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ARTICLE TYPE

Porous Co-P-Pd Nanotube Arrays for Hydrogen Generation by Catalyzing the Hydrolysis of Alkaline NaBH₄ Solution

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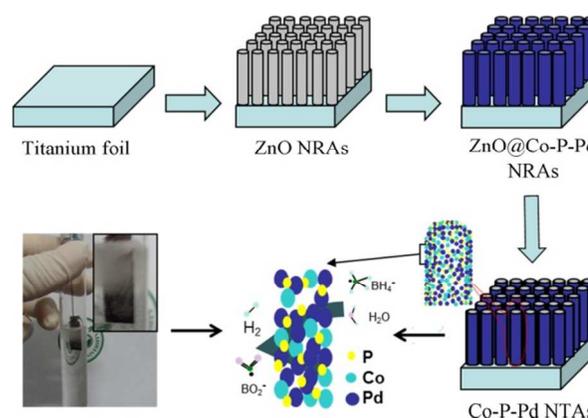
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Porous Co-P-Pd nanotube arrays (NTAs) are prepared and used for catalyzing the hydrolysis of alkaline NaBH₄ solution to generate H₂. Benefiting from the unique porous structure and synergistic effect, the Co-P-Pd NTAs show a maximum hydrogen generation rate of 4216 mL·min⁻¹·(g⁻¹ catalyst) and good cyclic stability.

The worsening climatic situation due to the combustion of hydrocarbons and fossil fuels has been of widespread public concern for decades. Thus, clean alternative fuel sources based on renewable energy have been developing rapidly in recent years. It is well known that hydrogen is the preferred fuel source, since it can provide energy by working as the anodic fuel for proton exchange membrane (PEM) fuel cells while gives the only by-product of water.^{1,2} However, the electrochemical application of hydrogen for power sources has been restrained, due to the challenges in convenient, efficient H₂ generation and storage. After decades of effort, high capacity hydrogen storage materials, including hydrides, hydrazine, ammonia borane, formic acid, alcohols and active metals, have been developed.³⁻⁵ Among chemical hydrides, NaBH₄ has been extensively investigated and regarded as a typical candidate for hydrogen storage materials, since it has many merits including theoretical hydrogen content of 10.8 wt.%, stability and non-flammability in alkaline solution,^{6,7} and can be readily produced by Brown-Schlesinger process, Bayer process, or more environment-friendly approaches.^{7,8} Moreover, the by-products of NaBH₄-based hydrogenation reaction can be reduced back to NaBH₄ such that NaBH₄ can be potentially recycled.² To generate H₂, NaBH₄ is catalytically hydrolyzed in alkaline solution, and various catalysts have proven to be able to accelerate the hydrolysis reaction, including noble metals (e.g. Rh,⁹ Ru,¹⁰ Pt,¹¹ Pd¹²), iron group metals (e.g. Co,¹³⁻¹⁵ Ni,¹⁵⁻¹⁷ Fe^{15, 18}) and metal-nonmetal composites (e.g. Co-P,¹⁹ Co-B,²⁰ Co-P-B,²¹ Co-Ni-P-B²²). While noble metal catalysts show excellent catalytic activity, their applications have been restricted by the high cost. In this context, inexpensive Co- and Ni-based catalysts which show high activities towards the catalytic hydrolysis of NaBH₄ have been developed, and their activities can be further improved, significantly, by doping P,²³ B,²⁴ and/or transition metals (e.g. Cu,²⁵ Cr,²⁶ Mo²⁷ and W²⁸) or noble metals (e.g. Pd²⁹ and Pt³⁰), and/or by exploiting porous/hollow structures (e.g. Raney Ni and Co,¹⁶ hollow/porous Co-B,^{31, 32} and porous Co-Ni-P³³). Another way to reduce the catalyst costs is to prepare substrate-supported

catalysts,³⁴⁻³⁶ which makes it easier yet more efficient to separate, collect and recycle the catalysts such that the overall costs are reduced.

