Journal of Materials Chemistry A



View Article Online

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COMMUNICATION

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Cite this: J. Mater. Chem. A, 2017, 5, 16580

Received 31st May 2017 Accepted 6th July 2017

DOI: 10.1039/c7ta04719c

rsc.li/materials-a

Electrodeposited cobalt phosphide superstructures for solar-driven thermoelectrocatalytic overall water splitting[†]

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We demonstrate solar-driven thermoelectrocatalytic water splitting using unique cobalt phosphide (Co₂P) sheet-on-leaf superstructures. Co₂P is synthesized through a one-step room-temperature electrodeposition technique that precludes the release of toxic PH₃ gas, where the *in situ* process warrants electron and mass transfer between Co₂P and the underlying substrate for effective electrocatalytic reactions. Facilitated by thermionic energy harvested from sustainable solar irradiance conversion, the electrocatalytic behaviours of Co₂P are remarkably increased. These superstructures are endowed with a higher electrical conductivity and electrochemical surface area, reduced activation energy and enhanced solar-to-heat conversion efficiency to accelerate electrocatalysis.

"Thermoelectrochemical" systems in a broad sense integrate thermal energy into electrochemical cells, where elevation of temperature usually enhances the entropy of chemical reactions as well as the thermodynamics and kinetics of the electron transfer process, hence surpassing the performances of either thermochemical or electrochemical reactions.^{1,2} Extensive heat sources have been adopted for isothermal or non-isothermal methods to achieve appropriate temperatures, such as direct bulk heating, laser heating methodologies^{2,3} and so forth. In view of their energy demands and high equipment cost, directly harvesting the abundant and inexhaustible sunlight by solar thermal techniques provides an inexpensive and competitive way to generate heat.4-8 The challenges to be addressed are, firstly, the design of effective reactors that are capable of converting sunlight into thermal energy to be readily utilized, and secondly, the pursuit of nanomaterials or nanostructures with

both high thermal conductivity and superior electrochemical responses to maximize thermoelectrochemical efficiency.

Transition metal phosphides (TMPs) interstitially alloyed from transition metals and phosphorus *via* M–P covalent bonds yield electronic structures around the Fermi level,⁹ which can serve as excellent thermal and electrical conductors.^{10–12} Recent reports have identified TMPs as highly active non-noble-metal electrocatalysts to split water into hydrogen gas, a clean and sustainable fuel for the future.^{13–22} However, the current synthetic methods of TMPs suffer from different drawbacks, for instance, vapour-phase deposition approaches involve multistep phosphidation that is accompanied by the release of flammable and toxic phosphine (PH₃) gas from thermal decomposition,^{23–29} while phosphate salt reduction methods require a high processing temperature up to 900 °C.^{30,31}

With this in mind, we describe herein a solar-driven thermoelectrocatalytic system for overall water splitting using cobalt phosphide (Co₂P) sheet-on-leaf superstructures, assisted by a simple passive optics design with a parabolic reflector to convert natural sunlight into heat. Co₂P is synthesized via a one-step room-temperature electrodeposition technique that enables facile incorporation of phosphorous atoms into cobalt lattices and accordingly averts the exposure to PH3 gas and high-temperature synthesis. The in situ deposition warrants intimate interfacial contact between Co2P and the underlying nickel foam (NF) substrate, thus favouring electron and mass transport to secure an effective binder-free electrocatalyst. Significantly, the electrocatalytic kinetics of both hydrogen and oxygen evolution reactions (HER and OER) are dramatically enhanced, as modulated by the thermal energy harvested from the sun. The increased electroactivities arise from the unique superstructures that afford a higher electrical conductivity and electrochemical surface area, lowered activation energy and increased solar-to-heat conversion. This proof-of-concept proposition that combines solar energy with electrochemistry will motivate the design of viable and costeffective thermoelectrochemical devices, and further bring about unforeseen and broad applications into other prospective thermoelectric, thermophotovoltaic and catalytic fields.

