Carbon nanodots modified cobalt phosphate as efficient electrocatalyst for water oxidation

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Received 20 May 2015; revised 22 June 2015; accepted 1 July 2015
Available online 19 August 2015

Abstract

High-activity and low-cost water oxidation electrocatalyst is of fundamental importance for the development of green energy technologies. Here, we demonstrated the carbon nanodots (phosphate functionalized carbon nanodots, PCDs) modified cobalt phosphate (CoPi) composite (CoPi/PCDs) could be served as high-efficiency oxygen evolution reaction (OER) catalyst in both neutral and alkaline conditions with low onset potential and high current density. This kind of improvement activity of CoPi/PCDs composite for OER may be attributed to the synergistic catalytic effect of CoPi and PCDs. In addition, the PCDs layer on the CoPi surface averted the CoPi from dissolution of enhancing the stability of the composite electrocatalyst.

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Keywords: Carbon nanodots; Cobalt phosphate; Oxygen evolution reaction; Neutral condition

1. Introduction

Electrochemical water oxidation is regarded as a key and promising energy conversion in many clean energy technologies, including solar fuel production, rechargeable metal-air batteries and electrolysis cells [1—4]. In this field, the pivotal challenges for enabling water electrolysis are the sluggish oxygen evolution reaction (OER) and the high cost of noble metal catalysts, including iridium (Ir) and ruthenium (Ru) oxides [5—9]. Considerable efforts have been devoted to developing high-efficient and cost-effective alternative catalysts. Recently, some nonprecious metal (Fe, Co, Ni, Mn, etc.)-based OER catalysts, including metal oxides, hydroxides, chalcogenides, selenides and borides have been investigated and demonstrated to be promising OER catalysts under mild reaction conditions [10—13]. Among them, cobalt phosphate (CoPi) as a scalable OER catalyst [14] has specifically drawn much attention, and their high electrocatalytic ability comes from the oxidation from Co2⁺ to Co3⁺ or Co4⁺ species, which results in the formation of high valent Co3⁺—O intermediates [15,16]. However, the stability of CoPi under alkaline conditions during the electrocatalytic process can not satisfy the future energy needs, which is still the critical challenge for their further practical application on high efficient water splitting.

Recently, carbon based materials have attracted much attention due to their potential application in electrochemistry [17,18]. Carbon nanodots (CDs), as a novel class of zero-dimensional (0D) carbon nanomaterials, have recently generated favorable interest owing to their outstanding chemical stability, eco-friendliness, favorable water solubility, and abundance photo-electrochemical properties [19—21]. Notably, CDs with abundant fluorescent properties are proved to be both electron acceptors and electron donors [22,23].

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Peer review under responsibility of The Chinese Ceramic Society.

http://dx.doi.org/10.1016/j.jmat.2015.07.003
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More important, the CDs can be acted as a promising component for the design of diverse composite catalysts. In our previous works, we have demonstrated the design of several complex catalysts (TiO$_2$/CDs, SiO$_2$/CDs, Fe$_2$O$_3$/CDs, NiFe-LDH/CDs and Ag$_3$PO$_4$/CDs) with high photocatalytic and/or electrocatalytic abilities [19,23–25]. On the other hand, phosphorus (with high electron-donating ability) can modify the electron transport properties of carbon, leading to an enhanced electrocatalytic performance [26,27]. Therefore, it may be a good choice to develop the PCDs and CoPi complex catalyst, which could be expected to enhance the electrocatalytic performance and stability as high-efficient electrocatalysts.

In this paper, we reported the design and synthesis of CoPi/PCDs composites, which performed highly catalytic activity with a fairly lower overvoltage and a substantial enhancement of the current density for OER under neutral and alkaline conditions. Moreover, the covering layer of PCDs on the surface of CoPi led to the excellent durability of the composites under neutral and alkaline conditions, making the hybrid a promising candidate in water electrolysis systems.

2. Experimental sections

All reagents were of analytical grade and used without any further purification.