In this paper, we propose a novel, inexpensive yet highly active catalyst, namely, porous Co-P-Pd nanotube arrays (NTAs). The porous Co-P-Pd NTAs compose of ~87 wt.% inexpensive P and Co, and feature unique porous nanotube structure that facilitates the mass transfer of reactants, provides large contact area, exposes more catalytic sites (particularly those located in the inner wall of Co-P-Pd nanotube), and significantly promotes the catalytic activity of the porous Co-P-Pd NTAs. Synergistic effect between Co, P and Pd are also found in the Co-P-Pd NTAs, which - together with unique porous nanotube structure - lead to the superior catalytic activity of the porous Co-P-Pd NTAs (maximum hydrogen generation rate, R_{\max} , ~4216 mL·min⁻¹·(g⁻¹ catalyst)). Moreover, the Co-P-Pd NTAs are robust during the recycling experiments, and the total volume of generated H₂ and R_{\max} only decrease slightly (~10%) even after 100 successive runs. The approach described in this paper provides an alternative way towards the fabrication of inexpensive yet highly active catalyst for the hydrolysis of alkaline NaBH₄ solution to produce H₂, and the as-prepared Co-P-Pd NTA catalyst may find promising applications in fuel cells.



Scheme 1 Schematic illustration of the fabrication of Co-P-Pd NTAs.

A schematic illustration of the fabrication of porous Co-P-Pd NTAs is presented in Scheme 1. Briefly, ZnO nanorod arrays (NRAs) were first prepared by electroplating at 70 °C, using titanium foil as substrate and zinc nitrate as source materials. The as-prepared ZnO NRAs were used as the template for the

fabrication of Co-P-Pd NTAs, through electrodeposition of Co, P, Pd on the outer surface of ZnO NRAs and subsequent removal of ZnO NRAs with NaOH solution.³⁷ All the electrodepositions were carried out in a regular two-electrode glass cell, in which a graphite rod was used as the counter electrode. Details of the electroplating conditions are listed in Table S1 in the Supplementary Information. Using a similar procedure, Co-P NTAs for control experiments were also fabricated.

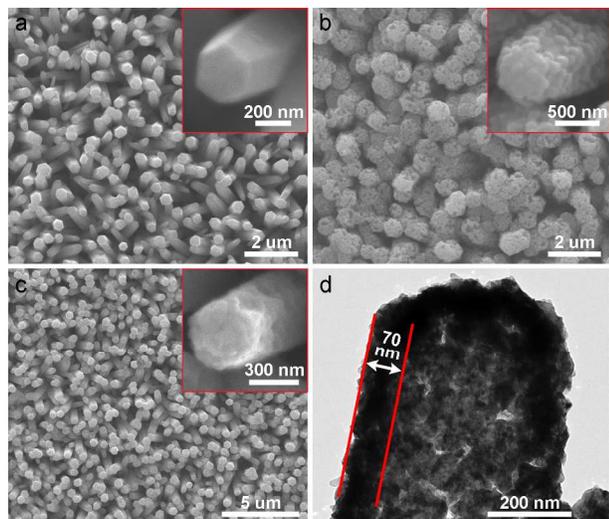


Fig. 1 SEM images of (a) ZnO NRAs, (b) Co-P NTAs, (c) Co-P-Pd NTAs, and (d) TEM image of Co-P-Pd NTAs. All inserts in (a), (b) and (c) are the corresponding SEM images at higher magnification.

Fig. 1a is the typical scanning electron microscopy (SEM) image of the as-prepared ZnO NRAs. With the electrodeposition approach, hexagonal ZnO NRAs with well-controlled length (700-900 nm) and diameter (~300 nm) can be readily grown (cf. the inserted image in Fig. 1a). The ZnO NRAs were used as the template for the fabrication of Co-P and Co-P-Pd NTAs that have hexagonal structures with rough outer surface (cf. Fig. 1b-d). The inner diameter of Co-P and Co-P-Pd NTAs is comparable and equal to the diameter of ZnO nanorod templates (~300 nm, cf. Fig. 1d). Transmission electron microscopy (TEM) image in Fig. 1d also shows that the wall thickness of the nanotubes is ~70 nm, and the porous wall of nanotubes consists of small nanocrystals of ~10 nm in diameter. As evidenced by the abundant H₂ bubbles generated on the surface of Co-P-Pd NTAs (cf. the optical image on the lower left panel in Scheme 1, H₂ bubbles in gray, Co-P-Pd NTAs in black),³⁸ such a unique, porous nanotube structure can significantly accelerate the catalytic hydrogenation reaction, since (1) the porous structure of Co-P-Pd nanotube walls facilitates the mass transfer of reactant through the walls, (2) nanocrystals located in the inner walls of Co-P-Pd nanotubes can also efficiently participate in catalytic reactions, and (3) the porous wall and rough surface of the Co-P-Pd nanotubes can provide larger contact area between catalyst and reactants and expose more catalytic sites. Indeed, under optimized hydrogen generation conditions (see more details in the following sections in this paper), the Co-P-Pd NTAs show a maximum hydrogen generation rate (R_{\max}) of 4216 mL·min⁻¹·(g⁻¹ catalyst). Actually, similar structure-activity effects have been reported in the case of Co-B hollow spheres and mesoporous Co-B nanocatalyst.^{31, 32}