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ta04719c

The electrodeposited cobalt phosphides fully covering NF surfaces present a unique morphology of homoepitaxially grown leaf-like superstructures that are uniformly coated by a thin layer of nanosheets (Fig. 1a-c). The TEM image apparently shows a well-defined branched leaf pattern with the leaflets enveloped in an outer layer (Fig. 1d and e). The HRTEM image indicates lattice fringes with an interplanar distance of 0.21 nm for both inner and outer areas (Fig. 1f), implying identical chemical compositions across the entire superstructures. Powder XRD analysis reveals three diffraction peaks at 2θ $= 41.6^{\circ}, 44.5^{\circ}$ and 47.4° (Fig. 1g), indexed to the (201), (211) and (031) crystalline planes of orthorhombic Co₂P (JCPDS card no. 32-0306),³² in which the (211) phase corresponds to the lattice spacing of 0.21 nm. Subsequently, the chemical information of these cobalt phosphides is obtained by using XPS spectra (Fig. 1h and i). The peaks at 778.5 eV in the Co 2p region and 129.4 and 130.5 eV in the P 2p region are ascribed to the binding energies of Co and P in Co₂P, respectively, whereas 780.5 and 132.5 eV are attributed to the oxidized cobalt and phosphorus species, respectively, likely arising from the superficial oxidation of Co₂P exposed to air. Notably, the binding energy of Co exhibits a positive shift with respect to metallic Co (778.2 eV), while that of P exhibits a negative shift as compared to elemental P (130.2 eV), suggesting the existence of electron transfer between Co and P.33,34 The EDX spectrum also corroborates the presence of Co, P and O elements (Fig. S3[†]). Collectively, the successful synthesis of Co₂P with sheet-on-leaf superstructures via a one-step room-temperature electrodeposition approach is demonstrated.

The formation mechanism of the Co_2P superstructures is explored. As illustrated in Fig. 2a, a large number of electrons are generated when a negative potential is applied, which accumulate on the surfaces of NF, the working electrode. Cobalt cations (Co^{2+}) and hypophosphite ($H_2PO_2^{-}$) anions in the solution react with the electrons and are reduced to their respective atomic forms:^{35,36}

$$\mathrm{Co}^{2^+} + 2\mathrm{e}^- \to \mathrm{Co} \tag{1}$$

$$H_2PO_2^- + 2H^+ + e^- \rightarrow P + 2H_2O$$
 (2)



Fig. 1 (a–c) Low- and high-magnification SEM images, (d and e) TEM and (f) HRTEM images, (g) XRD spectrum, and (h) Co 2p and (i) P 2p high-resolution XPS spectra of the as-synthesized Co_2P .



Fig. 2 (a) Schematic illustration of Co_2P formation mediated by electrodeposition. Morphology evolution of $Co_2P(C)$ at different deposition intervals of (b) 0.5, (c) 1, (d) 2 and (e) 5 min (scale bar: 500 nm).

The reduced atoms are adsorbed on the NF surfaces, where P atoms diffuse and incorporate into Co crystal lattices to form a Co–P phase,^{36,37} ultimately giving rise to cobalt phosphides:

$$2Co + P \to Co_2P \tag{3}$$

The formulation of the cobalt phosphides is determined to be Co₂P on the basis of the aforementioned analysis. The morphology evolution at different deposition intervals is recorded (Fig. 2b-e). Initially, the as-formed Co₂P nucleates into scarcely distributed irregular particles of <500 nm, which grow into flower-like clusters built up from nanoflakes. As the electrodeposition continues, these nanoflakes anisotropically grow larger and thicker, further transforming into quasi-leaf structures that are partially covered by thin nanosheets. The sheeton-leaf superstructures are eventually achieved when the electrodeposition time reaches 10 min (Fig. 1a). Comparatively, bare NF immersed in the same electrodeposition solution without an applied potential produces random morphologies (Fig. S4[†]), confirming that the Co₂P superstructures are mediated by electrodeposition. Regardless of the anions of cobalt precursors, electrodeposition from cobalt acetate and cobalt nitrate, which are labelled Co₂P(A) and Co₂P(N), creates branched leaf structures as well, yet their surfaces are smooth without nanosheets (Fig. S5 and S6[†]). This electrodeposition approach is generic in synthesizing a series of metal phosphides with different ensembles (Fig. S7[†]) and can be applied to various metal substrates, e.g. copper foil (Fig. S8[†]).