2.1. Preparation of PCDs and NCDs

The pristine CDs were prepared by an electrochemical etching method which was reported by our group [28]. The PCDs were synthesized by our reported method above by using dilute phosphoric acid as electrolyte. The reduced PCDs were prepared by a simple treatment of the obtained PCDs (about 6 nm) with hydrazine hydrate. A 250 mL flask containing 100 mL PCDs solution and 0.1 mL hydrazine hydrate was refluxed with magnetic stirring at 100 °C for 2 h. Then the mixture solution was treated by dialysis for 3 days. Finally, the reduced PCDs were obtained. The NCDs were prepared by heating the CDs with 30% ammonia solution. The solution containing 50 mL CDs and 50 mL ammonia solution was kept in Teflon autoclave at 150 °C for 10 h. The NCDs were collected and kept in air to get rid of the redundant ammonia. Finally, the solution was concentrated to 0.1 mg mL$^{-1}$ by rotary evaporation at 80 °C.

Three kinds of phosphate-modified carbon materials (phosphate-modified graphene, carbon nanotubes and carbon spheres) were prepared by the previous reported methods [29–31].

2.2. Preparation of CoPi/PCDs composites and CoPi

To prepare CoPi/PCDs composites, 5 mL sodium phosphate aqueous solution (0.2 M) and 1 mL cobalt nitrate aqueous solution (0.6 M) were added into 30 mL of PCDs aqueous solution, and followed by adding 5 mL polyvinyl pyrrolidone solution (PVP, 50 mg mL$^{-1}$). The mixture was constantly stirred and irradiated at room temperature for 3 h, and then the obtained CoPi/PCDs were washed several times with deionized water and ethanol. Finally, the sample was dried at 60 °C overnight.

The CoPi was prepared with the same process as above except using deionized water instead of the PCDs aqueous solution. The CoPi/NCDs were prepared by replacing PCDs solution with NCDs. CoPi with other three kinds of phosphate-modified carbon composites were prepared by replacing PCDs solution with different reference materials in 30 mL of deionized water.

2.3. Structural characterization

The scanning electron microscopy (SEM) images were taken on a FEI-quanta 200 (at 20 kV) with energy dispersive X-ray spectroscopy (EDS) analyses. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with a FEI-Tecnai F20 (at 200 kV). The TEM samples were prepared by dropping the solution onto a copper grid with polyvinyl formal support film and dried in air. Fourier Transform Infrared (FT-IR) spectrum was obtained with a Nicolet 360 spectrometer. Raman spectrum was collected on an HR 800 Raman spectroscope (J Y, France) equipped with a synapse CCD detector and a confocal Olympus microscope. UV–visible spectrum was measured with an Agilent 8453 UV–vis Diode Array Spectrophotometer. The photoluminescence (PL) study was conducted with a Horiba JobinYvon (FluoroMax 4) Luminescence Spectrometer and the fluorescence lifetime was measured by using a FluoroLog 3-211-TCSPC system. The X-ray photoelectron spectroscopy (XPS) was obtained by using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatized Mg K$_\alpha$ X-ray. The X-ray diffraction (XRD) patterns were obtained by an 8X/Pert-ProMPD (Holand) D/ max-$\gamma$A X-ray diffractometer with Cu K$_\alpha$ radiation ($\lambda = 0.154178$ nm).

