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NiCo₂S₄ sub-micron spheres: an efficient non-precious metal bifunctional electrocatalyst†Cite this: *Nanoscale*, 2014, 6, 3540Zhongyi Zhang,^{‡,ab} Xiaogang Wang,^{‡,a} Guanglei Cui,^{*a} Aihua Zhang,^d Xinhong Zhou,^c Hongxia Xu^a and Lin Gu^{*d}

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Urchin-like NiCo₂S₄ sub-micron spheres integrated with nano-sized and micro-sized structures, which were synthesized via a facile one-pot method, deliver efficient electrocatalytic activities for oxygen reduction and evolution reactions. The excellent electrocatalytic property of NiCo₂S₄ sub-micron spheres is originated from their unique urchin-like microstructure, composition and d-electronic configurations of the transition metal ions.

In the past decades, bifunctional electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are undoubtedly the pivot of advanced energy conversion and storage devices including rechargeable metal-air batteries and regenerative fuel cells.^{1–7} Presently, platinum-based electrocatalysts are known to be the preferred electrocatalysts with the highest electrocatalytic activity for ORR.⁸ Nevertheless, platinum-based electrocatalysts are generally claimed to be responsible for at least 50% of the total fuel cell cost due to the scarcity and preciousness of platinum.⁹ In addition to the high cost of Pt-based electrocatalysts, the limited electrocatalytic activity for OER inhibits their practical application in rechargeable metal-air batteries and regenerative fuel cells.^{10–12} Up to now, iridium oxide (IrO₂) and ruthenium oxide (RuO₂) are the best known OER electrocatalysts, and unfortunately possess poor ORR performance and consist of rare metal elements.^{13–15} Therefore, it is still a big challenge to develop low-cost

bifunctional electrocatalysts which can efficiently catalyze both ORR and OER.⁴ However, only few articles have been published, covering the synthesis and characteristics of non-precious metal bifunctional electrocatalysts including perovskite and spinel oxides.^{3,4,16}

Among various non-precious metal electrocatalysts, late transition metal chalcogenides consisting of transition metal atoms (Fe, Co, Ni) and chalcogen atoms (S, Se, Te) have attracted extensive attention, because of their low cost, high electrocatalytic activity for ORR and high tolerance to small organic molecules.^{17–20} Especially amongst these chalcogenides, bimetallic sulfides are considered as the most promising catalysts due to the synergistic effect of various transition metal atoms, often exhibiting superior catalytic activity towards many chemical transformations as compared to monometallic sulfides.^{21,22} Thiospinels with a general formula of AB₂S₄ is one typical group of bimetallic sulfides, which is known to be built around a closely packed array of S^{2–} ions, with A²⁺ and B³⁺ metal cations occupying the tetrahedral and octahedral sites, respectively.^{23–25} Recently, Suntivich *et al.* demonstrated that the bifunctional electrocatalytic activities of metal oxides primarily correlate to the σ*-orbital (e_g) occupation associated with the metal cations at octahedral centers.^{3,4} In some cobalt oxides, the surface Co(III) cations are considered to be electrocatalytic active centers for ORR/OER.^{4,26} As one of the rare bimetallic thiospinel, NiCo₂S₄ with a normal spinel structure is endowed more octahedral catalytic active sites of Co(III) cations compared to NiCo₂O₄ with the inverse spinel crystal structure. From this, NiCo₂S₄ is potentially provided with excellent bifunctional electrocatalytic activity for both ORR and OER. It is well known that the physicochemical properties of spinels are highly sensitive to the component, structural parameters, and distribution and oxidation state of cations,^{16,27} which depend mostly on the preparation conditions. Viable and facile routes to synthesize NiCo₂S₄ with specific nanostructured morphology are still lacking. Thereby, it is highly challenging and desirable to design and synthesize a NiCo₂S₄ material as an efficient bifunctional electrocatalyst for both ORR and OER.

