Heterogeneous nanocomposites consisting of Pt$_3$Co alloy particles and CoP$_2$ nanorods towards high-efficiency methanol electro-oxidation

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Abstract
Heterogeneous nanocomposites comprising chemically distinct constituents are particularly promising in electrocatalysis. We herein report a synthetic strategy that combines the reduction of Pt and Co ionic precursors at an appropriate ratio with the subsequent phosphating at an elevated temperature for forming heterogeneous nanocomposites consisting of quasi-spherical Pt$_3$Co alloy domains and rod-like CoP$_2$ domains for high-efficiency methanol electro-oxidation. The strong electronic coupling between Pt$_3$Co and CoP$_2$ domains in the nanocomposites render the electron density around Pt atoms to decrease, which is favorable for reducing the adsorption of poisoning CO-like intermediates on the catalyst surfaces. Accordingly, the as-prepared heterogeneous Pt$_3$Co–CoP$_2$ nanocomposites show good performance for methanol electro-oxidation both in acidic and alkaline media. In specific, at a Pt loading of only 6.4% on a common carbon substrate, the mass-based activity of Pt$_3$Co–CoP$_2$ nanocomposites in an acidic medium is about 2 and 1.5 times as high as that of commercial Pt/C catalyst (20% mass loading) and home-made Pt$_3$Co alloy nanoparticles (8.0% mass loading), while in the alkaline medium, these values are 3 and 2, respectively.

KEYWORDS
electrocatalysis, electronic coupling, methanol electro-oxidation, nanocomposite, Pt$_3$Co–CoP$_2$
1 | INTRODUCTION

Noble metal-containing heterogeneous nanomaterials with composite structures refer to those with noble metal domains and other different functional domains sharing intimate contacts at their interfaces, which are particularly useful for electrocatalysis.1–4 The adjacent domains of the noble metals in the heterogeneous nanocomposites endow them with suitable electronic configuration or appropriate d-band center, favorable for catalyzing electrochemical reactions. A very early example is the synthesis of dumbbell-like Pt–Fe3O4 nanocomposites via epitaxial growth of Fe onto Pt nanoparticles followed by an oxidation treatment, which exhibit a 20-fold increase in mass activity for electrocatalytic oxygen reduction in comparison with the commercial Pt particles due to the electronic interaction between Pt and Fe3O4 domains, vividly proving that the electrocatalytic performance of Pt metal could be greatly enhanced by integrating it with a vastly different material.5 Subsequently, the nanocomposites formed by depositing Pt on Ag2S nanocrystals are shown to have superior activity and durability for electro-oxidation of methanol due to the electronic coupling between Pt and Ag2S domains.6–8 The electivity of Ag2S–Pt nanocomposites for methanol electro-oxidation could even be used to establish a direct methanol fuel cell without the proton exchange membrane through combining them with an oxygen reduction-selective electrocatalyst,9 or to run a direct methanol fuel cell model under high concentration of methanol.10

The synthesis and electrocatalytic evaluations of noble metal-containing heterogeneous nanocomposites bloom in recent years upon recognition of their huge potentials in electrocatalysis, for example, alcohol oxidation,11–22 oxygen reduction,23–25 and hydrogen evolution.26–32 Typically, as revealed by in situ-attenuated total reflection surface-enhanced infrared radiation absorption spectroscopy, in nanocomposites composed of Pt and CoP components, the presence of CoP can promote the full oxidation of methanol to CO2, endow the Pt domains with high activity and improved anti-poisoning capability in methanol electro-oxidation.33 In another example, alloying the Pt metal with Ru in Pt–CoP nanocomposites can further enhance its performance in methanol electro-oxidation.34 The presence of CoP in the nanocomposites dramatically slow down the dissolution loss of Pt and Ru, making them highly durable in the electrochemical oxidation of methanol.

