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Facile synthesis of Pd–Co–P ternary alloy network nanostructures and their enhanced electrocatalytic activity towards hydrazine oxidation[†]

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Porous ternary Pd–Co–P alloy network nanostructures were synthesized by reducing $K_2PdCl_4/K_3Co(CN)_6$ cyanogel with a mixture of NaH₂PO₂ and NaBH₄ at room temperature, which show superior electrocatalytic activity and stability towards hydrazine oxidation reaction.

Three-dimensional (3D) porous Pt or Pd (Pt/Pd) nanostructures with a high density of atomic scale defects have attracted increasing interest in the field of electrochemistry because of their improved electrocatalytic activity and stability.¹⁻⁶ Specifically, (i) the particular interconnected structure restrains the dissolution/aggregation of Pt/Pd nanoparticles driven by Ostwald ripening effect; (ii) the unique 3D network structure facilitates mass exchange and gas diffusion during the electrochemical reactions; (iii) the abundant defect atoms, including steps, edges and kinks, usually are much more active than terrace atoms. For example, Jia's group has successfully synthesized 3D Pt network nanostructures, which exhibit superior electrochemical activity and stability towards methanol oxidation.¹ Also, 3D Pd network nanostructures prepared by Xu's group show excellent electrocatalytic performance towards formic acid oxidation.²

Over the past few decades, alloying Pt/Pd with early transition metals has became an effective way for reducing the utilization of Pt/Pd and simultaneously improving electrocatalytic activity and stability because of the modified geometric and electronic structures of Pt/Pd atoms.⁷⁻¹³ Besides Pt/Pd-based bimetallic alloy nanostructures, the controllable synthesis of Pt/Pd-based trimetallic nanostructures has attracted much attention.^{14–18} The introduction of a third element can further tune the atomic scale structures (bond distance and coordination number), morphologies and electronic structures of bimetallic alloys, and consequently improve electrocatalytic activity and stability. For example, Dong's group has synthesized Au-Pt-Pd trimetallic alloy nanowires, which exhibited enhanced electrocatalytic activity towards ethanol oxidation than both Pd-Pt and Pd-Au bimetallic alloy nanowires.¹⁵ Therefore, ternary Pt/Pd-based alloy nanostructures are being considered as promising nanomaterials with enhanced electrocatalytic performance.14 Although alloying Pt/Pd with phosphorus (P) can improve electrocatalytic activity of Pt/Pd nanostructures for many important reactions such as oxygen reduction, formic acid oxidation, and ethanol oxidation reactions,19-22 Pt/Pd-P-based ternary alloy electrocatalysts are rarely reported.17,18

The essential challenge for the synthesis of alloy nanostructures is the diverse nucleation and growth rates of different element precursors owing to their distinct standard reduction potentials.7 Large differences in reduction potentials result in the preferential reduction of the metal with a higher reduction potential and the formation of a core-shell structure. The cyanogel, a kind of coordinate inorganic polymer, is a special class of 3D double-metal cyanide (see eqn (1)).4,7,8 The intimate interconnection between R and M metal precursors facilitates the combination between R⁰ and M⁰ crystal nuclei upon chemical reduction. Moreover, the solid nature of a cyanogel also effectively suppresses the Brownian motion of R⁰ and M⁰ crystal nuclei, which facilitates the formation of R⁰-M⁰ alloy. Our laboratory recently successfully synthesized porous Pt-Co and Pd-Co alloy network nanostructures by cyanogel-reduction method.7,8 In view of our successful preparation of Pt/Pd bimetallic alloy network nanostructures (BANNs), herein, we successfully synthesize Pd-Co-P ternary alloy network nanostructures (TANNs) via one-step cyanogel-reduction method. The as-prepared Pd-Co-P TANNs exhibit remarkably enhanced electrocatalytic activity and stability towards hydrazine oxidation.

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Pd–Co–P TANNs were readily achieved by reducing light yellow $K_2PdCl_4/K_3Co(CN)_6$ cyanogel with a mixture of NaH_2PO_2 and $NaBH_4$ ($NaH_2PO_2/NaBH_4$ molar ratio is 0.42:1) at room temperature (Scheme 1, see Experimental in ESI† for details). Scanning electron microscopy (SEM) image shows the products have 3D network-like architectures, very similar to the morphology of Pd–Co bimetallic alloy network nanostructures (Pd–Co BANNs) obtained by control experiment without NaH_2PO_2 .⁸ Upon reduction, Pd and Co crystal nuclei grow oneby-one along the 3D scaffold direction of the $K_2PdCl_4/K_3Co(CN)_6$ cyanogel, which results in the interconnected 3D structure.