We emphasize that the unique, porous nanotube structure is not the only factor that contributes to the high activity of our Co-P-Pd NTAs catalyst. Under identical, optimized hydrogen generation conditions, Co-P NTAs with similar structure gives a R_{\max} of ~2868 mL·min⁻¹·(g⁻¹ catalyst), which is only 68% of the R_{\max} of Co-P-Pd NTAs (see more details in the following sections in this paper). The compositions of Co-P-Pd NTAs and Co-P NTAs were quantified with energy-dispersive X-ray spectroscopy (EDX), and the results show that the contents of P in these two NTAs are close (7.6 wt.% in Co-P NTAs and 7.8 wt.% in Co-P-Pd NTAs, cf. Fig. 2a,b), suggesting that the 13.4 wt.% Pd in Co-P-Pd NTAs plays an important role in the catalytic activity. Given that the Pd itself is a poor catalyst for the hydrolysis of NaBH₄,^{39, 40} synergistic effect is expected to exist between Co, P and Pd, which enhances the catalytic activity of Co-P-Pd NTAs and accounts for the great activity difference between Co-P-Pd NTAs and Co-P NTAs. As demonstrated in literatures, Pd is believed to contribute to the synergistic effect by working as a promoter metal to efficiently activate Co and P through electronic effects.⁴¹⁻⁴³

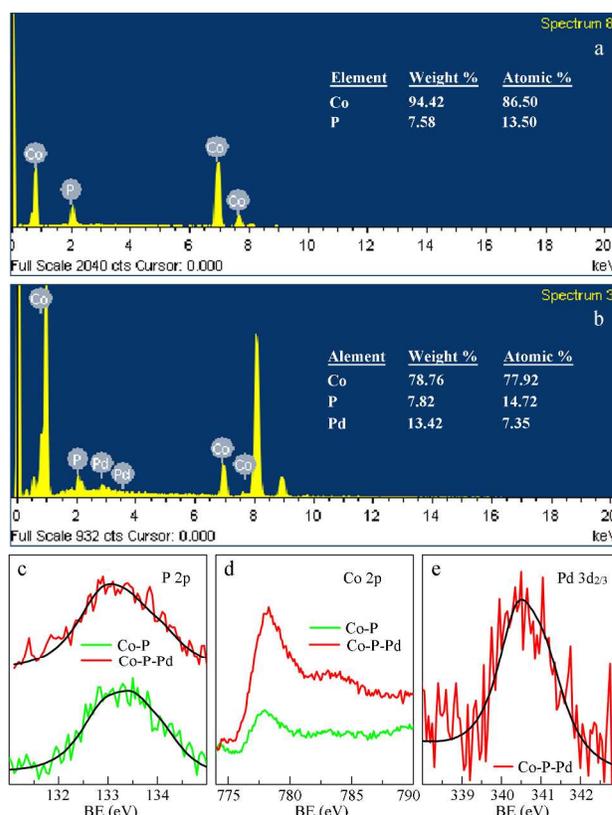


Fig. 2 EDX profiles of (a) Co-P and (b) Co-P-Pd NTAs, and XPS spectra of (c) P 2p, (d) Co 2p of Co-P-Pd and Co-P NTAs and (e) Pd 3d of Co-P-Pd NTAs. Black curves in (c, e) are the corresponding fitting curves.