In principle, the function can be expected to scale remarkably with an increase in the complexity of nanocomposites that can be produced.35 The optimization on both the composition and morphology of the domains for a composite catalyst is an effective route to boost its performance for a given electrochemical reaction. In addition, the synthesis of heterogeneous nanocomposites constituted by earth-abundant elements but with superior catalytic properties is always desired. Therefore, we herein report the construction of heterogeneous nanocomposites comprised by Pt3Co alloy nanoparticles and CoP2 nanorods towards high-efficiency methanol electro-oxidation, the key anodic reaction in direct methanol fuel cells. The synthetic strategy combines the reduction of Pt and Co ionic precursors at an appropriate ratio with the subsequent phosphating at an elevated temperature. The X-ray photoelectron spectroscopy (XPS) characterizations disclose that there is strong electronic interaction between the alloy and phosphide domains, which promote the Pt3Co alloys in the nanocomposites to efficiently catalyze the electro-oxidation of methanol in both acidic and alkaline media. In specific, in acidic medium, at a Pt loading of only 6.4% on XC-72 carbon support, the mass-based activity of Pt3Co–CoP2 is about 2 and 1.5 times as high as that of commercial Pt/C catalyst (20% mass loading) and home-made Pt3Co alloy nanoparticles (8.0% mass loading), while in alkaline medium, these values are 3 and 2, respectively. The study here offers another vivid example to show the potential of heterogeneous nanocomposites in electrocatalysis and may provide a promising way to produce electrocatalysts with cost-effectiveness and desired efficiency.

2 | MATERIALS AND EXPERIMENTAL

2.1 | Materials

Platinum(II) acetylacetonate (Pt(acac)2, 98%) and oleylamine (OLA, 95.4%) from J&K Scientific, cobalt(II) acetylacetonate (Co(acac)2, 97%), 1-octadecene (>90.0%),Tri-n-octylphosphine (TOP, 90%), aqueous HClO4 solution (70%, ACS reagent) and Nafion 117 solution (5% in a mixture of lower aliphatic alcohols and water) from Aladdin, methanol (99%), ethanol (>99.7%) and n-hexane (>99.5%) from Beijing Chemical Works, Vulcan XC-72 carbon powders (XC-72C, 40–50 nm in particle sizes) from Cabot, and commercial Pt/C (20 wt% of Pt on Vulcan XC-72 carbon supports) from Johnson Matthey were used as received. Ultrapure water was used throughout this study.

2.2 | Synthesis of Pt3Co–CoP2 nanocomposites

For the synthesis of Pt3Co–CoP2 nanocomposites, 0.033 mmol of Pt(acac)2 and 0.1 mmol Co(acac)2 were added to a mixture composed of 10 ml of 1-octadecene and 2.5 ml of OLA in a 3-necked flask, followed by heating to 250°C and keeping there for 2 h under
vigorously stirring and flowing \( \text{N}_2 \) to reduce the Pt and Co ions. Then, 2.5 ml of TOP was injected and the reaction mixture was heated to 280°C and continuously kept there for 2 h. Subsequently, the as-formed \( \text{Pt}_3\text{Co}–\text{CoP}_2 \) nanocomposites were precipitated with methanol, collected by centrifugation, washed twice with methanol, and redispersed into 10 ml of \( n \)-hexane. It should be noted that the coreduction of Pt and Co ionic precursors at other Pt/Co ratios followed by phosphating under the same conditions were also conducted for investigating the formation mechanism of \( \text{Pt}_3\text{Co}–\text{CoP}_2 \) nanocomposites.

### 2.3 Synthesis of \( \text{Pt}_3\text{Co} \) nanoalloys

The home-made \( \text{Pt}_3\text{Co} \) nanoalloys were used to benchmark the as-formed \( \text{Pt}_3\text{Co}–\text{CoP}_2 \) nanocomposites for methanol electro-oxidation. For the synthesis of \( \text{Pt}_3\text{Co} \) nanoalloys, 0.1 mmol of \( \text{Pt(acac)}_2 \) and 0.033 mmol of \( \text{Co(acac)}_2 \) were added to a 3-necked flask containing 10 ml of 1-octadecene and 2.5 ml of OLA. The mixture was heated to 250°C and kept there under vigorous stirring and flowing \( \text{N}_2 \) for 2 h to fulfill the reduction of Pt or Co ionic precursors by OLA. Then, the obtained alloy products were precipitated with methanol, collected by centrifugation, washed twice with methanol, and redispersed in 10 ml \( n \)-hexane.

### 2.4 Characterization

The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images taken from a JEOL JEM-2010F electron microscope were used to observe the size and morphology of all composite and alloy samples. An energy-dispersive X-ray spectroscopy (EDX) analyzer attached to the TEM operated in the scanning TEM (STEM) mode was used to analyze the distributions of relevant elements in the nanocomposites. Powder X-ray diffraction (XRD) patterns recorded on a Bruker D8 diffractometer using Cu K\( \alpha \) radiation (\( \lambda = 0.154,056 \text{ nm} \)) were used to determine the crystal structure of all samples, while XPS conducted on a VG ESCALAB MKII spectrometer was used to characterize the chemical states of the relevant elements.