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In this research, urchin-like NiCo_2S_4 sub-micron spheres (SMS) were synthesized through a facile one-pot solution-based approach (detailed experiment see ESI†). These unique urchin-like NiCo_2S_4 SMS as non-precious metal electrocatalyst exhibit comparable electrocatalytic activity for ORR and higher electrocatalytic activity for OER compared with commercial Pt/C electrocatalyst in alkaline solutions.

Fig. 1 shows the typical powder X-ray diffraction (XRD) pattern of the as-synthesized NiCo_2S_4 SMS. The experimental pattern agrees very well with the standard data of linnaeite-type NiCo_2S_4 with a space group of $Fd-3m$ (227) and cubic lattice parameter of $a = 9.387 \text{ \AA}$ (JCPDS card no. 20-0782). The inset of Fig. 1 schematically illustrate the crystal cell structure of NiCo_2S_4 . The morphology of the NiCo_2S_4 SMS was examined by SEM and TEM. Fig. 2 gives a panoramic picture of the NiCo_2S_4 SMS characterized by low-magnification SEM, which shows that the as-synthesized NiCo_2S_4 sample consists of almost entirely monodisperse spherical sub-micron particles (100% morphological yield). As shown in Fig. 3a, the NiCo_2S_4 sample exhibits uniform morphologies of SMS with an average diameter of $0.25 \mu\text{m}$ and they present an urchin-like appearance as a whole.

From the TEM image shown in Fig. 3b, it was observed that the surface of the urchin-like NiCo_2S_4 SMS is decorated by many nano-papillae primary particles with diameters in the range between 10 and 25 nm in a radial form, expanding the specific surface area of NiCo_2S_4 SMS (Fig. S1†). Such uniform urchin-like structure not only guarantees desirable mechanical stability of NiCo_2S_4 particles but also facilitates the redox species rapid transport to the electrocatalytic active sites of the NiCo_2S_4 particles. Also, the selected-area electron diffraction (SAED) pattern for a single sphere (Fig. 3c) shows the ring patterns, which are well indexed to planes of (111), (220), (311), (400), (422), (511) and (440). A typical HRTEM image of the nano-papillae primary particles with the corresponding SAED is shown in Fig. 3d. The well-defined crystalline lattice spacing of $2.83 \text{ \AA}$ is clearly observed, which is consistent with the diffraction peak of (311) plane in the XRD. The elemental mapping images (Fig. 3e–i) did not show any elemental segregation of Ni, Co or S. Energy dispersive spectra (EDS) was used to examine

Fig. 1 XRD patterns of the as-prepared NiCo_2S_4 SMS.

Fig. 2 SEM image of the NiCo_2S_4 SMS in wide range.

the element composition of the as-prepared NiCo_2S_4 SMS (Fig. 3j). It is shown that the atomic ratio of Ni to Co and S is 1.16 : 2.00 : 3.96, which is approximately the integer ratio of 1 : 2 : 4, confirming the formation of a stoichiometric NiCo_2S_4 compound. The above characterizations of structure and composition credibly demonstrate that the as-prepared NiCo_2S_4 SMS possess high purity and uniform morphology.

To understand the formation mechanism of NiCo_2S_4 SMS, time-dependent composition and morphology evolution through interception of intermediate products were performed. The SEM images (Fig. 4a–c) show the observed morphologies of intermediate products at three reaction stages. The corresponding reaction stages were marked with I, II and III in Fig. 4d, which exhibits the evolution of various element concentrations with reaction time (based on EDS analysis of intermediate products). As shown in Fig. 4a, the morphology of intermediate products corresponding to reaction stage I can be described as the grass-like configuration. After that, namely in stage II, the grass-like structure dissociated and assembled to form flower-like spheres as shown in Fig. 4b. After 50 minutes reaction that is in stage III, as shown in Fig. 4c, the intermediate products with flower-like spheres evolved into the final urchin-like SMS. As shown in Fig. 4d, the element concentration of C and O was relatively high in the early stage (I, II) and gradually declined with the reaction progress. This indicates that the reaction is probably accompanied with a decomposition process. After 80 minute reaction, the element concentration of C and O in the intermediate products gradually decreased to the minimum values. The element concentration of S continuously increased with the slightly decreased element concentrations of Ni and Co. After 120 minute reaction, the composition and morphology evolution process is accomplished. Consequently, these three elements' concentrations attained the stoichiometric value of $\text{Ni} : \text{Co} : \text{S} = 1 : 2 : 4$. The sum of element concentrations of Ni, Co and S tended to be more than 90%, which corresponded to above 96% of the total mass content. After 120 minutes, the reaction achieved a high-yield of above 97% for generating NiCo_2S_4 SMS (measured by weighting the final products). Thus, the optimum synthesis process was performed at 220°C for 120 minutes.