These Co₂P superstructures manage to serve directly as electrocatalysts for overall water splitting. The volumes of the generated gases, confirmed to be hydrogen and oxygen by gas chromatography, respectively, are constantly kept at 2:1 (Fig. S9†). Their electrocatalytic performances are evaluated, in which the current densities (*j*) are normalized by geometric areas of the electrodes. As shown in Fig. 3a, all Co₂P electrodes outperform bare NF in current densities across the potentials,



Fig. 3 (a) LSV curves, (b) HER Tafel plots, and (c) EIS spectra of different Co_2P structures. (d) CV curves of $Co_2P(C)$ at scan rates of 10, 20, 50, 100 and 200 mV s⁻¹. (e) Charging current density differences of the Co_2P plotted against the scan rates.

demonstrating their good HER and OER responses. To deliver a current density of 10 mA cm⁻², Co₂P(C) requires a lower overpotential (n) of 108 mV for the HER and 440 mV for the OER than ca. 170 mV and 480 mV of both Co₂P(A) and Co₂P(N), showing its highest electrocatalytic activity towards hydrogen and oxygen evolution. The fitted Tafel plots derived from $\log(j) \sim \eta$ indicate slopes as small as 69 and 78 mV dec^{-1} for the HER and OER, respectively (Fig. 3b and S10[†]). The Co₂P(C) electrode exhibits superior HER performance to most of the recently reported metal-phosphide-based electrocatalysts measured in alkaline electrolytes (Table S2[†]). Essentially, the occurrence of electron transfer between Co and P demonstrates that the negatively charged P centers can act as the proton acceptor, while the positively charged Co centers as the hydride acceptors, functioning as active sites for the HER and OER, respectively.38-40 The higher electroactivity of Co₂P(C) possibly originates from its secondary nanosheets that provide more interconnected networks for faster electron mobility and further more effective electrode kinetics.41-43 As validated by their EIS analysis in Fig. 3c, the smallest semicircle diameter of Co2P(C) indicates its lowest charge transfer resistance amongst the three cobalt phosphides.44,45 Moreover, the electrochemical double layer capacitances (C_{dl}) of Co₂P(C) is calculated to be 18.6 mF, approximately three times larger than 6.7 and 5.5 mF of Co₂P(A) and Co₂P(N), respectively (Fig. 3d, e and S11⁺), indicating its highest electrochemical surface area (ECSA). To clarify the uniqueness of the sheet-on-leaf superstructures, we have also synthesized a series of different Co₂P structures, typically nanosheet clusters, under the same electrodeposition conditions for comparison (Fig. S12-S14[†]). These clusters exhibit a larger overpotential of 191 mV and a Tafel slope of 106 mV dec⁻¹ for the HER, and a lower C_{dl} of 2.1 mF. Hence, the sheet-on-leaf superstructures are endowed with a higher electrical conductivity and ECSA than other ensembles for enhanced electrocatalytic performances. Moreover, $Co_2P(C)$ shows good durability with the current density well maintained (Fig. S15[†]).

Finally, a solar-to-heat conversion process is performed in the electrocatalytic cell by harnessing natural sunlight with a simple parabolic solar concentrator, aiming at accelerating the electrocatalytic kinetics. Fig. 4a depicts the design of the thermoelectrocatalytic reactor involving an underlying parabolic reflector that concentrates sunlight onto a vial filled with KOH electrolyte. The outdoor time-dependent solar intensity and the corresponding temperatures of the KOH electrolyte are displayed in Fig. 4b, based on which the electrocatalytic activities of $Co_2P(C)$ are concurrently measured. The solar intensity fluctuates in the range of 70–95 mW cm⁻² due to variable cloud cover, leading to a temperature increase from 25 to 65 °C in 40 min by virtue of the parabolic reflector, whereas the KOH solution measured strictly under identical conditions without the reflector reaches the maximum temperature of 37 °C only. Fig. 4c shows the polarization curves of the $Co_2P(C)$ electrode measured from the thermoelectrocatalytic reactor under the real sun (the applied potentials are converted to the RHE with the consideration of the temperature effect on the SCE). The HER activity of $Co_2P(C)$ is found to be greatly boosted, which is evidenced by higher current densities across all potentials and gradually decreased overpotentials from 108 mV (25 °C) to 68 mV (65 °C). Similar OER improvement at elevated temperatures



Fig. 4 (a) Schematic illustration of the thermoelectrocatalytic reactor. (b) Outdoor time-dependent solar intensity and temperature curves of the KOH solution with and without a parabolic reflector. (c) HER LSV curves of Co₂P(C) measured at different temperatures of KOH solution heated by sunlight. Inset shows the decrease of overpotential at j = 10 mA cm⁻² with the increase of temperature. (d) Semilogarithmic dependence of current density *versus* temperature (Arrhenius plots) at the overpotentials of 50, 100, 150 and 200 mV. (e) Linearly fitted activation energy curve of Co₂P(C). (f) Infrared images of Co₂P(C) and bare NF irradiated at 0.5, 1, 2 and 4 min and (g) temperature increase of Co₂P(C)/NF and bare NF measured under ambient conditions.