### 2.5 Electrochemical measurements

Before the electrochemical tests of all relevant samples, they were loaded on the XC-72 carbon substrates. Specifically, a calculated amount of carbon powder was added to the hexane solution of the nanocomposites or nanoalloys. After stirring for 6 h, the carbon-supported samples were collected by centrifugation and dried at room temperature. The accurate contents of Pt in all samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), as summarized in Table S1.

Electrochemical measurements for methanol electro-oxidation were carried out in a standard three-electrode cell connected to a Bio-logic VMP3 potentiostat. A saturated calomel electrode (SCE) and a Pt mesh (1 \( \times \) 1 cm\(^2 \)) attached to a Pt wire were used as the reference electrode and counter electrode, respectively. The working electrode was a thin layer of Nafion-impregnated catalyst cast on a glassy carbon disk electrode. This electrode was prepared as follows: 5 mg of the relevant catalyst (\( \text{Pt}_3\text{Co}–\text{CoP}_2/C \), \( \text{Pt}_3\text{Co}/C \), or \( \text{Pt}/\text{C-JM} \)) was dispersed ultrasonically in 1 ml of the aqueous solution containing 0.8 ml of ethanol and 0.05 ml of Nafion solution. Then, 5 \( \mu \)L of the ink was dropped onto the 5-mm glassy carbon disk electrode, followed by drying in a stream of warm air at 70°C.

The electrochemically active surface areas (ECSAs) and the tolerance to CO poisoning were estimated by the CO stripping voltammograms. In detail, the CO was introduced into an electrolyte solution (0.1 mol/L HClO\(_4\) or 1.0 mol/L KOH) for 15 min to complete the absorption of CO onto the relevant catalyst. Then, excessive CO in the electrolyte was purged with high purity \( \text{N}_2 \) for 15 min. The amount of CO\(_{\text{ads}}\) was measured by integrating the CO\(_{\text{ads}}\) peak and corrected for electric double-layer capacitance. The specific ECSAs could be calculated using the equation of ECSA = \( Q/420G \), where \( Q \) is the charge of CO desorption-electro-oxidation in microcoulomb (\( \mu \)C), which is calculated by dividing the scan rate with the integral area of CO desorption peak, \( G \) represents the total amount of Pt (\( \mu \)g) loaded on the electrode, and 420 is the charge (\( \mu \)C/cm\(^2 \)) required to oxidize a monolayer of CO on the catalyst.

The electrocatalytic performance including activity and durability of relevant catalysts for methanol electro-oxidation was evaluated at room temperature by cyclic voltammetry (CV) and chronoamperometry. The CV curves were obtained at a scan rate of 50 mV/s from −0.25 to 1.0 V versus SCE in an acidic electrolyte (0.1 mol/L HClO\(_4\) and 1 mol/L CH\(_3\)OH) or from −1.05 to 0.2 V versus SCE in an alkaline electrolyte (1.0 mol/L KOH and 1 mol/L CH\(_3\)OH). The current densities were normalized by ECSAs and mass loading of the relevant catalysts to obtain their specific activities.

### 3 RESULTS AND DISCUSSION

We first characterize the product using XRD obtained by combining the reduction of Pt and Co ions at a Pt/Co ratio of 1/3 with the subsequent phosphating at an elevated temperature. Instead of a uniform compound
comprising Pt, Co, and P after phosphating, two distinct crystal phases in the final product are clearly discerned, that is, cubic phase of Pt₃Co alloys (JCPDS Card No. 290499) and monoclinic phase of CoP₂ species (JCPDS Card No. 260481), as shown in Figure 1, in which the (111), (200), and (220) facets indexed to cubic Pt₃Co alloys and the (11̅1), (200), (210), and (113) facets indexed to monoclinic CoP₂ species could be easily identified. In addition, the XRD pattern also confirms that the products thus produced are of high crystallinity.

TEM observations were conducted on a JEOL JEM-2010F electron microscope to address the detailed structure of the products obtained by combining the reduction of Pt and Co ions at a Pt/Co ratio of 1/3 with the subsequent phosphating at an elevated temperature.

