Behavior of gold-enhanced electrocatalytic performance of NiPtAu hollow nanocrystals for alkaline methanol oxidation

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ABSTRACT The Pt-based catalyst tends to be poisoned by carbon monoxide (CO)-like intermediates produced in fuel cell reactions, which seriously deteriorates its catalytic performance. Herein, noble metal Au with the capacity of resistance to CO-like intermediates poisoning was employed to construct multi-element Pt-based catalysts. Two trimetallic NiPtAu hollow nanocrystals (HNCs) with different surface Au contents were synthesized to explore the role of Au in electrocatalysis for alkaline methanol oxidation reaction (MOR). The trimetallic NiPtAu-SR_{Au} HNCs catalyst with the relative rich Au content (15.17 at%) on surface exhibits a much lower CO oxidation peak potential than the other HNCs counterpart and 20 wt% Pt/C, which indicates the more exceptional CO-resisting performance. Besides, the MOR specific activity of NiPtAu-SR_{Au} HNCs (31.52 mA cm⁻²) is 7 times higher than that of 20 wt% Pt/C (4.50 mA cm⁻²). This enhancement in catalytic activity as well as anti-CO poisoning capability for NiPtAu-SR_{Au} HNCs can be mainly ascribed to the weakened CO adsorption due to the exposure of Au atoms on NiPt surface evidenced by the experimental data and density functional theory calculations. This study not only investigates the role of Au in MOR catalysis but also could be helpful for designing and optimizing the electrocatalysts for high-active and robust fuel cell applications.

Keywords: trimetallic NiPtAu, hollow nanocrystals, methanol oxidation, carbon monoxide poisoning

INTRODUCTION

The direct methanol fuel cells (DMFCs) are expected to be one of the most significant new resource fuel cells for

their higher utilization efficiency, higher power density, and intrinsically lower environmental pollution than that of traditional energy sources to meet the energy and environmental challenges [1–3]. It is vital to get an appropriate catalyst to improve the efficiency of the methanol oxidation reaction (MOR) of DMFCs. It is believed that platinum (Pt) is the most effective element employed in the design and synthesis of the catalyst for MOR [4–6]. Up to now, a series of Pt-based catalysts with various structures have been synthesized, including alloy nanoparticles [7–9], core-shell nanostructures [10,11], and hollow nanostructures [12–14]. Among these, hollow nanostructures have many advantages in improving the electrocatalytic performance with a large specific surface area and abundant active sites [15]. There are several strategies for synthesizing the hollow nanostructures [16,17], including the Kirkendall effect [18], seed-mediated growth followed by etching [19], and galvanic replacement [20]. The last approach has been proposed that the metal with a relatively low redox potential can be facilely used as the sacrificial templates to reduce the deposition of noble metal atoms on their surfaces when the atoms of the template are oxidized and dissolved into the reaction solution [21]. Additionally, another strategy to enhance the catalytic performance is to control the composition of the catalyst surfaces for their great influences on the adsorption/desorption behavior of the reactants and intermediates during the electrochemical reaction [22,23]. Thus, it is significant to design novel electrocatalysts with hollow nanostructures and optimize the surface composition to boost the electrocatalytic

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performance for MOR.

Gold (Au) has been extensively applied for a variety of electrocatalytic reactions due to its unique properties [24]. Recent studies indicate a possible relevance between Au and catalytic stability where the long-term stability of catalysts can be assured by incorporating Au into Pt-based nanocatalysts because of up-shifting the dissolution potential of Pt [25–27]. More importantly, Au has great resistance to CO-like intermediates poisoning by decreasing the adsorption energy of CO [28–30]. Therefore, the appropriate Au content and status of the Pt-based nanocatalysts are the key factors to improve their catalytic activity and stability. Currently, many important Pt-based catalysts employed for MOR tend to be poisoned by CO-like carbonaceous intermediates generated in the reaction process, resulting in rapid decay of their catalytic activity. This is a great challenge to Pt-based catalysts for MOR. However, it is expected that catalysts with high activity and excellent durability should be synthesized *via* appropriate incorporation of Au.