To further investigate the electronic states and interactions between surface Co, P and Pd atoms, X-ray photoelectron spectroscopy (XPS) spectra of Co-P NTAs and Co-P-Pd NTAs were recorded and presented in Fig. 2c-e. In Fig. 2c, the P 2p peaks centred at 133.1 eV suggest that P, which can promote the Co active sites on catalyst surface,^{21, 44} exists in oxidized state in Co-P NTAs and Co-P-Pd NTAs.^{44, 45} As shown in the XPS spectra of Co 2p (Fig. 2d), the peaks centered at 778.1 and 781.9

eV indicate that Co exists in both metallic (Co^0) and oxidized (Co^{II}) states in Co-P NTAs and Co-P-Pd NTAs.^{44, 46} The oxidized Co probably formed through the oxidation of metallic Co by dissolved oxygen in solution during the fabrication of NTAs.⁴⁷ The oxidized Co, however, can be easily reduced to metallic Co by NaBH_4 during H_2 generation,⁴⁴ and in such a way Co is reactivated to function as highly active catalyst. It is worth noting that the content of oxidized Co relative to metallic Co in Co-P-Pd NTAs is significantly higher than that in Co-P NTAs (cf. Fig. 2d), indicating that the Co atoms in Co-P-Pd NTAs are much more active such that they are prone to oxidation. Given that Co-P-Pd NTAs and Co-P NTAs were prepared under similar experimental conditions, such a Co^{II} content difference may suggest that Pd significantly activates Co and synergistic effect does exist in Co-P-Pd NTAs. The Pd $3d_{3/2}$ spectrum in Fig. 2e shows that Pd, as expected to be stable against ambient oxygen, exists in elemental state (340.4 eV).⁴⁸

Besides the unique, porous nanotube structure and synergistic effect, it is also worth mentioning that by growing the Co-P-Pd NTAs on titanium foil, our catalyst can be easily and completely separated from solution and recycled so that the catalyst cost can be further reduced, which is an advantage over those catalysts in the form of particles or powders,^{12, 22, 49-52} particularly for long-term catalyst operation.

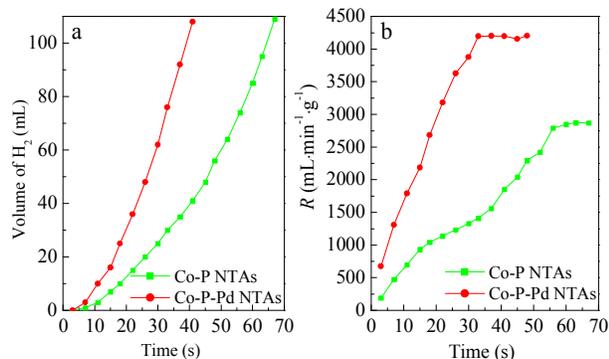


Fig. 4 (a) The volume of generated H_2 and (b) the hydrogen generation rate, R , as a function of time when using Co-P and Co-P-Pd NTAs as the catalysts in a 10 mL of solution of NaBH_4 (10 wt.%) and NaOH (2 wt.%) at 30°C .

The catalytic activities of Co-P-Pd NTAs and Co-P NTAs (as control experiment) were evaluated in hydrogen generation experiments performed in a reactor containing 50 mL of aqueous solution of NaOH and NaBH_4 at 30°C (see more experimental details in Section S3, Supplementary Information). Under optimized experimental conditions (2 wt.% NaOH and 10 wt.% NaBH_4), the volume of generated H_2 as a function of reaction time obtained by hydrolysis of alkaline NaBH_4 with Co-P-Pd and Co-P NTAs catalyst under otherwise identical experimental conditions are recorded and shown in Fig. 4a. A numerical procedure, described elsewhere,⁵³ was utilized to obtain the hydrogen generation rate, R , for all the catalysts, and the results are plotted in Fig. 4b. As shown in Fig. 4, the H_2 generation rate of Co-P-Pd NTAs is significantly faster than that of Co-P NTAs. Moreover, the maximum hydrogen generation rate, R_{max} , of Co-P-Pd NTAs reaches $4216 \text{ mL}\cdot\text{min}^{-1}\cdot(\text{g}^{-1} \text{ catalyst})$, which is higher than that of Co-P NTAs ($\sim 2868 \text{ mL}\cdot\text{min}^{-1}\cdot(\text{g}^{-1} \text{ catalyst})$) by 47%, indicating that our Co-P-Pd NTAs have excellent catalytic

activity towards catalyzing the hydrolysis of alkaline NaBH_4 solution for H_2 generation. As discussed in previous sections, such a significant improvement in performance/catalytic activity can be attributed to the unique porous structure consisting of small nanocrystals and the synergistic effect between Co, P and Pd.