![Figure 1](image)

**Figure 1** X-ray diffraction pattern of the products obtained by combining the reduction of Pt and Co ions at a Pt/Co ratio of 1/3 with the subsequent phosphating at an elevated temperature.
process continues, the CoP₂ domains gradually grow. However, the growth of the CoP₂ domains might be inhibited in the direction that connects with the remaining bimetallic particles. As a result, rod-like CoP₂ domains are formed instead in the heterogeneous structures. In addition, one likely possibility for the formation of dimeric Pt₃Co–CoP₂ nano-composites is to reduce the interfacial energy of the hybrid interface, as there exists a lattice mismatch between cubic phase Pt₃Co and monoclinic phase CoP₂. The formation of Pt₃Co–CoP₂ heterodimers reduces the interfacial area of two domains in the nanocomposites, circumventing their large interfacial strain. This result is consistent with the findings reported previously, where Au–Cu₂S, Pt–CuS, and Pt–Ag₂S nanocomposites all exhibit heterodimeric structures.⁷,⁴¹,⁴²

The extraction of Co from bimetallic PtₓCoᵧ nanoparticles ceases when a robust Pt₃Co alloy phase is reached, giving rise to final heterogeneous nanocomposites constituted by quasi-spherical Pt₃Co and rod-like CoP₂ domains. In addition, the extraction of Co by TOP also satisfactorily interprets the size decrease from the 11.4 nm original PtₓCoᵧ particles to 5.1 nm quasi-spherical Pt₃Co domains of the final nanocomposites.

Obviously, the original Pt/Co precursor ratio has a significant effect on the final composite products. At an initial Pt/Co precursor ratio of 3/1, the robust Pt₃Co alloy phase renders the extraction of Co from bimetallic particles to be impossible, and therefore no heterogeneous nanocomposites are produced after phosphating at 280°C for 2 h, as proved by Figure S2 for their TEM and HRTEM images. As the ratio of Co increases (Pt/Co of 1/1), the extraction of Co from the bimetallic particles becomes feasible, but due to relatively lower Co contents, the as-synthesized heterogeneous Pt₃Co–CoP₂ nanocomposites have bigger Pt₃Co quasi-spherical domains and shorter CoP₂ rod-like domains in comparison with those in Pt₃Co–CoP₂ nanocomposites prepared from Pt/Co precursor ratio of 1/3, as displayed by TEM and HRTEM images in Figure S3. It is noteworthy that in the absence of Pt ionic precursors, direct phosphating of Co ions with TOP at 280°C would only give rise to an unknown product with leek-like morphologies, as shown by Figure S4 for their microscopic characterizations. Their XRD pattern (Figure S5) presents some broad and weak peaks that do not correspond to any already known samples, indicating that the phosphating process is actually more complicated and its details are yet to be explored.

We determined the chemical states of Pt in the as-prepared heterogeneous Pt₃Co–CoP₂ nanocomposites using XPS and compared them with those of the Pt in the home-
made Pt₃Co nanoalloys and commercial Pt/C catalyst. As shown in Figure 5A, the 4f spectra of Pt for all samples can be deconvoluted into two pairs of doublets. As summarized in Table S2, the more intense doublet (at 72.3 and 75.6 eV for Pt₃Co–CoP₂, 71.8 and 75.1 eV for Pt₃Co, 71.6 and 75.0 eV for commercial Pt/C) correspond to the Pt at a zero-valent state, while the weaker doublets, with binding energies higher than those of metallic Pt, are an indication of the oxidized Pt (e.g., PtO). Compared with those of commercial Pt/C catalyst, a slight shift to higher values is observed for the 4f⁷/₂ and 4f⁵/₂ binding energies of Pt in the home-made Pt₃Co nanoalloys. This shift is able to be expected because transition metals, for example, Fe, Ni, and Co, usually have more 5d vacancies than Pt and could attract electrons from the latter, inducing the decrease in electron density around Pt atoms.43 Interestingly, the comparison between the Pt 4f XPS spectra of Pt₃Co–CoP₂ nanocomposites and home-made Pt₃Co nanoalloys reveals that the CoP₂ domains in the heterogeneous nanocomposites could further promote the positive shift of Pt binding energies, indicating that there is additional electronic coupling between the alloy and semiconductor domains in the nanocomposites, analogous to that in noble metal–metal oxide or chalcogenide nanocomposites.44–47 The shift to a higher value in Pt binding energies is a welcome feature for the electro-oxidation of methanol. As have been well documented, a major deficiency for Pt-based nanomaterials used as catalysts for methanol electro-oxidation is they are susceptible to poisoning by CO-like intermediates.45,47 In this sense, the decrease in electron density around Pt atoms that means their higher binding
energies could weaken the adsorption of poisoning CO-like intermediates generated from methanol electro-oxidation on the Pt catalyst surfaces as the decreased electron density is not capable enough to back-donate the antibonding orbitals of CO, thus improving their intrinsic electrocatalytic properties.48