For these reasons, we demonstrate a facile pathway to construct two trimetallic NiPtAu hollow nanocrystals (HNCs) with different surface compositions and structures. In this study, two trimetallic NiPtAu HNCs exposing different Au contents on the surfaces were produced by controlling the order of replacement in the chemical synthesis process (Fig. 1). The action mechanism of Au on electrocatalytic performance for MOR was investigated by comparing the two NiPtAu HNCs with different amounts of Au on the surface and traditional HNCs. Meanwhile, the adsorption energy of CO could be weakened by the surface Au which facilitated the removal of CO on Pt. As expected, the results demonstrate that the NiPtAu-SR_{Au} HNCs catalyst displays greatly enhanced catalytic performance towards MOR, much superior to the NiPtAu-SP_{Au} or bimetallic NiPt HNCs owing to the rich surface exposure of atoms and their oxidation status. Furthermore, it is also found that the NiPtAu-SR_{Au} HNCs possess negative oxidation potential and onset potential in CO-stripping and less current attenuation in chronoamperometry measurements at different potentials for MOR with CO gas. Meanwhile, density functional theory (DFT) calculations illustrate that Au atoms doped on the surface of the NiPt nanocatalysts can effectively decrease the adsorption energy of CO so that the NiPtAu-SR_{Au} HNCs have an exceptional capability of anti-CO poisoning. These preliminary results are more favourable for mechanism understanding of elemental content and valence of Au in trimetallic catalysts for enhanced catalytic performance and provide a reference for the fabrication

of high-performance MOR catalysts through the reasonable design and construction of surface component and states of trimetallic catalysts.

RESULTS AND DISCUSSION

Characterization of the morphology, nanostructure, and composition of nanocatalysts

The synthetic process is schematically illustrated in Fig. 1. Ni possesses a lower electronegativity than Au and Pt. For the NiPtAu-SR_{Au} HNCs, NiPt HNCs were produced by galvanic replacement between Ni and Pt, and then, a mild galvanic replacement reaction between Au(III) and Ni atom in NiPt HNCs was carried out at first accompanying with adding the HAuCl₄ solution. Au atoms formed isolated clusters or small nanoparticles on the surface of NiPt HNCs. Similarly, for the NiPtAu-SP_{Au} HNCs, NiAu HNCs were obtained by the same principle. Excessive Pt (IV) reacted with the Ni atoms in NiAu HNCs after adding the H₂PtCl₆ solution and a portion of Pt(IV) was directly reduced to atoms which assembled or even developed; another portion of Pt(IV) diffused onto the surfaces of HNCs, and a similar chemical reaction took place and then the reduced Pt atoms clustered or grew *in situ* [31–33].

The morphologies of the as-prepared NiPtAu HNCs were observed using transmission electron microscopy (TEM). Fig. 2 shows the morphology and the elemental distribution of NiPtAu-SP_{Au} and NiPtAu-SR_{Au} HNCs. As

Figure 1 Schematic diagram of the synthetic route of NiPtAu-SR_{Au} and NiPtAu-SP_{Au} HNCs. Two trimetallic NiPtAu HNCs with different surface compositions and structures prepared by the diagrammatic process have different resistance to CO, one of the MOR intermediate products.

Figure 2 (a, c) TEM images, (b, d) HRTEM images of NiPtAu-SP_{Au} and NiPtAu-SR_{Au} HNCs, respectively. (b1–b4) and (d1–d4) correspond to the marked areas in (b) and (d) encoded sequentially with 1 to 4 (scale bars: 1 nm). Yellow and white boxes represent the lattice fringes of Au and Pt, respectively. (e–h) EDS elemental mapping images of NiPtAu-SR_{Au} HNCs.

can be seen, both samples had plenty of typical HNCs with an average size of 22.87 and 24.12 nm, respectively (see Fig. S1) and displayed similar dendritic nanostructures (Fig. 2a, c). The X-ray diffraction (XRD) patterns of NiPtAu HNCs and NiPt HNCs are displayed in Fig. S2 and the four peaks are mainly assigned to the Pt (111), (200), (220), and (311) planes of face-centered-cubic (fcc) phase (Pt JCPDS No. 04-0802, Ni JCPDS No. 04-0850, and Au JCPDS No. 04-0784) [34]. The peak positions of NiPtAu-SR_{Au} and NiPtAu-SP_{Au} HNCs shifted to lower angles relative to those of the NiPt HNCs, indicating that Au atoms were introduced into the NiPt HNCs [28,35].