2.4. Electrochemical characterization

Electrochemical measurements were performed at ambient temperature in nitrogen-saturated solutions with an electrochemical analyzer (CHI 920C, CH Instruments Co. Ltd., China). A conventional three-electrode electrochemical cell was used, including a glassy carbon electrode (GCE, geometric area = 0.07 cm$^2$) as the working electrode, an Ag/AgCl (saturated KCl) electrode as the reference electrode and polished platinum wire as the counter electrode. The GCE was polished to a mirror finish and thoroughly cleaned before use. To prepare the working electrode, 1.4 mg catalyst was dispersed in 800 μL of deionized water, and then the mixture was given an ultrasonic treatment for 30 min to generate a homogeneous solution. After that, 10 μL of catalyst solution was dropped onto the GCE followed by coating with 4 μL of Nafion solution (0.5 wt%), which was allowed to dry in air, leading to the catalyst loading about 0.2 mg cm$^{-2}$. The electrolyte solutions were 0.1 M potassium phosphate at pH 7 and
In the followed study, the morphology of as-prepared CoPi/PCDs composites was identified by scanning electron microscopy (SEM) and TEM. The SEM image of the CoPi/PCDs in Fig. 2a shows that the composites display uniformly spindle-like morphology with 1.5–2.0 μm in size. The rough edges of one particle CoPi/PCDs in the typical TEM image of Fig. 2b shows the thin surface layer composed of PCDs covered the CoPi particles, which confirms the formation of CoPi/PCDs composites. In contrast, the pure CoPi shows a smooth surface, which displays an obvious difference in the morphology between CoPi/PCDs composites and CoPi (Fig. S5). The further detailed EDS element mappings and profile reveal the CoPi/PCDs composites are composed of C, O, and P elements (Figs. S6 and S7), and their elements are all uniformly distributed in the composites. Fig. 3a exhibits the typical X-ray diffraction (XRD) patterns of CoPi and CoPi/PCDs composites. The characteristic peaks shown in the black curve can be well indexed to Co3(PO4)2·8H2O (JCPDS card no. 33-0432), which was formed due to the precipitation of Co2+ ions by the phosphate anions [37]. The XRD patterns of the CoPi/PCDs for the red curve reveal no obvious change in crystalline structure compared to that of CoPi. Owing to the small amount of PCDs in the CoPi/PCDs composite, the characteristic peak for carbon is hardly to be observed. Fig. S8 shows the high resolution XPS spectra of Co 2p and P 2p of the sample are shown in Fig. S9. As shown in Fig. S9a, it can be observed that the two characteristic peaks of Co 2p at about 781 and 797 eV; the former represents Co2+(2p3/2), while the latter represents Co3+(2p1/2). CoPi/PCDs and CoPi have similar Co2+ and Co3+ band intensities. Fig. 3b shows the FT-IR spectra of PCDs and the CoPi/PCDs. In the black line of PCDs, the peaks at 3442 and 1632 cm⁻¹ correspond with the O−H and C−O stretching vibrations, respectively [29,34]. The peaks at 1399 and 1108 cm⁻¹ show the asymmetric and symmetric stretching vibrations of C=O−C and P−O bonds, respectively [38–40]. Compared with PCDs, the peak at 1399 cm⁻¹ shows a shift of ~35 cm⁻¹ in the CoPi/PCDs composites (red line), which may be due to the formation of a new Co−O−C species besides the pristine C=O−C species [25,38]. These results further suggest that the PCDs have additional strong interaction (i.e., chemical bonding) with CoPi rather than simply mix with it or normal physical absorption. In addition, the peaks in the range of 500−1000 cm⁻¹ of the red line belong to the CoPi component in the FT-IR curve of the CoPi/PCDs composites [47]. As shown in Fig. 3c, except for the peaks coming from the CoPi at 969 and 1056 cm⁻¹ in the Raman spectrum (black trace) [41], two characteristic peaks located at 1334 and 1610 cm⁻¹ are clearly observed in the Raman spectrum of CoPi/PCDs composites (red trace), corresponding to the typical D- and G-band of carbon, respectively [24,39]. The photoluminescence (PL) of PCDs has been proved to quench efficiently by either electron acceptors or electron donors (Fig. S10), which indicates that PCDs are both excellent electron donors and electron acceptors. The PL spectra of PCDs and the CoPi/PCDs composites in Fig. 3d show the luminescence of PCDs.

3. Results and discussion

The transmission electron microscopy (TEM) image of PCDs (Fig. 1a) shows uniformly dispersed particles of ~6 nm in diameter (size distribution of PCDs shown in Fig. S1). The energy dispersive X-ray spectroscopy (EDS) spectrum in Fig. S2 shows the PCDs consist of C, O, and P elements. The high resolution TEM (HRTEM) image of PCDs (Fig. 1b) exhibits the crystal lattice spacing of approximately 0.212 nm, which agrees well with the (100) lattice planes of graphitic carbon [32]. As shown in Fig. S3, the XRD profile of PCDs shows a broad characteristic peak of carbon at approximately 24°, which is consistent with the HRTEM analysis. The UV–visible spectrum (red line) of PCDs in Fig. 1c displays an absorption peak at 245 nm, indicating the π−π* transition of aromatic sp² domains [21]. The Raman spectrum (black line) in Fig. 1c reveals two conspicuous peaks at 1334 and 1610 cm⁻¹, representing the typical D- and G-band of carbon materials, respectively [27]. The I_D/I_G peak intensity ratio obtained for PCDs is about 1.13, suggesting the presence of structural defects and disorders within the material [29]. X-ray photoelectron spectroscopy (XPS) was further performed to analyze the chemical environment of various elements in PCDs. From the XPS survey spectrum of PCDs (Fig. S4), the P, C and O elements are detected, which consist with the EDS analysis. The high-resolution P 2p peak located at 133.9 eV in Fig. 1d should be assigned to the P−O bonding [33], which indicated the successful modification of phosphate radical on the surface of CDs. As shown in Fig. 1e, the C1s peak can be resolved into three different component peaks, representing C−C (284.7 eV), C−O/C−O−C (286.2 eV) and O=O−C (288.7 eV) groups, respectively [34,35]. The O1s spectrum (Fig. 1f) can be divided into three main types of chemical states. The peaks at 533.9 eV and 531.5 eV are ascribed to O−C and C−O bonding, respectively [35]. While, the peak at 532.8 eV is associated with P−O bonding [36], which is also in agreement with the P 2p peak in phosphate radical.

