N-doped TiO$_2$ nanotube arrays with uniformly embedded Co$_x$P nanoparticles for high-efficiency hydrogen evolution reaction$^\dagger$

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Efficient and stable non-precious metal based electrocatalysts are crucial to the hydrogen evolution reaction (HER) in renewable energy conversion. Herein, Co$_x$P nanoparticles (NPs) are uniformly embedded in N-doped TiO$_2$ nanotube arrays (Co$_x$P/N-TiO$_2$ NTAs) by low-temperature phosphorization of the precursor of metallic cobalt NPs embedded in N-doped TiO$_2$ NTAs (Co/N-TiO$_2$ NTAs) which were fabricated by phase separation of CoTiO$_3$ NTAs in ammonia. Owing to the abundant exposed surface active sites of Co$_x$P NPs, tight contact between the Co$_x$P NPs and TiO$_2$ NTAs, fast electron transfer in N-doped TiO$_2$, and channels for effective diffusion of ions and H$_2$ bubbles in the tubular structure, the Co$_x$P/N-TiO$_2$ NTAs have excellent electrocatalytic activity in HER exemplified by a low overpotential of 180 mV at 10 mA cm$^{-2}$ and small Tafel slope of 51 mV dec$^{-1}$ in 0.5 M H$_2$SO$_4$. The catalyst also shows long-term cycling stability and is a promising non-precious metal catalyst for HER.

Introduction

Because of environmental pollution and greenhouse gas emission derived from the consumption of fossil fuels, alternative green energy is attracting tremendous interest.$^{1,2}$ For example, hydrogen energy is very promising due to the harmless byproducts, high energy density, abundant resource, and recyclability, and electrochemical water splitting is an important technology.$^3$ Electrocatalysts play key roles in electrochemical water splitting which includes two half reactions: hydrogen evolution reaction (HER) on the cathode and oxygen evolution reaction (OER) on the anode.$^4$ It is well known that platinum (Pt)-based electrocatalysts are ideal for HER because of the low overpotentials and large exchange current densities,$^5$ but the high cost and terrestrial scarcity of Pt are hurdles for large-scale industrial application.$^6$ Therefore, noble metal-free electrocatalysts having good activity and stability,$^7$ such as transition metal chalcogenides,$^{8-10}$ nitrides,$^{11,12}$ and phosphides,$^{13-15}$ are attractive alternatives.

Transition metal phosphides (TMPs) are attractive non-precious metal based electrocatalysts for HER in acidic media, for instance, cobalt phosphide,$^{16}$ nickel phosphide,$^{17}$ and molybdenum phosphide,$^{18}$ have been studied intensively and exhibited excellent HER performance,$^{19-22}$ because the negatively charged P atoms in TMPs could trap positively charged protons during HER.$^{18}$ However the poor conductivity of TMP-based catalysts is a crucial obstacle to limit the HER performance. Hybrid structure composed of TMP nanoparticles anchored on conductive substrate is desirable, for example, CoP nanoparticles grown on graphene oxide$^{23}$ and carbon nanotubes decorated with CoP nanocrystals$^{24}$ exhibit excellent HER activity in acid solution. Although the hybrid electrocatalysts shows improved HER activity,$^{25}$ the random distribution of nanosize TMP nanoparticles on conductive agent without good adhesion and coupling compromised their HER activity and stability. Meanwhile, the fast electron transport pathways as well as effective channels for ions and gas bubbles diffusion are still challenge. Titanium oxide nanotube arrays (TiO$_2$ NTAs) have been proposed as a support substrate for superior electrochemical electrodes in many field because of the unique hollow structure, effective electron transfer pathways, and excellent physical and chemical stability under a wide variety of conditions.$^{26-33}$ More important, the highly ordered TiO$_2$ NTAs prepared by anodization of Ti substrate exhibits large surface areas, and they do not require additional binders to adhere to Ti substrates. Recently, there are many literatures on the incorporation of noble metal or economic electrocatalysts on TiO$_2$ NTAs to decrease their overpotential for water splitting, such as RuO$_2$ doped TiO$_2$ NT for OER application, amorphous MoS$_2$ coated TiO$_2$ NTAs and Ru$_{0.03}$Se nanoparticles decorated TiO$_2$ NTAs for enhanced HER activity.$^{34-35}$
Herein, we describe a novel electrocatalyst, Co₃P NPs uniformly embedded in N-doped TiO₂ NTAs (Co₃P/N-TiO₂ NTAs). First, the CoTiO₃ NTAs was fabricated by hydrothermal treatment of amorphous TiO₂ NTAs in cobalt acetate solution. Second, metallic cobalt is in situ segregated and anchored in/on the wall of the N-doped TiO₂ nanotubes (Co/N-TiO₂ NTAs) after thermal reduction of the CoTiO₃ NTAs under ammonia by phase separation. Then, the Co₃P/N-TiO₂ NTAs with original morphology was obtained after phosphorization of Co/N-TiO₂ NTAs. In this unique structure, the N-doped TiO₂ NTAs provide the fast electron transfer pathways and the original hollow channels is in favor of fast diffusion of ions and generated H₂ bubbles. More important, the formed Co₃P NPs are confined and tightly anchored in/on the wall of TiO₂ NTAs resulting in low contact resistance and excellent structural stability. The catalyst shows a low overpotential of 180 mV at 10 mA cm⁻² with a small Tafel slope of 51 mV dec⁻¹ under acidic conditions and a long lifetime suggesting large potential in water splitting and related applications.