In order to distinctly illustrate the Pt and Au distributions in NiPtAu-SP_{Au} and NiPtAu-SR_{Au} HNCs, herein, the lattice fringe spacing of the shells was further analyzed by high-resolution TEM (HRTEM) (Fig. 2b, d). The well-resolved lattice fringe spacing regions in the HRTEM images of the hollow nanosphere edge were enlarged and the representative results were selected for detailed annotation in Fig. 2b1–b4, d1–d4 (the lattice fringe and crystal index of other squares were not repeatedly marked in detail for these areas were consistent with those marked in the images). Two of six regions

were the lattice fringe of Au on the edge of the NiPtAu-SP_{Au} HNCs; however, six of eight regions of NiPtAu-SR_{Au} HNCs were the lattice fringe of Au, and the lattice fringes of 0.21 and 0.23 nm were closed to the (200) and (111) planes of fcc Au, respectively. These results revealed that the surface-exposed Au of NiPtAu-SR_{Au} HNCs was relatively rich in comparison with that of NiPtAu-SP_{Au} HNCs by analyzing the number of the yellow boxes at the edges in the images. Furthermore, the energy dispersive spectroscopic (EDS) elemental mapping of NiPtAu-SR_{Au} HNCs verified that the Pt, Ni, and Au uniformly coexisted in the shell (Fig. 2e–h). It also demonstrates that a much higher content of Pt was distributed on the external surfaces of NiPtAu-SP_{Au} HNCs and formed a Pt-rich surface layer. On the contrary, the Ni and Au were enriched mainly on the internal surfaces of the NiPtAu-SP_{Au} HNCs (Fig. S3). For comparison, the morphology and the elemental characterizations of NiPt and NiAu HNCs from the synthetic process of the trimetallic NiPtAu HNCs are shown in Figs S4, S5.

The X-ray photoelectron spectroscopy (XPS) results reflect the elemental compositions of the sample surface and EDS results display the whole elemental compositions. The composition analysis by EDS and XPS pro-

vided further evidence that there was a distinct difference in the surface contents of Au between NiPtAu-SR_{Au} and NiPtAu-SP_{Au} HNCs (Table S1). The former consisted of 69.43 at% Pt, 14.24 at% Ni, and 16.33 at% Au according to the results of EDS. It was found that there was slight distinction in the overall alloy compositions between the two trimetallic catalysts (72.86 at% Pt, 11.04 at% Ni, and 16.10 at% Au for NiPtAu-SP_{Au} HNCs). Moreover, XPS surface analysis indicated that there was a significant difference in the surface contents of Au between the two samples. The surface Au contents of NiPtAu-SR_{Au} and NiPtAu-SP_{Au} HNCs were 15.17 and 8.00 at%, respectively. The EDS and XPS results indicated that Au element in NiPtAu-SR_{Au} HNCs distributed mainly on the external surfaces of the hollow nanospheres. For the NiPtAu-SP_{Au} HNCs, only a trace of Au on the surface was detected by XPS for its low detection sampling depth in comparison with EDS. It was confirmed that these two NiPtAu HNCs with similar compositions had different Au contents on their surfaces.

Electrocatalytic performance

Given the above verification of different surface contents of Au in the two NiPtAu HNCs samples, the following question is whether this difference has a profound effect on the electrocatalytic performances for MOR. In this

regard, the electrocatalytic performances of the as-prepared samples for MOR in alkaline electrolytes were assessed. As a contrast, the same measurements of NiPt HNCs and Pt/C were also performed (the results of NiAu HNCs are shown in Fig. S6).

Fig. 3a shows the cyclic voltammogram (CV) of these four catalysts activated in N₂-saturated 1 mol L⁻¹ KOH. The catalytic performances of the activated catalysts were measured in 1 mol L⁻¹ KOH + 1 mol L⁻¹ CH₃OH (Fig. 3b, c), and insights into MOR performance can be gained by quantitatively comparing the oxidation peak corresponding to the current density and onset potential in the forward scan. Notably, NiPtAu-SR_{Au} HNCs exhibit the highest specific activity (31.52 mA cm⁻²) normalized according to the electrochemical surface area (ECSA), compared with NiPtAu-SP_{Au} (30.03 mA cm⁻²), NiPt HNCs (18.81 mA cm⁻²) and Pt/C (4.50 mA cm⁻²). Combining with the results of inductively coupled plasma mass spectrometry (ICP-MS), the mass activities of NiPtAu-SR_{Au}, NiPtAu-SP_{Au}, NiPt HNCs, and Pt/C reached 1184.64, 1066.78, 993.53, and 749.64 mA mg_{Pt}⁻¹, respectively (Fig. 3d). Moreover, the specific activities and mass activities combined with the ECSA and the mass of Pt loading are summarized in Table S2. NiPtAu-SR_{Au} HNCs display the best performance compared with other recently reported catalysts in alkaline MOR (Table S3).

