the electronic properties and the unpaired spin density in this material before and/or after hydrogenation was also complemented by magnetization measurements. The interactions between 3d transition metal Co and P atoms are described with the Vanderbilt ultra-soft pseudo-potential. The exchange and correlation functional are treated by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). The Brillouin zone is sampled with the Monkhorst-pack scheme  $(6 \times 8 \times 4 \text{ k-mesh})$ . Optimization of atomic positions and lattice parameters is achieved by minimization of forces and stress tensors. We chose a cutoff energy of 500 eV, which gives an energy convergence of less than 10<sup>-5</sup> eV atom<sup>-1</sup>. The maximum force tolerance, the maximum stress, and the maximum displacement tolerance are selected as 0.03 eV Å<sup>-1</sup>, 0.05 GPa, and 10<sup>-3</sup> Å, respectively. Four unit cells of model  $(2 \times 2)$  are simulated in our calculation, which contains 4 Co and 8 P atoms.

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Communication

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