Fig. 3 (a) SEM images of the NiCo_2S_4 SMS. (b) TEM images of the NiCo_2S_4 spheres. (c) SAED patterns for a single NiCo_2S_4 sphere. (d) HRTEM images of typical nano-papillae on the surface of the NiCo_2S_4 sphere. Inset is the corresponding SAED pattern. (e) Typical STEM image of the NiCo_2S_4 SMS. (f) STEM image taken from the square region marked in (e). (g–i) The corresponding elemental mapping images are for (g) Ni, (h) Co and (i) S, respectively. (j) EDS of the NiCo_2S_4 spheres measured by loading on the Al foil.

The electrocatalytic activity of NiCo_2S_4 SMS for ORR was characterized by cyclic voltammetry (CV) in 0.1 M KOH aqueous solution on a glassy carbon disk electrode (GC). All electrocatalyst loadings on electrode for electrochemical experiment were uniformly 0.7 mg cm^{-2} . As it can be seen from Fig. 5a, the CV curves of NiCo_2S_4 SMS obtained in O_2 -saturated solution show that the detected currents increased rapidly in the mixed kinetic-diffusion control region (-0.1 V to -0.22 V), then reached the peak value and next gradually decreased. This observed current was attributed to ORR electrocatalyzed by NiCo_2S_4 SMS through comparison with CV curve recorded in Ar-saturated aqueous solution, which show no distinguishable cathodic current over the measured potential range. Furthermore the CV

Fig. 4 SEM images showing three growth stages of the NiCo_2S_4 SMS: (a) early stage I (b) middle stage II (c) final stage III. (d) The plots of element concentrations versus reaction time (based on EDS analysis).

curves of NiCo_2S_4 SMS show that an ORR onset potential is at -0.05 V (versus Ag/AgCl electrode) and the peak potential is at -0.22 V . The CV curves of commercial Pt/C electrocatalysts (10 wt

Fig. 5 Cyclic voltammetry curves of (a) the NiCo_2S_4 and (b) the Pt/C electrocatalyst in Ar or O_2 saturated 0.1 M KOH aqueous solution at a scan rate of 10 mV s^{-1} . (c) LSV curves of the NiCo_2S_4 electrocatalyst in O_2 -saturated 0.1 M KOH aqueous solution at different rotation rate with a sweep rate of 10 mV s^{-1} . (d) Corresponding Koutecky–Levich plots (j^{-1} vs. $\omega^{-0.5}$) at different potential from (c) LSV curves. (e) LSV curves of oxygen evolution reaction electrocatalyzed by NiCo_2S_4 and Pt/C electrocatalysts in 0.1 M KOH aqueous solution at a sweep rate of 10 mV s^{-1} . (f) Tafel plot of the OER specific activity of NiCo_2S_4 and Pt/C.

% Pt), as shown in Fig. 5b, exhibit the ORR onset potential and peak potential located at 0.05 V and -0.13 V, respectively.