Figure 3 CV curves of NiPtAu-SR_{Au}, NiPtAu-SP_{Au}, NiPt HNCs, and Pt/C in N₂-saturated (a) 1 mol L⁻¹ KOH and (b) 1 mol L⁻¹ KOH + 1 mol L⁻¹ CH₃OH at a scan rate of 50 mV s⁻¹. (c) Blow-ups of (b) from -0.8 to -0.3 V. (d) Summary of specific activities and mass activities. (e) CA curves recorded at -0.3 V. (f) EIS measurements in 1 mol L⁻¹ KOH + 1 mol L⁻¹ CH₃OH at the potential of -0.3 V.

Besides, the durability of the as-prepared samples was also investigated by chronoamperometric (CA) measurements. As shown in Fig. 3e, NiPtAu-SR_{Au} HNCs display a higher initial specific activity and a much slower current decay than the other three samples. This result reveals NiPtAu-SR_{Au} HNCs retain the most remarkable catalytic performance for quite a long time and it has the best capacity of tolerating CO-like intermediates from MOR. Furthermore, electrochemical impedance spectroscopy (EIS) measurements were performed at -0.3 V (vs. saturated calomel electrode (SCE)) to evaluate the electrochemical reaction processes (Fig. 3f). The diameter impedance arc (DIA) of catalysts as an important index can be employed to evaluate the charge-transfer resistance (R_{ct}) during the process of MOR [36,37]. It is clear that the DIA of the as-prepared samples increases in the following order: NiPtAu-SR_{Au} HNCs < NiPtAu-SP_{Au} HNCs < NiPt HNCs < Pt/C. The remarkably smaller DIA of NiPtAu-SR_{Au} HNCs indicates it has a lower R_{ct} during MOR, corresponding to its higher catalytic activity.

The possible mechanism of MOR in alkaline media can be briefly described as follows [38,39]: methanol molecules are initially adsorbed on the surfaces of the NiPtAu HNCs and then dissociated to generate various carbonaceous intermediates, such as CO. The carbonaceous species are eventually oxidized to produce the final product CO₂. This process can be accelerated by the electronic, geometric, and synergistic effects in the

multicomponent catalysts [38]. So, the performance variation of the two NiPtAu HNCs with different surface Au contents may be due to the following possible factors: (i) the capacities of samples are different in resisting the intermediates poisoning produced during MOR. By the direct electronic coupling between different elements, the third kind of metal has indeed a strong influence on the adsorption energy of the surfaces as adsorption substrate on the surface of bimetallic catalysts. The CO is one of the significant intermediate products [31,35,40]. (ii) The electron structures and their synergistic effects in NiPtAu-SR_{Au} HNCs possibly differ from NiPtAu-SP_{Au} HNCs.

Mechanism of Au-enhanced electrocatalytic performance

In order to uncover the reasons for the enhanced electrocatalytic performance of NiPtAu-SR_{Au} HNCs, the near-surface compositions and status of the catalysts were detected by XPS. Pt, Ni, and Au were confirmed by the XPS survey of the two NiPtAu HNCs catalysts in Fig. S7. The Pt 4f peaks of these two catalysts can be assigned to Pt 4f_{7/2} and Pt 4f_{5/2}, and can be further divided into two peaks, associated with metallic state Pt(0) and Pt oxide (Fig. 4a, d). The 4f_{7/2} peaks of Pt(0) in NiPtAu-SR_{Au} and NiPtAu-SP_{Au} HNCs are located at 71.14 and 71.15 eV, respectively, and both of them positively shift compared with that of pure Pt(0) (71.00 eV) reported previously [41,42]. It is demonstrated that synergistic effects in the

Figure 4 XPS spectra of (a, d) Pt 4f, (b, e) Ni 2p, (c, f) Au 4f peaks of NiPtAu-SR_{Au} and NiPtAu-SP_{Au} HNCs, respectively.

NiPtAu catalyst lead to a downshifting of the Pt d-band center and it is usually related to the weak binding of the intermediates on the catalyst's active sites [43,44]. Fig. 4b, e show the Ni 2p peaks in deconvoluted XPS spectra of NiPtAu-SR_{Au} and NiPtAu-SP_{Au} HNCs and they can be split into three pairs of peaks, associated with metallic Ni, Ni oxide, and satellite peak, respectively [45].