Using the as-prepared Co-P-Pd NTAs as catalyst, the effect of NaOH concentration on the H_2 generation kinetics of the catalytically hydrolysis of NaBH_4 solution (10 wt.%) at 30°C was explored. As shown in Fig. 5, the R_{max} increases remarkably from $3750 \text{ mL}\cdot\text{min}^{-1}\cdot(\text{g}^{-1} \text{ catalyst})$ to a maximum of $4216 \text{ mL}\cdot\text{min}^{-1}\cdot(\text{g}^{-1} \text{ catalyst})$, as the concentration of NaOH increases from 1 to 2 wt.%. Then R_{max} decreases persistently and rapidly to $1260 \text{ mL}\cdot\text{min}^{-1}\cdot(\text{g}^{-1} \text{ catalyst})$ as the concentration of NaOH increases to 10 wt.%. Such deterioration in R_{max} can be attributed to the fact that excessive NaOH can lead to a decrease in the solubility of the NaBO_2 by-product formed in the hydrolysis reaction, which subsequently precipitates from solution, deposits on the surface of Co-P-Pd NTAs, blocks the active site on catalyst surface, and decrease the H_2 generation rate.²⁹

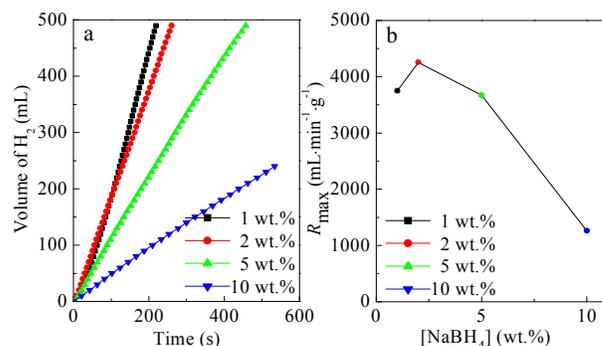


Fig. 5 Effects of NaOH concentration on (a) the volume of generated H_2 and (b) the maximum H_2 generation rate, R_{max} , when Co-P-Pd NTAs were used as the catalyst for the hydrolysis of 10 wt.% NaBH_4 solution at 30°C .

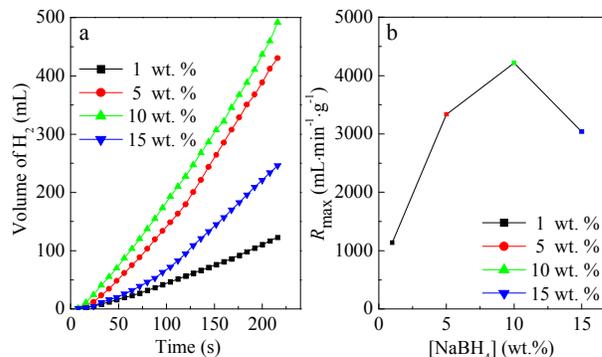


Fig. 6 Effects of the NaBH_4 concentration on (a) the volume of generated H_2 and (b) the maximum H_2 generation rate, R_{max} , when Co-P-Pd NTAs were used as the catalyst for the hydrolysis of NaBH_4 in 2 wt.% NaOH solution at 30°C .

The influence of the NaBH_4 concentration on H_2 generation kinetics at 30°C was also investigated, and the results are shown in Fig. 6. Briefly, R_{max} increases rapidly from 1137 to 4216, and then decreases to $3041 \text{ mL}\cdot\text{min}^{-1}\cdot(\text{g}^{-1} \text{ catalyst})$ as the concentration of NaBH_4 increases from 1 to 10 wt.%, and finally to 15 wt.%. A R_{max} of $4216 \text{ mL}\cdot\text{min}^{-1}\cdot(\text{g}^{-1} \text{ catalyst})$ can be

achieved in a solution of 10 wt.% NaBH₄ and 2 wt.% NaOH, when using Co-P-Pd NTAs as the catalyst. Excessive NaBH₄ (over 10 wt%) is unfavourable for the H₂ generation kinetics, since it leads to increased solution viscosity, inevitably retarded mass transfer in solution and consequently reduced hydrolysis efficiency. Such a trend in our experiments is similar to previous studies.⁵⁴