**Experimental methods**

Ti plates (purity: 99.6%) with dimensions 10 mm × 10 mm × 1 mm were used as the substrates. Cobaltous acetate (Co(Ac)₂), sodium hypophosphite (NaH₂PO₂) were obtained from Aladdin Company and nitric acid, hydrofluoric acid and other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All the chemicals were analytical reagent grade and used without further purification. Deionized water (DIW) was used throughout the experiments.

**Materials preparation**

**Synthesis of TiO₂ nanotube arrays (TiO₂ NTAs)**

The TiO₂ NTAs were prepared according to the process described in the literature. The Ti plates were ultrasonically cleaned successively with acetone, ethanol, and DIW. Electrochemical anodization was carried out using a two-electrode configuration with a graphite plate being the cathode and Ti plate being the anode. After anodization in an ethylene glycol solution containing 5 vol% DI water and 0.5 wt% ammonium fluoride (NH₄F) at 60 V for 1 h using a power supply (IT6834, ITECH, China) at room temperature, the samples were washed with DIW and dried in air.

**Synthesis of CoTiO₃ nanotube arrays (CoTiO₃ NTAs)**

The CoTiO₃ NTAs were prepared by a hydrothermal method. The as-prepared amorphous TiO₂ NTAs were placed vertically and immersed in 30 ml of a 0.2 M cobalt acetate (Co(Ac)₂) aqueous solution in a 40 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and heated in an oven to 200 °C for 6 h. Afterwards, the product was removed from the autoclave and ultrasonically washed with DIW for 5 minutes. The sample was then annealed at 450 °C for 2 h in air to improve the crystallinity of the CoTiO₃ NTAs.

**Synthesis of Co/N-doped TiO₂ nanotube arrays (Co/N-TiO₂ NTAs)**

The as-prepared CoTiO₃ NTAs were calcined in an ammonia ambient at 600 °C (5 °C min⁻¹) for 3 hours in a tube furnace to prepare Co NPs decorated N doped-TiO₂ NTAs. After natural cooling, black Co/N-TiO₂ NTAs were obtained.

**Synthesis of Co₃P/N doped-TiO₂ nanotube arrays (Co₃P/N-TiO₂ NTAs)**

The as-prepared Co/N-TiO₂ NTAs were placed downstream from NaH₂PO₂ (0.2 g) in a furnace tube at a distance of about 20 cm and treated at different temperature for 3 h under flowing Ar. After phosphorization, the Co₃P/N-TiO₂ NTAs were collected after the furnace cooled down to room temperature. The
samples were denoted as CoₓP/N-TiO₂-300, CoₓP/N-TiO₂-450, CoₓP/N-TiO₂-550, respectively.

**Materials characterization**

The morphology and microstructure of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, FEI Nova 400 Nano), transmission electron microscopy (TEM, JEOL 2010, Tokyo, Japan), X-ray diffraction (XRD, Philips X’Pert Pro) with Cu Kα radiation, X-ray photoemission spectroscopy (XPS, ESCALAB MK-II, VG Instruments, London, UK, calibrated with the C 1s peak at 284.6 eV).

**Electrochemical measurements**

The electrochemical measurements were carried out using a three-electrode system in 0.5 M H₂SO₄ with carbon as the counter electrode, saturated calomel electrode (SCE) as the reference electrode, and the sample with an exposed surface area of 1 cm² as the working electrode (CHI 760e, Shanghai CHI Company, China). The HER activity was evaluated by linear sweep voltammetry (LSV) at a scanning rate of 5 mV s⁻¹ and the potentials were referenced to the reversible hydrogen electrode (RHE) according $E_{RHE} = E_{SCE} + 0.2415 + 0.0591 \times \text{pH}$. The electrochemical impedance spectra (EIS) were acquired at an overpotential of 100 mV in the frequency range between 100 kHz and 0.01 Hz with an AC perturbation of 5 mV. The stability of the electrocatalyst was assessed by cyclic voltammetry (CV) at a scanning rate of 200 mV s⁻¹. All the potentials in the polarization curves and Tafel plots were $iR$ corrected using $R_s$ from EIS.