The Au 4f peaks of NiPtAu-SR_{Au} HNCs can be divided into two pairs of peaks in Fig. 4c, indicating the presence of both metallic and cationic Au species [46,47]. One pair of peaks with the binding energies located at 84.02 and 87.70 eV are assigned to Au 4f_{7/2} and Au 4f_{5/2}, respectively, corresponding to Au(0). The other peaks located at 84.78 and 88.59 eV are distributed to Au 4f_{7/2} and Au 4f_{5/2} corresponding to oxidized Au species in NiPtAu-SR_{Au} HNCs [48–51]. Nevertheless, as shown in Fig. 4f, there is only metallic state Au(0) in the Au 4f peak for NiPtAu-SP_{Au} HNCs. The oxidized Au species may be related to the order of substitution during the preparation of catalysts. As previously studied [52–54], cationic Au plays a crucial role in catalyzing CO oxidation. For the higher adsorption energy of CO on cationic Au than that on Au(0), it is demonstrated that the Au in the cationic state may be kinetically more significant than that in the metallic state under some reaction conditions [52]. Therefore, the evidence suggests that the NiPtAu-SR_{Au} HNCs may have superior performance of CO tolerance for MOR in alkaline solution, resulting from the oxidation state of Au 4f. The surface electronic structures of NiPt HNCs as the reference sample are shown in Fig. S8.

In order to verify that the superior performance of MOR is due to the strongly resistant ability to CO, a series of experiments on the oxidative removal of CO were conducted. The CO-stripping measurements of NiPtAu-SR_{Au}, NiPtAu-SP_{Au}, and NiPt HNCs were carried out in a 1 mol L⁻¹ KOH solution (Fig. 5a–c). It is found that there is a sharp oxidation peak during the first forward scan, suggesting the CO adsorption on the surface of catalysts. Subsequently, these sharp oxidation peaks disappear in the second cycle because of the oxidative removal of CO from the catalysts. The value of the potential corresponding to the sharp oxidation peak and onset oxidation potential are standards of CO tolerance [55]. Obviously, the onset oxidation potential and the CO oxidation potential of NiPtAu-SR_{Au} HNCs are located at -0.646 and -0.375 V, respectively, and more negative than those of NiPtAu-SP_{Au} and NiPt HNCs. This significant negative shift reveals that the CO strips more easily from the surfaces of NiPtAu-SR_{Au} HNCs. The total amount of active sites available for CO adsorption decreases, when

Au is introduced into the Pt-based catalysts [56]. It also proves that the CO oxidation peak potential of NiPtAu-SP_{Au} HNCs roughly equals to that of NiPt HNCs (-0.367 and -0.370 V, respectively). It suggests that the CO resistance strongly depends on the amount of Au exposed on the surface rather than that in the interior of NiPtAu-SP_{Au} HNCs, in which Au could not play a full role in resisting the toxicity of CO. Based on these results, the presence of Au on the surfaces of the as-prepared catalysts has a positive effect on tolerating CO (the result of CO-stripping of Pt/C is shown in Fig. S9).

After the first experiment of CA under the N₂-saturated condition for 3600 s, the second one for durability of the catalysts on the degree of CO tolerance was borne out immediately in the electrolyte, in which CO gas was bubbled uninterruptedly [57]. As shown in Fig. 5d–f, there is no sharp attenuation for the current value of NiPtAu-SR_{Au} HNCs during MOR, in stark contrast to that of NiPtAu-SP_{Au} and NiPt HNCs. These further reveal that the NiPtAu-SR_{Au} HNCs have a superior anti-CO poisoning capability, and the content of surface Au is more important for CO resistance. Moreover, the CA experiments at different potentials (-0.3 and -0.5 V) present a similar variation tendency of current (Fig. S10).