0.1 M KOH at pH = 13, which were degassed by bubbling with high-purity nitrogen for at least 30 min prior to the start of experiments. The solution resistance in electrochemical experiments was corrected by the iR compensation. The cyclic voltammetry (CV) and linear sweep voltammograms (LSV) measurements were performed with the scan rate of 5 mV s⁻¹. Tafel plots were measured with the scan rate of 0.1 mV s⁻¹. The potentials were converted to Normal Hydrogen Electrode (NHE) scale by using E (NHE) = E (Ag/AgCl) + 0.197 V. Additionally, the overpotential values were calculated by the difference between the iR corrected potential (V = V_app − iR) and the thermodynamic potential of water oxidation. The chronoamperometry tests were performed at a constant potential (1.4 V, vs NHE) at pH = 7. The electrochemical impedance spectroscopy (EIS) measurements were carried out from 10,000 to 0.01 Hz with the AC voltage amplitude of 5 mV at an open circuit in 0.1 M potassium phosphate solution at pH = 7.
effectively quenches in the CoPi/PCDs composites. The obvious quenching of PL intensity proves that an ultrafast electron transfer process exists in the CoPi/PCDs composites system.

To assess the electrochemical catalytic properties of the CoPi/PCDs, the composites were dropped onto a glassy carbon electrode (GCE) followed by coating with Nafion solution. The cyclic voltammetry (CV) measurement was carried out at a scan rate of 5 mV s$^{-1}$ in a 0.1 M potassium phosphate solution (pH = 7). The same measurements were also performed for PCDs, CoPi and bare glassy carbon (BGC) electrodes as control. The water oxidation occurred at potential over 0.82 V (vs. NHE, the theoretical OER potential at pH = 7) according to the following formula: 1.23 V$ - 0.059$ (pH) V vs. NHE [41]. Fig. 4a shows the CV curves of CoPi/PCDs, CoPi, PCDs and BGC. The OER onset potential, which reflects the resistance of the catalysts, can be determined by the extrapolation of the OER catalytic curves. As can be seen from the red trace in Fig. 4a, the CoPi/PCDs composites show the onset potential of a large anodic current upon reaching the potential of water oxidation at ca. 1.09 V (vs. NHE), which is superior to the previous studies (Table S1) [42–46]. In contrast, both BGC

Fig. 1. TEM (a) and HRTEM (b) images of PCDs. (c) UV–vis absorption (red line) and Raman (black line) spectra of PCDs. High-resolution XPS (d) P 2p, (e) C 1s and (f) O 1s spectra of PCDs.
(pink trace) and PCDs (blue trace) turn out to be catalytically inactive towards OER even when the potential extends to 1.5 V (vs. NHE). The above discussion proves that the inherent characteristic of PCDs shows a little contribution for the OER catalytic activity of the complex. So, the CoPi and PCDs among the composites reveal the synergistic catalysis effect. Compared the PCDs and BGC with CoPi/PCDs, the composites exhibit remarkable enhancement of the current intensity. Due to the oxygen evolution ability of CoPi itself, we further compare the OER performance of the CoPi/PCDs composite with CoPi (black trace). It can be seen that the CoPi gives an OER onset potential of ca. 1.24 V (vs. NHE), which is 150 mV higher than that of CoPi/PCDs electrode. The negative shift of onset potential of CoPi/PCDs was unambiguously attributed to the presence of PCDs in the composites. The CoPi/PCDs composites also exhibit distinct enhancement of the current intensity compared with CoPi, which may be due to the introduction of PCDs. Moreover, the CoPi/PCDs composite also displays intensive electrocatalytic activity in terms of current density and onset potential compared with pure composite.