The electrocatalytic activity can be illustrated by the net peak current density (NPCD), which is calculated by subtracting the background current from the peak current.⁶ According to Fig. 5a and b, the NPCD reaches to 0.71 mA cm^{-2} for the NiCo_2S_4 SMS, while the commercial Pt/C electrocatalysts exhibit an NPCD of 0.77 mA cm^{-2} . Therefore, the electrocatalytic activity of NiCo_2S_4 SMS for ORR approaches that of Pt/C electrocatalyst. To further investigate the ORR kinetics of NiCo_2S_4 SMS electrocatalyst, the linear sweep voltammetry (LSV) was carried out on a rotating disk electrode (RDE) at different rotation speeds in O_2 -saturated 0.1 M KOH aqueous solution. As shown in Fig. 5c, the LSV curves exhibit similar profiles except the limiting current density increasing with the increasing RDE rotation speed. The corresponding K - L plot of j^{-1} versus $\omega^{-0.5}$ yields straight and parallel lines (Fig. 5d), which implies first-order dependence of O_2 kinetics, as described by Stamenković *et al.*^{28,29} The number of electrons transferred per O_2 molecule was calculated from the K - L plots to be 3.98, which is approximately the theoretical value of 4 throughout the potential range studied (see ESI†). Thereby, the NiCo_2S_4 SMS show excellent electrocatalytic activity for ORR through favorable direct four-electron reaction pathway. The electrocatalytic activity of NiCo_2S_4 SMS electrocatalyst for oxygen evolution reaction (OER) was investigated by LSV and Tafel plot, as shown in Fig. 5e and f. In comparison with the Pt/C electrocatalyst, the NiCo_2S_4 SMS electrocatalyst exhibits a more negative onset potential for OER with a higher OER current density under the same potential (as shown in Fig. 5e), which indicates that NiCo_2S_4 SMS electrocatalyst possesses excellent electrocatalytic activity for OER. The Tafel plot (Fig. 5f) also demonstrates that the measured intrinsic electrocatalytic activity of NiCo_2S_4 is higher than that of Pt/C electrocatalyst for OER. Moreover, the summary of ORR and OER activities in 0.1 M KOH for NiCo_2S_4 and other non-noble electrocatalyst is presented in the ESI,† which was characterized by LSV on RDE at 1600 rpm. It can be seen from Tables S1 and S2† that the bifunctional catalytic performance of NiCo_2S_4 SMS is outstanding in the non-precious metal electrocatalysts. It was also demonstrated that NiCo_2S_4 SMS electrocatalyst possess the advantages of methanol tolerance compared with the strong methanol response in the case of Pt/C electrocatalyst³⁰ (see ESI†, Fig. S5†). In order to gain a better insight into the electrocatalytic mechanism of NiCo_2S_4 SMS electrocatalyst for both ORR and OER, the detailed analysis of the crystal and electronic structure of NiCo_2S_4 was discussed in ESI.† The excellent electrochemical properties of NiCo_2S_4 is originated from the unique d-electronic configuration of Co(III) at the surface of NiCo_2S_4 , for which the single electron in the e_g energy level selectively occupies the e_g-z^2 orbit pointing to the surface sulfur vacancy and interacting with the frontier orbital of oxygen.

Conclusions

In summary, urchin-like NiCo_2S_4 SMS were prepared *via* a facile synthetic approach. These NiCo_2S_4 SMS possess uniform urchin-like morphologies with an average diameter of $0.25 \mu\text{m}$

and the surface of NiCo_2S_4 SMS is decorated by many nanopillae particles. These urchin-like NiCo_2S_4 SMS as non-precious metal electrocatalyst exhibit comparable electrocatalytic activity for ORR and excellent electrocatalytic activity for OER compared with commercial Pt/C electrocatalyst in alkaline solutions. The excellent electrocatalytic property of NiCo_2S_4 is originated from the unique d-electronic configuration of Co(III) at the surface of NiCo_2S_4 . These results will guide the future rational design and development of transition metal thiospinels as highly efficient bifunctional non-precious metal electrocatalysts to replace precious metal electrocatalysts applied in advanced energy conversion and storage devices.

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