To check the cyclic stability of our Co-P-Pd NTAs catalyst, recycling experiments were operated at 30 °C in 5 mL of aqueous solution containing 10 wt.% NaBH₄ and 2 wt.% NaOH. The results show that both the total volume of generated H₂ and R_{\max} of the H₂ generation reaction are quite comparable in 5 successive runs (Fig. 7a). In fact, even after 100 runs in the recycling experiments, the total volume of generated H₂ and R_{\max} only decrease slightly (~10%). In fact, we checked the Co-P-Pd NTAs after 100 runs with SEM and TEM and found out that the overall structure of Co-P-Pd NTAs were well preserved (Fig. 7b). All these results indicate that the Co-P-Pd NTAs are robust catalyst for rapid H₂ generation by the hydrolysis of alkaline NaBH₄ solution. However, it is also worth noting that the surfaces of Co-P-Pd NTAs become smoother after 100 runs (Fig. 8b,c), which is likely due to the formation of an oxide layer consisting of the by-products of potassium borate (NaB_xO_y) and boron oxide (B₂O₃) on the catalyst surface during the catalyst recycling.³³ Moreover, cavities can be found in Co-P-Pd NTAs after 100 runs, as shown in Fig. 7b and 7d, which can be rationalized by the fact that few catalyst particles were broken away from the Co-P-Pd NTAs during the filtration and washing process (for catalyst recycling), and/or the H₂ generation process. Both the formation of by-product layer and the loss of catalyst particles are unfavourable for H₂ production, and contribute to the decrease in the total volume of generated H₂ and the R_{\max} of the H₂ generation reaction.

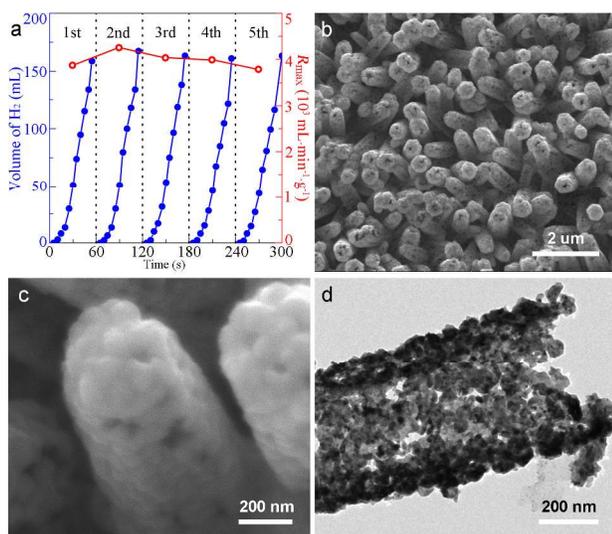


Fig. 7 (a) The volume of generated H₂ over time and R_{\max} of the H₂ generation reaction in 5 successive runs. (b, c) SEM and (d) TEM images of the Co-P-Pd NTAs after 100 runs.

Conclusions

In conclusion, we prepared a novel, inexpensive Co-P-Pd NTA catalysts by introducing Pd to inexpensive Co and P and using

template-assisted electrodeposition approach. The Co-P-Pd NTAs were used to catalyze the hydrolysis of alkaline NaBH₄ solution to produce hydrogen, and the operation conditions were optimized to be 10 wt.% NaBH₄ and 2 wt.% NaOH at 30°C. Under such optimized condition, the Co-P-Pd NTAs showed superior catalytic activity ($R_{\max} \sim 4216 \text{ mL} \cdot \text{min}^{-1} \cdot (\text{g}^{-1} \text{ catalyst})$) to Co-P NTAs catalysts, and good cyclic stability during the recycling experiments. Such excellent performance is attributed to the unique, porous nanotube structures of Co-P-Pd NTAs consisting of small nanocrystals and the synergistic effect between Co, P and Pd. We believe that this low-cost, high-performance Co-P-Pd NTA catalyst should be of interests and importance for portable devices or vehicles that are driven by hydrogen.

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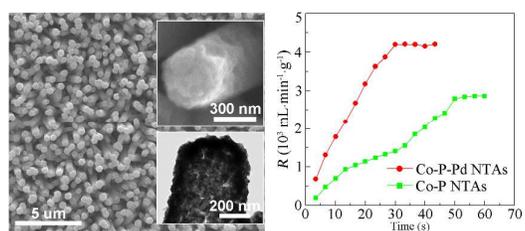
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- † Electronic Supplementary Information (ESI) available: Bath composition and electroplating conditions for fabricating Co-P and Co-P-Pd NTAs, characterization and procedure for the hydrogen generation experiments. See DOI: 10.1039/b000000x/
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