![Fig. 2. SEM (a) and TEM (b) images of CoPi/PCDs composites.](image)

![Fig. 3. (a) XRD patterns of CoPi and CoPi/PCDs composites. (b) FT-IR spectra of PCDs and CoPi/PCDs composites. (c) Raman spectra of CoPi and CoPi/PCDs composites. (d) PL spectra of PCDs and CoPi/PCDs composites.](image)
CoPi and PCDs in 0.1 M KOH (Fig. 5a). It also can be seen that the CoPi/PCDs composite performs comparable OER activity with the RuO$_2$ catalyst. The current density of 10 mA cm$^{-2}$ can be achieved at a small overpotential of 0.35 V for CoPi/PCDs composites, which is a metric relevant to solar fuel synthesis [47]. As control, the CoPi catalyst synthesized without PCDs affords much lower OER activity and PCDs alone also affects the OER activity rarely.

In order to ascertain the advantage of the CoPi/PCDs composites, it is necessary to further evaluate their catalytic performance of OER by using the Tafel plot under neutral condition. As calculated from Fig. 4b, the Tafel slope of pure CoPi is 62 mV per decade, while the CoPi/PCDs composites affords a small Tafel slope down to 59 mV per decade, which is also lower than those of previously reported Co-based catalysts for OER under neutral condition (Table S1). This

Fig. 4. (a) CV curves of CoPi/PCDs, CoPi, PCDs and BGC electrodes. The vertical dashed line at 0.82 V for theoretical OER potential at pH = 7. (b) Tafel plots of CoPi and CoPi/PCDs catalysts. (c) CV curves of CoPi/PCDs catalyst under the 1st and 100th cycle. (d) Chronamperometry curves of CoPi and CoPi/PCDs catalysts.

Fig. 5. (a) LSV curves of CoPi/PCDs, CoPi, PCDs and RuO$_2$ electrodes. (b) Stability test of CoPi/PCDs catalyst. The vertical dashed line at 0.46 V for theoretical OER potential at pH = 13.
observed Tafel slope is a characteristic of an O\textsubscript{2} evolution mechanism and can be regarded as one electron pre-equilibrium transfer process followed by a rate limiting reaction step, which facilitates the formation of the O–O bond [16]. The observed decrease in the Tafel slope values also demonstrates the synergistic enhancement of the OER activity taking effect in the CoPi/PCDs composites.

To illustrate the stability of CoPi/PCDs composites, we further performed continuous OER CV measurements both under neutral and alkaline conditions. In the 0.1 M potassium phosphate solution, as shown in Fig. 4c, the CV current of CoPi/PCDs composites remains constant after 100 cycles between the same potential ranges. After 1500 cycles of continuous operation, the CoPi/PCDs catalyst still shows a little negligible decay in the electrocatalytic current density (Fig. S11), indicating the excellent OER activity with long-term stability. Additionally, the chronocapacitometry curves at a constant potential (1.4 V, vs. NHE) in Fig. 4d also indicates the CoPi/PCDs catalyst merely shows a slight degradation (4.7\%) of current density within a 2700 s period, while the pure CoPi catalyst shows an evident degradation (27.4\%). Fig. 5b reveals after 100 cycles in the 0.1 M KOH solution, the CoPi/PCDs catalyst affords almost the same LSV curve as the initial cycle, only with a negligible drop of the current density. These results show the CoPi/PCDs catalyst exhibits superb stability for OER under neutral and alkaline conditions. In addition, the SEM image and XRD patterns of the CoPi/PCDs composites shows no obvious change after long-time test, which also confirms that the structure of composites remains nearly no change (Fig. S12).

In the followed study, the electrochemical impedance spectroscopy (EIS) measurements were further performed to confirm the influence of PCDs on CoPi among the as-synthesized composites. The Nyquist plots of pure CoPi and CoPi/PCDs samples are shown in Fig. 6. The charge transfer resistance (R\textsubscript{ct}) is fitted by the Nyquist plots with Zsimpwin software. By fitting the EIS data, the obtained R\textsubscript{ct} value of CoPi/PCDs (2.6 k\Omega) is much lower than that of pure CoPi (16.3 k\Omega). The lower R\textsubscript{ct} value of CoPi/PCDs indicates a faster reaction rate [48], suggesting that CoPi/PCDs composites catalyst holds lower charge transfer resistance than that of pure CoPi. These results are in accordance with the much higher current density of CoPi/PCDs in the CV curves in Fig. 4a and can be attributed to the fluent electron transfer between PCDs and CoPi during the electrocatalytic reaction.