**Results and discussion**

Fig. 1a schematically illustrates the synthesis of the CoₓP/N-TiO₂ NTAs. Uniform TiO₂ NTAs are fabricated on the Ti plates by electrochemical anodization and the CoTiO₃ NTAs are prepared by a simple hydrothermal treatment of the as-prepared amorphous TiO₂ NTAs and Co(Ac)₂. The Co/N-TiO₂ NTAs are produced by thermal reduction of CoTiO₃ NTAs under ammonia and the CoₓP/N-TiO₂ NTAs are obtained after phosphorization. Fig. 1b–e display the morphology and microstructure of the TiO₂ NTAs after different steps. After anodic oxidation, the ordered TiO₂ NTAs with a uniform diameter of 90 nm are vertically aligned on the Ti plate. After the hydrothermal treatment in 0.2 M Co(Ac)₂ at 200 °C for 6 h, Fig. 1c shows that the diameter of CoTiO₃ NTAs decreases because of the thick wall of the NTAs. It is due to self-crystallization of amorphous TiO₂ to titanate in the presence of corresponding salts as previously reported. After the thermal treatment at 600 °C in NH₃ (Fig. 1d), NPs with a diameter of about 80 nm are formed uniformly on the surface of the NTAs by the phase
Subsequently, the morphology is maintained after phosphorization, as shown in Fig. 1e.

The structural evolution of the products is monitored by XRD as in Fig. 2. The XRD pattern of as-anodized TiO₂ NTAs shows a series of peaks (green line) at 38.4°, 40.2°, 53.0°, 62.9°, 70.6°, 76.1°, and 82.2° assigned to the substrate Ti (JCPDS no. 89-2762) reflecting the amorphous structure of the as-anodized TiO₂ NTAs (Fig. 2a). However, there is no peak from as-hydrothermal cobalt titanate can be observed in Fig. 2b suggesting the amorphous nature and the obvious phase assigned to CoTiO₃ (JCPDS no. 77-1373) can be formed at a high annealing temperature (Fig. S1†). After nitridation, several new XRD peaks at 44.2°, 51.5°, 75.8° corresponding to the (111), (200), and (220) planes of metallic Co (JCPDS no. 89-7093) are observed, as shown Fig. 2c (purple line), confirming segregation of metallic Co from the hydrothermal product. After phosphorization (Fig. 2d), the XRD pattern shows characteristic peaks of cobalt phosphide (CoP, JCPDS no. 89-2747 and Co₂P, JCPDS no. 89-3030) in addition to the TiO₂ and Ti substrate indicating that metallic Co is converted to cobalt phosphide.⁴³

Fig. 3 presents the microstructure and morphology of CoₙP/N-TiO₂-300 examined by SEM and TEM. The cross-sectional SEM image of CoₙP/N-TiO₂-300 in Fig. 3a discloses a large amount of CoₙP NPs with a large exposed surface and uniformly embedded in the NTAs. The tubular channels allow for fast diffusion of ions and gas bubbles in a stable structure benefiting the electrochemical activity and durability during HER. Fig. 3b depicts the cross-sectional TEM image of CoₙP/N-
TiO$_2$-300 clearly showing the tubular structure after phosphorization. Fig. 3c shows a well assembled and porous structure and the high-resolution TEM image (Fig. 3d) reveals lattice spacings of 0.351 nm, 0.206 nm, and 0.171 nm corresponding to the (101) plane of anatase TiO$_2$, (211) plane of Co$_2$P, and (103) plane of CoP, respectively. Fig. 3e shows the energy-dispersive X-ray spectroscopy (EDS) maps of Ti, O, N, Co, and P disclosing that Ti, N and O are uniformly distributed through the entire NTAs benefiting the conductivity and electrochemical properties. In contrast, Co and P are scattered at the same positions demonstrating that Co$_2$P NPs are embedded in the N-doped TiO$_2$ NTAs and there is no doped P in the NTAs after phosphorization.