Both the as-prepared Pt$_3$Co–CoP$_2$ nanocomposites and home-made Pt$_3$Co nanoalloys were loaded on Vulcan carbon substrates for estimating their catalytic performance in methanol electro-oxidation at room temperature. As shown by the representative TEM images in Figure S6, the as-prepared Pt$_3$Co–CoP$_2$ nanocomposites and home-made Pt$_3$Co nanoalloys are uniformly dispersed on the carbon substrate. The accurate mass loadings (Pt base) on carbon substrate determined by ICP-AES are 6.4% and 8.0% for as-prepared Pt$_3$Co–CoP$_2$ nanocomposites and home-made Pt$_3$Co nanoalloys, respectively.

Figure 5B shows the cyclic voltammograms with and without CO$_{ad}$ on as-prepared Pt$_3$Co–CoP$_2$ nanocomposites, home-made Pt$_3$Co alloy nanoparticles, and commercial Pt/C catalyst. As observed, the peak potential of CO-stripping on as-prepared Pt$_3$Co–CoP$_2$ nanocomposites is apparently more negative than that on the home-made Pt$_3$Co nanoalloys and Pt/C catalyst. This shift to a lower value is ascribed to the decrease of electron density around Pt atoms in the Pt$_3$Co–CoP$_2$ nanocomposites, which weakens the interaction between Pt and CO-like intermediates,49,50 suggesting a higher poisoning tolerance of Pt$_3$Co–CoP$_2$ nanocomposites than that of the home-made Pt$_3$Co nanoalloys and commercial Pt/C catalyst. In an acidic electrolyte (0.1 mol/L HClO$_4$), based on the CO stripping peaks shown in Figure 5B, the ECSAs normalized by the mass of Pt are calculated to be 47.6, 55.2, and 80.0 m$^2$/g for the as-prepared Pt$_3$Co–CoP$_2$ nanocomposites, home-made Pt$_3$Co alloy nanoparticles, and commercial Pt/C catalyst, respectively. The relatively smaller ECSAs of the as-prepared Pt$_3$Co–CoP$_2$ nanocomposites compared with that of home-made Pt$_3$Co alloy nanoparticles and commercial Pt/C catalyst are most likely attributed to the Pt surface dilution by Co and the intimate contact between their quasi-spherical Pt$_3$Co and rod-like CoP$_2$ domains. For the CO-stripping tests conducted in alkaline medium, the peak potentials of as-prepared Pt$_3$Co–CoP$_2$ nanocomposites, home-made Pt$_3$Co nanoalloys, and Pt/C catalyst show the same trend (Figure S7), and the ECSAs calculated based on the CO stripping voltammograms are 26.5 m$^2$/g for Pt$_3$Co–CoP$_2$ nanocomposites, 38.0 m$^2$/g for home-made Pt$_3$Co nanoalloys, and 44.0 m$^2$/g for commercial Pt/C catalyst, respectively.

The ECSA- and mass-based voltammograms for methanol electro-oxidation on the as-prepared Pt$_3$Co–CoP$_2$ nanocomposites, home-made Pt$_3$Co alloy nanoparticles, and commercial Pt/C catalyst in an acidic medium are
given in Figure 6A,B, respectively. The current densities for all catalysts in the voltammograms normalized by ECSA and mass in the forward scans are compared by the histogram in Figure 6C, and as well as summarized in Table S3. As expected, due to the favorable electronic configuration of Pt in the nanocomposites, the comparison of current densities shows that the as-prepared Pt₃Co–CoP₂ nanocomposites have much higher specific activity and mass activity than those of home-made Pt₃Co nanoalloys and commercial Pt/C catalyst for methanol electro-oxidation. The ECSA-based activity of the as-prepared Pt₃Co–CoP₂ nanocomposites is about two and three times as high as that of home-made Pt₃Co nanoalloys and commercial Pt/C catalyst, respectively, while this value is about 1.5 and 2 for mass-based activity. It should be pointed out that the electronic coupling in nanocomposites is only the most possible explanation for the catalytic enhancement of Pt₃Co–CoP₂ heterogeneous nanocomposites toward methanol electro-oxidation. The limitation of using this explanation is apparent since the stability of other species, for example, Co and P species in the methanol electro-oxidation environment is yet to be known and they might also play important roles in determining the electrocatalytic performance of the nanocomposites. Therefore, thorough material characterization is of necessity before the experimental observations are used to generalize even a phenomenological theory.