The composition of Pd-Co-P TANNs was investigated by energy dispersive spectroscopy (EDS). The appearance of Pd-L, Co-K and P-K peaks illustrates the products are ternary Pd-Co-P nanostructures (Fig. 1A, the Pd/Co/P atomic ratio is 82.7:11.6:5.7). X-ray photoelectron spectroscopy (XPS) measurements show the percentages of Pd⁰ and Co⁰ species are 88.5% and 90.4%, respectively (Fig. 1B-a and B-b), demonstrating that Pd^{II} and Co^{II} precursors are successfully reduced in our synthesis. In particular, elemental state phosphorus (P^0) is observed in Pd-Co-P TANNs samples (Fig. 1B-c, P2p peaks at 130.4 and 134.3 eV are assigned to elemental state phosphorus and oxidized phosphorus (Pv), respectively²⁰), which is indicative of metal-P alloy formation.19-24 Specifically, the inclusion of P atoms in the PdCo matrix can be ascribed to the codeposition of Pd-Co and P. The elemental phosphorus generated via hydrogenous free radical (eqn (2)) and/or hydrogenous radical anion (eqn (3)) mechanisms can react with Pd and Co crystal nuclei generated via cyanogel reduction to form Pd-Co-P alloy, similar to the case of Pd-P alloy formation.19,20,23,24 Of course, Pd nanoparticles also work as catalyst to promote P electroless deposition during reactions.²⁴ It is worth noting that K₂PdCl₄/ K₃Co(CN)₆ cyanogel cannot be reduced by single-component NaH₂PO₂ at room temperature. Thus, in our synthesis, NaBH₄ acts as reducing agent whereas NaH2PO2 acts as phosphorusintroducing reagent.

Scheme 1 Schematic representation of synthetic procedure of Pd– Co–PTANNs. (A) Photograph of $K_2PdCl_4/K_3Co(CN)_6$ cyanogel. (B) SEM image of Pd–Co–P TANNs.



Fig. 1 (A) EDS spectrum and (B) XPS spectra of Pd-Co-P TANNs in the (a) Pd 3d, (b) Co 2p, and (c) P 2p regions.

$$H_2PO_2^- + 2H^+ + H^- \rightarrow 2H_2O + 1/2H_2 + P$$
 (2)

$$H_2 P O_2^- + H^+ + H^{\bullet} \rightarrow 2 H_2 O + P \tag{3}$$

Compared with Pd–Co BANNs obtained by control experiment without NaH₂PO₂,⁸ the Pd 3d binding energies in Pd–Co–P TANNs negatively shift *ca.* 0.29 eV (Fig. S1, ESI[†]), indicating the introduction of P element can effectively tune the electronic structures of Pd–Co bimetallic alloy because of the chemical interactions between Pd, Co and P atoms. This change decreases 2π electron donation from O₂ to the Pd atoms, and consequently results in weakened O₂ adsorption.^{25,26} As observed, the percentage of Pd⁰ species in Pd–Co–P TANNs (88.5%) is higher than that in Pd–Co BANNs (83.1%), confirming a weaker oxophilicity in Pd–Co–P TANNs.

The crystal structure of Pd-Co-P TANNs is investigated by Xray diffraction (XRD). With the incorporation of phosphorus, the diffraction peaks of Pd-Co-P TANNs become wider compared to Pd-Co BANNs (Fig. 2A), indicating Pd-Co-P TANNs have a low crystallinity degree or rather small particle size (or both).16 According to the Scherrer equation, the average particle sizes of Pd-Co-P TANNs and Pd-Co BANNs are calculated to be 2.1 and 3.9 nm, respectively. Because of easy oxidation of elemental state phosphorus, the phosphonic acid groups are easily generated on the Pd-Co-P crystal nuclei surface during synthesis (e.g., zeta potential of Pd-Co-P TANNs is -20 mV in a pH 3.0 solution). The strong electrostatic repulsion between phosphonic acid groups restrains the aggregation of Pd-Co-P crystal nuclei during synthesis, which results in low crystallinity degree and small particle size. Moreover, the Pd(111) diffraction peak of Pd-Co-P TANNs shifts to a higher angle compared to both JCPDS 05-0681 Pd and Pd-Co BANNs (insert in Fig. 2A), which clearly confirms the formation of

NaBH₄

NaH₂PO₂



Fig. 2 (A) XRD patterns of (a) Pd–Co–P TANNs and (b) Pd–Co BANNs. (B) TEM image of Pd–Co–P TANNs. Insert: SAED image. (C) HRTEM image of Pd–Co–P TANNs. Inserts: magnified HRTEM images recorded from regions marked by squares. (D) Representative large-area TEM image of Pd–Co–P TANNs and corresponding EDS mapping patterns of Pd (red), Co (yellow) and P (green) elements.