is also observed (Fig. S17†). The overpotentials of the overall water splitting system also decline with the temperature increase, close to the sum of respective HER and OER overpotentials at different temperatures (Fig. S18†). To justify the thermo-effect on electrocatalysis, direct heating of KOH solution to the same temperatures is carried out. The temperature increase results in the decrease of HER and OER overpotentials (Fig. S19†), simulating the solar-to-heat conversion scenario. Moreover, a full-spectrum LED lamp is used to illuminate the $Co_2P(C)$ electrode for electrocatalysis at room temperature. The polarization curve remains almost unchanged compared to the non-illumination case (Fig. S20 and S21†), excluding the light influence in electrocatalysis. Therefore, the enhanced electrocatalytic HER and OER behaviours of $Co_2P(C)$ are evidently associated with the heat converted from sunlight.

As reported, the efficiency of electrocatalytic water splitting is impeded by the slow kinetics of the OER that involves the transfer of four electrons and protons over a large thermodynamic potential (1.23 V).^{46,47} The introduction of heat is expected to speed up the sluggish reactions by increasing the entropy and accelerating electron transfer of the electrocatalytic system.^{1,2} The activation energy (E_a) at $\eta = 0$ is a key factor to assess the electrocatalytic performance, which can be evaluated by a modified Arrhenius equation:^{1,48}

$$j = A e^{-E_a/RT} \tag{4}$$

where A is the pre-exponential factor, R is the gas constant and T is the temperature (kelvin). Derived from the LSV curves in Fig. 4c, Arrhenius plots displaying the semilogarithmic dependence of current densities versus temperature at different overpotentials of 50, 100, 150 and 200 mV are plotted. The current densities and temperatures exhibit a linear relationship at varied overpotentials (Fig. 4d). Accordingly, E_a ($\eta = 0$) of Co₂P(C) is calculated to be 25.91 KJ mol⁻¹ for the HER (Fig. 4e) and 65.20 KJ mol⁻¹ for the OER (Fig. S17[†]), respectively, much lower than 52.38 KJ mol⁻¹ and $80.94 \text{ KJ mol}^{-1}$ of bare NF (Fig. S22 and S23[†]), demonstrating that the Co₂P(C) electrode needs to overcome reduced energy barrier to initiate electrocatalytic reactions. To elucidate the thermoresponses of the superstructures, the temperature evolution of $Co_2P(C)$ and bare NF under a solar simulator (100 mW cm⁻²) is recorded by infrared imaging (Fig. 4f and g). The temperatures of both samples ascend with the illumination time, but $Co_2P(C)$ constantly exhibits 6-8 °C higher temperature than NF throughout the irradiation. The UV-vis spectra (Fig. 4h) show that the absorption edge of Co₂P(C) dramatically extends to beyond 1000 nm, while that of bare NF is located at around 500 nm, suggesting that $Co_2P(C)$ is capable of utilizing and then converting more sunlight to heat under solar irradiation. Furthermore, by virtue of the superstructures, $Co_2P(C)$ can efficiently preserve the converted heat, as the temperature remains unchanged for two seconds after taking it out from hot KOH electrolyte (see the thermal images in Fig. S24[†]). Consequently, the HER and OER kinetics of $Co_2P(C)$ are markedly promoted at elevated temperatures.

In conclusion, we present a successful example of solardriven thermoelectrocatalytic water splitting using Co₂P sheet-on-leaf superstructures. The one-step electrodeposition technique accomplished in merely 10 min deters the release of PH_3 gas and high temperature, providing a convenient, ecofriendly and generic approach to synthesizing transition-metal semiconductors. Assisted by a simply designed thermoelectrocatalytic reactor, the electrocatalytic activity of the Co_2P is considerably enhanced, with the overpotentials declining from 108 (25 °C) to 68 mV (65 °C) for the HER. The superstructures with a high electrical conductivity and electrochemical surface area, along with lowered activation energy, are able to utilize and convert heat from sunlight more efficiently, thus favouring electrocatalytic kinetics. The facile supplement of thermal energy to electrocatalysis is anticipated to provide new insights into thermoelectric, thermophotovoltaic and catalytic fields.

Acknowledgements

This work is supported by MOE R-263-000-B38-112 and R-263-000-B63-112 (Ministry of Education, Singapore).

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