Next we evaluated the effects of the functional groups on the catalytic activities of CDs. As shown in Fig. 7a, CoPi/NCDs composites (red curve) exhibit lower activity compared with CoPi/PCDs, indicating that the phosphate radical on PCDs should be a key factor for its high OER catalytic ability. In addition, we also utilized the hydrazine hydrate as the reductant to eliminate the hydroxys and carboxyls of PCDs to verify their catalytic effects. As shown in the blue curve (Fig. 7a), the OER activity of the CoPi and the reduced PCDs composite are poorer when compared with that of CoPi/NCDs composites (black curve), which proves that the oxygen-containing groups (including phosphate radical, hydroxide radical and carboxyl groups) promotes the interaction between PCDs and CoPi and further improves the OER performance. In order to further verify the influential role of PCDs in the composites, other phosphate functionalized carbon materials (phosphate-modified graphene, carbon nanotubes and carbon spheres) were prepared and used for comparison. As shown in Fig. 7b, three kinds of synthesized hybrids with CoPi exhibit worse OER activities both in current density and onset potential than that of CoPi/PCDs composites, which prove that the PCDs as vital component in the hybrids improves the OER performance for the strong interaction with CoPi. We also investigated different sizes of phosphate functionalized carbons to form composites with CoPi using the same preparation method and under the same test condition for comparison. As shown in Fig. S13, the increase of the size of phosphate functionalized carbons decreased the electrocatalytic activity. The CoPi/PCDs composites exhibit the best current density and earliest OER onset. Thus, we can conclude that the PCDs and CoPi display the synergistic catalysis effect of the electrocatalytic activity toward OER.

Based on the results and discussions above, the possible reasons for the enhanced OER activity of CoPi/PCDs composites may be attributed to the factors as follows. Basically, the superior catalytic activity for OER can be ascribed to the intrinsic property of CoPi and further enhanced by the synergistic effect between CoPi and PCDs. As shown in Fig. S10, the luminescence decays of PCDs by either electron acceptors (2, 4-dinitrotoluene) or electron donors (N, N-diethylaniline, DEA) confirm that PCDs can act as both electron donors and electron acceptors, which means the electrons can be easily transferred to the surface of CoPi, and the redundant electrons on CoPi can also be easily transferred to PCDs. The ultrafast electron transfer process in the CoPi/PCDs system restrains the electron–hole recombination and effectively promotes the formation of peroxide species, which act as the precursor of O\textsubscript{2} molecules. The combination of PCDs and CoPi also endues the CoPi/PCDs composites catalyst with high electrical conductivity, which also affords the high activity during the OER performance. The abundant

![Fig. 6. Nyquist plots of CoPi and CoPi/PCDs from 10000 to 0.01 Hz measured in 0.1 M potassium phosphate solution (pH = 7).](image-url)
surface functional groups on PCDs including hydroxyls, carboxyls and phosphates groups promotes the formation of CoPi/PCDs composites due to the additional strong interaction (i.e., chemical bonding) between PCDs and CoPi rather than the simply mix and/or physical absorption. Moreover, the phosphate radicals on both PCDs and CoPi lead to the excellent compatibility between them, which are beneficial to the combination of the hybrid and ensure the stability during the long-term test.

4. Conclusions

We demonstrated the design and fabrication of CoPi/PCDs composite catalyst, and then their high OER activity in neutral phosphate electrolyte was distinctly observed from the reduced onset potential, increased current density, small Tafel slope, and enhanced stability. In comparison with CoPi, the CoPi/PCDs composites exhibited prominently better OER activity for the interaction between CoPi and PCDs, and extraordinary stability under both neutral and alkaline conditions after long-time test owing to the protection of the covering layer of PCDs on the CoPi surface. Our results also will provide a potential alternative approach to get the high efficient and low-cost electrocatalysts by replacing the components in present system, such as introducing new metal nanoparticles or metallic oxide, and other heteroatom doped carbons.

Acknowledgments

This work was supported by Collaborative Innovation Center of Suzhou Nano Science and Technology, the National Basic Research Program of China (973 Program) (2012CB825803, 2013CB932702), the National Natural Science Foundation of China (51422207, 51132006, 21471106), the Specialized Research Fund for the Doctoral Program of Higher Education (20123201110018), a Suzhou Planning Project of Science and Technology (ZXG2012028), and a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jmat.2015.07.003.

References


Fig. 7. (a) CV curves of CoPi/PCDs, CoPi/NCDs and CoPi/PCDs reduced with hydrazine hydrate. (b) Comparisons of CoPi with different phosphate functionalized carbon materials for the OER activity.


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