The durability of the electrocatalysts is also an important indicator to estimate their performance in electrocatalysis. The CA tests in a 0.1 mol/L HClO₄ with 1.0 mol/L methanol

![Graphs showing ECSA-based cyclic voltammograms and mass-based cyclic voltammograms of Pt₃Co–CoP₂ nanocomposites, Pt₃Co nanoalloys and commercial Pt/C catalyst in argon-purged HClO₄ (0.1 mol/L) with 1 mol/L methanol.](image-url)

**FIGURE 6** ECSA-based cyclic voltammograms of Pt₃Co–CoP₂ nanocomposites, Pt₃Co nanoalloys and commercial Pt/C catalyst in argon-purged HClO₄ (0.1 mol/L) with 1 mol/L methanol (A); mass-based cyclic voltammograms of Pt₃Co–CoP₂ nanocomposites, Pt₃Co nanoalloys and commercial Pt/C catalyst in argon-purged HClO₄ (0.1 mol/L) with 1 mol/L methanol (B); histogram showing the comparison of ECSA- and mass-based current densities of Pt₃Co–CoP₂ nanocomposites, Pt₃Co nanoalloys and commercial Pt/C catalyst for methanol electro-oxidation (C); chronoamperograms of Pt₃Co–CoP₂ nanocomposites, Pt₃Co nanoalloys and commercial Pt/C catalyst at 0.4 V versus SCE in argon-purged HClO₄ (0.1 mol/L) with 1 mol/L methanol (D). ECSA, electrochemically active surface area; SCE, saturated calomel electrode.
at 0.4 V for 6000 s were used to examine the durability of the as-prepared Pt₃Co–CoP₂ nanocomposites, home-made Pt₃Co alloy nanoparticles, and commercial Pt/C catalyst. As from Figure 6D, the performance of the three electrocatalysts decline to a certain extent after 6000 s, but the as-prepared Pt₃Co–CoP₂ nanocomposites still maintain a relatively higher electrochemical activity than that of the home-made Pt₃Co alloy nanoparticles, and commercial Pt/C catalyst, indicating that they have better stability.

It is noteworthy that the as-prepared Pt₃Co–CoP₂ nanocomposites also perform very well for methanol electro-oxidation in an alkaline medium, as evinced by Figure S8A,B for their ECSA- and mass-based voltammograms in 1.0 mol/L KOH with 1.0 mol/L methanol. The details are listed by the histogram in Figure S8C and Table S4 for convenient comparison. In brief, the ECSA-based activity of the as-prepared Pt₃Co–CoP₂ nanocomposites in the alkaline medium is about three and four times as high as that of home-made Pt₃Co nanoalloys and commercial Pt/C catalyst, respectively, while this value is about 2 and 3 for mass-based activity.

4 | CONCLUSIONS

In summary, we have demonstrated a strategy that combines the reduction of Pt and Co ionic precursors at an appropriate ratio with the subsequent phosphating at an elevated temperature for constructing heterogeneous nanocomposites comprising quasi-spherical Pt₃Co alloy domains and rod-like CoP₂ domains for high-efficiency methanol electro-oxidation. The strong electronic coupling between different domains renders the electron density to decrease around Pt atoms in the nanocomposites, favorable for weakening the adsorption of poisoning CO-like intermediates on the catalyst surfaces. Therefore, the as-prepared heterogeneous Pt₃Co–CoP₂ nanocomposites exhibit good performance for methanol electro-oxidation both in acidic and alkaline media. In specific, in an acidic medium, at a Pt loading of only 6.4% on a common carbon substrate, the mass-based activity of Pt₃Co–CoP₂ nanocomposites is about 2 and 1.5 times as high as that of commercial Pt/C catalyst (20% mass loading) and home-made Pt₃Co alloy nanoparticles (8.0% mass loading), while in alkaline medium, these values are 3 and 2, respectively. By optimizing the composition, size, and morphology of each domain in the nanocomposites, further enhancement in their electrocatalysis could be optimistically expected.

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CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

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