X-ray photoelectron spectroscopy (XPS) is conducted to characterize the chemical state of the phosphatized sample and shown in Fig. 4. The survey spectrum shows Co, P, Ti, N, and O (Fig. 4a) consistent with EDS mapping. A fitted weak peaks at 458.8 and 464.8 eV in the Ti 2p spectrum (Fig. 4b) and that at 398.3 eV in the N 1s spectrum (Fig. 4c) are related to N–Ti–O confirming formation of N-doped TiO$_2$. The high-resolution Co 2p spectrum shows two pairs of double peaks and two satellite peaks (Fig. 4e). The peaks at 777.8 and 792.7 eV can be assigned to Co in cobalt phosphide and those at 781.4 eV and 797.3 eV are associated with Co$^{2+}$. The peaks at 785.5 eV and 802.4 eV are satellite peaks. The P 2p spectrum can be deconvolved into three peaks (Fig. 4f). The ones at 129.1 eV and 129.9 eV are low valence P in Co$_3$P NPs and that at 133.5 eV can be attributed to PO$_4^{3-}$ or P$_2$O$_5$ because of oxidation. The XPS results confirm that the hybrid composite composed of Co$_2$P and N-doped TiO$_2$, in consist with the XRD and TEM analysis.

The electrocatalytic activity of Co$_2$P/N-TiO$_2$ NTAs in HER is evaluated using a three-electrode system in 0.5 M H$_2$SO$_4$. Fig. 5a shows the polarization curves after removing the effect of solution resistance by $iR$ compensation (Fig. S2†). As expected, the Pt sheet exhibits excellent HER activity with a very low onset overpotential of $-34$ mV for 1 mA cm$^{-2}$ and only needs $-59$ mV to reach the benchmark current density of 10 mA cm$^{-2}$. The bare Ti plate has no electrocatalytic activity. After nitridation, the Co/N-TiO$_2$ NTAs show poor electrocatalytic properties with a current density of 10 mA cm$^{-2}$ at a large overpotential of $-380$ mV. After phosphorization at 300 °C for 3 h, the optimal HER activity is achieved. A small onset potential of $-123$ mV for 1 mA cm$^{-2}$ is observed and only $-180$ mV is needed to reach the current density of 10 mA cm$^{-2}$. By further increasing the phosphorization temperature, the HER activity of the Co$_2$P/N-TiO$_2$ NTAs decline dramatically due to insufficient phosphorization as a result of quick decomposition of NaH$_2$PO$_2$ as well as fast segregation of Co NPs on the surface blocking the mouth of the NTs (Fig. S3 and S4†). Fig. 5b presents the Tafel slopes derived from the polarization curves by fitting the Tafel equation $\eta = b \log j + a$, where $j$ is the current density and $b$ is the
Tafel slope, in different overpotential ranges. The Pt sheet shows a low Tafel slope of 30 mV dec$^{-1}$ close to that reported previously. In comparison, the Tafel slopes of the Co$_3$P/N-TiO$_2$ NTAs are 51, 57, and 70 mV dec$^{-1}$ when phosphorization is carried out at 300 °C, 450 °C, and 550 °C, respectively. Co$_3$P/N-TiO$_2$ NTAs-300 has better HER properties than other transition metal phosphides based electrocatalysts, as shown in Fig. S5.† Electrochemical impedance spectroscopy (EIS) is employed to determine the charge transfer resistance as shown in Fig. 5c. The Nyquist plots are fitted with an equivalent circuit (inset in Fig. 5c), where the $R_s$ is the solution resistance of the electrochemical system, $R_{ct}$ is the charge transfer resistance, and CPE is the constant phase element. Co$_3$P/N-TiO$_2$ NTAs-300 has a lowest resistance of 8 Ω implying efficient electron transport. The stability which is also a critical factor in HER catalyst is evaluated by continuous CV cycling at 200 mV s$^{-1}$. After 3000 cycles (Fig. 5d), the polarization curve exhibits negligible degradation, demonstrating superior stability under acidic conditions. The excellent HER activity of Co$_3$P/N-TiO$_2$ NTAs-300 with uniformly dispersed Co$_3$P NPs stems from the unique nanostructure which provides not only fast charge transfer pathways and low contact resistance between the catalyst and electrode, but also effective hollow channels for diffusion of ions and H$_2$ bubbles.

**Conclusion**

Co$_3$P NPs are uniformly embedded in N-doped TiO$_2$ NTAs by nitridation and phosphorization of CoTiO$_2$ NTAs. Co$_3$P/N-TiO$_2$ NTAs-300 delivers excellent electrocatalytic performance in HER in 0.5 M H$_2$SO$_4$, for instance, a low overpotential of 180 mV at a current density of 10 mA cm$^{-2}$, small Tafel slope of 51 mV dec$^{-1}$, and long-term durability. The Co$_3$P NPs confined in the N-doped TiO$_2$ NTs provide high structural stability and low contact resistance between the catalyst and electrode. The N-doped TiO$_2$ NTs provide fast electron transfer pathways as well as channels for effective diffusion of ions and H$_2$ bubbles. The novel electrocatalyst has excellent HER activity and our results reveal a different approach to design and synthesize non-noble-metal electrocatalysts.

**Conflicts of interest**

The authors declare no conflicts of interest.

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