Pd-Co-P ternary alloy. The lattice parameter value (a) of Pd-Co-P TANNs is calculated to be 0.3817 nm, smaller than that of Pd–Co BANNs (a = 0.3875 nm), reflecting that the introduction of P element can also effectively tune the surface structure of Pd-Co bimetallic alloy. The morphology and structural features of Pd-Co-P TANNs were further investigated by transmission electron microscopy (TEM). As observed, small primary nanoparticles are interconnected to each other to form 3D nanonetworks with abundant pores (Fig. 2B). The selected area electron diffraction (SAED) image shows an irregularly and discretely dotted pattern (insert in Fig. 2B), indicating Pd-Co-P TANNs are polycrystalline. High-resolution TEM (HRTEM) image shows Pd-Co-P TANNs consist of irregular nanochains with a diameter of 3-8 nm (Fig. 2C). Also, the HRTEM image of Pd-Co-P TANNs shows the obvious lattice fingers corresponding to Pd(111) facets and large numbers of the defects such as boundary, vacancy and dislocation (insert). The high density of defects can effectively improve catalytic activity owing to the open coordination nature of defect atoms.^{10,27} Nanoscale EDS elemental mapping patterns clearly show that Pd, Co and P are evenly distributed through the nanostructures (Fig. 2D), which is a strong evidence for the formation of ternary Pd-Co-P alloy.14 It is worth noting that particle size, alloying degree and P amount of Pd-Co-P TANNs can be adjusted by controlling the molar ratio of NaH₂PO₂/NaBH₄ (the molar amount of NaBH₄ remains constant). In detail, the particle size of Pd-Co-P TANNs decreases with increasing NaH₂PO₂/NaBH₄ molar ratio (Table S1 and Fig. S2, ESI[†]), whereas both the alloying degree and P amount of Pd-Co-P TANNs increase with NaH₂PO₂/NaBH₄ molar ratio (Table S1 and Fig. S3, ESI[†]). After increasing NaH₂PO₂/NaBH₄ molar feeding ratio to 0.42 : 1, however, the

particle size, alloying degree, and P amount of Pd–Co–P TANNs remain unchanged (Table S1, ESI†). Considering that Pd–Co–P TANNs prepared under present experimental conditions have smallest particle size and highest alloying degree and P amount, the present experimental parameters are selected (*i.e.*, NaH₂PO₂/NaBH₄ molar ratio is 0.42 : 1).

The electrochemical properties of Pd-Co-P TANNs and Pd-Co BANNs were firstly investigated by cyclic voltammetry (CV) in N₂-saturated 0.1 M HClO₄ solution (Fig. 3A). The characteristic reduction peak in higher potential region (ca. 0.40 V) is attributed to reduction of Pd(OH)₂ on the Pd surface, which can reflect the number of Pd sites.²⁸⁻³⁰ By measuring the reduction charge of surface $Pd(OH)_2$ and assuming a value of 420 μ C cm⁻² for the reduction charge of a Pd(OH)₂ monolayer,²⁸⁻³⁰ the electrochemical surface areas (ECSA) of Pd-Co-P TANNs and Pd-Co BANNs are calculated to be 27.2 and 22.1 m² g_{Pd}⁻¹, respectively. The larger ECSA value of Pd-Co-P TANNs is most likely due to the smaller size $(d_{xrd}-Pd-Co-P = 2.1 \text{ nm } \nu s. d_{xrd}-Pd-Co =$ 3.9 nm). The electrocatalytic activities of Pd-Co-P TANNs and Pd-Co BANNs were examined by taking hydrazine as a model molecule. It is clear that the mass activity of electrocatalysts (i.e., the currents are normalized to the metal mass) is taken as an index to assess the applicability of electrocatalysts. The mass normalized cyclic voltammograms (Fig. 3B) show the anodic oxidation peak current of hydrazine (758.1 A g_{Pd}⁻¹) on Pd-Co-P TANNs is 1.5 times higher than that $(521.4 \text{ A g}_{Pd}^{-1})$ on Pd–Co BANNs, implying that the Pd loading can be markedly reduced if Pd-Co-P TANNs replace Pd-Co BANNs as electrocatalysts. The high mass activity of Pd-Co-P TANNs likely originates from the big ECSA of Pd-Co-P TANNs. Indeed, both Pd-Co-P TANNs and Pd-Co BANNs have also much better mass activity than commercial Pd black (Fig. S4, ESI[†]), further indicating Pd-Co-P



Fig. 3 (A) Cyclic voltammograms of (a) Pd–Co–P TANNs and (b) Pd–Co BANNs in N₂-saturated 0.1 M HClO₄ solution at the scan rate of 50 mV s⁻¹; (B) mass activity and (C) specific activity of (a) Pd–Co–P TANNs and (b) Pd–Co BANNs in N₂-saturated 0.1 M HClO₄ + 0.05 M N₂H₄ solutions at the scan rate of 50 mV s⁻¹. (D) Chronoamperometric curves of (a) Pd–Co–P TANNs and (b) Pd–Co BANNs in the N₂-saturated 0.1 M HClO₄ + 0.05 M N₂H₄ solution at 1000 rpm rotation rate at 0.30 V.