The CO resistance of the trimetallic NiPtAu with Ni, Pt, and Au atoms occupied at different locations was evaluated by DFT calculations. We merely considered the adsorption of CO on the surface of the catalysts, due to the adsorbed CO only on the surfaces of catalysts in the experimental conditions. The adsorption of CO at four different sites of atoms including Ni, Pt, and Au, was calculated to qualitatively evaluate the adsorption capacity of the NiPtAu surfaces. As shown in Fig. 5g, it can be found that the adsorption energy (E_{ads}) of CO on Au (-0.98 eV) is much lower than that on Ni (-1.97 eV) and Pt sites (-2.06 or -2.08 eV), which means that the CO molecules are likely adsorbed on Pt atoms, instead of Au or Ni. Therefore, the doping of Au could induce a strong resistance to CO. These data are also confirmed by the experimental results of the trimetallic NiPtAu HNCs, that is, the greatly reduced CO poisoning has been observed in Fig. 5a, d. Significantly, the adsorption of CO on Pt was influenced by the Au atoms. The E_{ads} of CO at Pt-1 is -2.06 eV, slightly weaker than that at Pt-2, and more approximate to the value at Au, which indicates that the Au-doping can reduce the CO adsorption around them [28,58], although Au atoms are not doping on the top surface. Overall, the Au atoms on NiPt nanocatalysts can effectively weaken the adsorption of CO, leading to superior capability of anti-CO poisoning during the MOR

Figure 5 (a–c) CO-stripping curves of NiPtAu-SRAu, NiPtAu-SPAu, and NiPt HNCs in 1 mol L⁻¹ KOH solution at a scan rate of 50 mV s⁻¹. (d–f) CA curves of the NiPtAu-SRAu, NiPtAu-SPAu, and NiPt HNCs recorded at -0.4 V in 1 mol L⁻¹ KOH + 1 mol L⁻¹ CH₃OH with and without CO gas during the tests. (g) DFT calculations about the E_{ads} of CO on Ni, Pt, and Au.

processes on the NiPtAu-SRAu catalyst.

CONCLUSIONS

In conclusion, two trimetallic NiPtAu HNCs with different surface exposure contents of Au were fabricated through a facile synthesis to enhance the electrocatalytic performance and anti-CO poisoning ability for MOR. The trimetallic NiPtAu-SRAu HNCs exhibit highly cata-

lytic performance and CO tolerance in comparison with other HNCs counterparts and 20 wt% Pt/C. The MOR specific activity of NiPtAu-SRAu HNCs (31.52 mA cm⁻²) is 7 times higher than that of Pt/C (4.50 mA cm⁻²). Additionally, NiPtAu-SRAu HNCs also display more negative oxidation potential and onset potential in CO-stripping and less current attenuation in CA measurements for MOR with CO gas than other catalysts. Moreover, the

experimental result of the CO resistance of NiPtAu-SR_{Au} is further supported by the results of the theoretical analysis of the E_{ads} of CO, revealing that the superior anti-CO poisoning ability correlates well with the lower E_{ads} . This enhancement in catalytic activity as well as the anti-poisoning capability of NiPtAu-SR_{Au} HNCs can be mainly ascribed to the synergistic effects and the weakened CO adsorption due to the exposure of Au atoms on the catalyst surface. And this is well demonstrated with the experimental data and DFT calculations. It confirms the Au on the surface of the bimetallic NiPt HNCs plays a positive role in the electrocatalytic enhancement, and the improvement in electrocatalytic performance is strongly dependent on the exposure content of Au atoms on the surfaces. Especially, the electrocatalytic activities and anti-CO poisoning rely heavily on the existing content and status of Au. This paper provides new insight on the synergistic effects of trimetallic or multi-metallic nanocatalysts and a feasible pathway to design and optimize the nanostructure of electrocatalysts in the future.

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- Supporting Information** The experimental details, particle diameters, morphologies, compositions, and phases of obtained samples; electrochemical performances and XPS spectra of contrast samples; CA curves; summary of MOR performance from the literature are available in the online version of the paper.

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Au增强NiPtAu中空纳米晶体电催化碱性甲醇氧化性能的行为研究

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摘要 甲醇氧化反应中产生的CO等中间体是导致Pt基催化剂中毒而丧失催化活性的重要原因. 针对该问题, 本文利用具有较强抗CO中毒能力的贵金属Au构建多元Pt基催化剂. 采用置换法合成了两种表面Au元素含量不同的NiPtAu中空纳米晶体(HNCs), 分析了其电催化性能及抗CO毒化性能, 并探讨了Au在电催化碱性甲醇氧化反应中的作用. 研究表明, 相比于其他样品, 表面Au含量相对较高的NiPtAu-SR_{Au} HNCs (15.17 at%)展现出更优异的电催化性能以及抗CO毒化性能. NiPt表面暴露的Au能削弱催化剂表面对CO的吸附, 有利于提高电催化甲醇氧化的性能和抗CO中毒能力. 这一研究结果不仅有助于深化认识Au在电催化甲醇氧化反应中的作用机理, 同时也为燃料电池用新型高性能电催化剂的结构设计和优化提供了参考.