TANNs hold promise as potentially practical electrocatalysts towards hydrazine oxidation. On the other hand, the specific activity of electrocatalysts (i.e., the currents are normalized to the ECSA of metal nanoparticles) demonstrates the actual value of the intrinsic activity of electrocatalysts. ECSA-normalized cyclic voltammograms (Fig. 3C) show the specific peak current density of hydrazine (27.6 A ${m_{Pd}}^{-2})$ on Pd–Co–P TANNs is 1.2 times higher than that (23.5 A m_{Pd}^{-2}) on Pd–Co BANNs, indicating that Pd-Co-P TANNs have better electrocatalytic activity than Pd-Co BANNs. Considering the identical synthetic route and similar morphology, the higher electrocatalytic activity of Pd-Co-P TANNs compared to Pd-Co BANNs can be mainly ascribed to synergetic effects among Pd, Co, and P, including the slight change of Pd electronic structure and Pd lattice parameter, high percentage of Pd⁰ species, and enrichment of hydrazine at Pd-Co-P TANNs surface due to the electrostatic attraction between the positively charged N₂H₅⁺ and the negatively charged phosphonic acid groups.

The electrocatalytic stabilities of Pd-Co-P TANNs and Pd-Co BANNs were investigated by chronoamperometry at 0.3 V applied potential (Fig. 3D). In order to obtain better control of mass transport and prevent a large extent of the accumulation of small gas bubbles on catalyst surfaces, the rotating disk electrode in this work is adopted.30 The overall oxidation reaction of hydrazine in acid can be written as $NH_2NH_3^+ \rightarrow N_2 + 5H^+$ + 4e.³¹⁻³³ Since N₂ is the oxidation product of hydrazine electrooxidation, the Pd electrocatalysts should not suffer from any poisoning effects. At 6000 s, however, the oxidation currents of hydrazine on Pd-Co-P TANNs and Pd-Co BANNs decrease to 12.7% and 3.1% of their initial values, respectively. Considering the existence of some impurities in the hydrazine solution, it is reasonable to suggest that the decreasing of the electrocatalytic current results from the contamination of the solution.³⁴ The previous investigations have demonstrated alloying Pd with P can effectively facilitate the oxidation of generated CO_{ads} and/or unidentified non-CO_{ads} organic species intermediates during the electrooxidation reactions of various small fuel molecules, owing to the "synergistic effect" between Pd and P atoms (such as electronic effect, geometric effect, and bifunctional mechanism, etc.).^{20,35,36} Thus, introduction of P in Pd-Co alloy should be responsible for improved durability of Pd-Co-P TANNs towards hydrazine oxidation. Although the ESCA of Pd-Co-P TANNs is smaller than that of commercial Pd/C catalyst (27.2 vs. 47.3 m² g_{Pd}⁻¹, Fig. S5, ESI[†]), Pd-Co-P TANNs show superior electrocatalytic stability than commercial Pd/C catalyst. As showed by chronoamperometry tests, the hydrazine oxidation current on commercial Pd/C decreases to 0.5% of the initial value at 6000 s, which is much larger than the attenuation degree (decreases to 12.7%) of Pd-Co-P TANNs for hydrazine oxidation (Fig. S6, ESI[†]). This shows that the electrocatalytic stability of Pd-Co-P TANNs is much better than that of commercial Pd/C catalyst, further indicating Pd-Co-P TANNs is a promising and practical electrocatalyst for hydrazine oxidation.

We successfully synthesized porous Pd–Co–P TANNs through a surfactant-free cyanogel-reduction route with $NaH_2PO_2/NaBH_4$ mixed reductants at room temperature.

During reduction, introduction of NaH₂PO₂ not only acts as an efficient phosphorus-introducing reagent, but also decreases the particle size of Pd–Co–P TANNs because of the electrostatic repulsion between phosphonic acid groups. Introduction of P in Pd–Co BANNs can effectively tune geometric, electronic and superficial structures of Pd–Co BANNs. As a result, Pd–Co–P TANNs exhibit higher electrocatalytic activity (mass activity and specific activity) and durability towards hydrazine oxidation compared to Pd–Co BANNs. This work demonstrates that Pd–Co–P TANNs are indeed promising electrocatalysts towards hydrazine oxidation. The cyanogels-reduction method with NaBH₄/NaH₂PO₂ mixed reductant can be applied to other cyanogels to synthesize various multimetallic metals–P alloy network nanostructures.

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