



# Hierarchical urchin-like peapodded core-shell-structured NiCo<sub>2</sub>@Ni<sub>1/3</sub>Co<sub>2/3</sub>S<sub>2</sub>@C catalyst with synergistically high-efficiency electrocatalytic properties toward hydrogen evolution reaction

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## ABSTRACT

Designing and developing earth-abundant, low-price and high-efficiency catalysts for hydrogen evolution reaction (HER) is remaining a great challenge from the standpoint of energy. Herein, we have synthesized, firstly, three-dimensional (3D) urchin-like NiCo<sub>2</sub>@Ni<sub>1/3</sub>Co<sub>2/3</sub>S<sub>2</sub>@C catalyst composed of one-dimensional (1D) peapod-like structure, in which the nanoparticles of the peapod are characterized with a special structure: NiCo<sub>2</sub> alloy as the core and thin Ni<sub>1/3</sub>Co<sub>2/3</sub>S<sub>2</sub> layer as the shell. Notably, the internal NiCo<sub>2</sub> core offers efficient routes for electron transfer and the external Ni<sub>1/3</sub>Co<sub>2/3</sub>S<sub>2</sub> shell provides a great number of active sites for HER. Owing to the synergistic effect between the inner core and the outer shell, NiCo<sub>2</sub>@Ni<sub>1/3</sub>Co<sub>2/3</sub>S<sub>2</sub>@C catalyst displays excellent catalytic performance, including a low overpotential of ~41.0 mV at 10 mA cm<sup>-2</sup>, a corresponding small Tafel slope of ~39.2 mV dec<sup>-1</sup>, and an excellent stability in acidic medium for 200 h, which is greater than many reported transition metal chalcogenides (TMCs). Simultaneously, the free energy of H<sup>+</sup> adsorption ( $\Delta G_{H^+}$ ) for NiCo<sub>2</sub>@Ni<sub>1/3</sub>Co<sub>2/3</sub>S<sub>2</sub>@C (about -0.10 eV) is extremely near to that for Pt (~0.09 eV) by density functional theory (DFT) calculated results, which is significantly beneficial to HER performance.

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## 1. Introduction

The urgent issues of environment due to the greenhouse effect and water pollution have always been the international focus [1,2]. Recently, based on that, many countries have introduced schedule policy of disabling petroleum. Considering that hydrogen is a clean sustainable energy, most studies have been revealed that it's one of the most potentially alternative energy candidates to keep a balance between energy loss and environmental pollution for interchanging scarce fossil fuels [3,4]. Owing to its merits of high efficiency and eco-friendly to environment, water electrolysis has been regarded as a greatly prospective pathway to collect hydrogen [5]. Furthermore, hydrogen evolution reaction (HER) is the key step to produce hydrogen for water electrolysis, and electrochemical catalyst directly plays an extremely vital role during the catalytic process [6,7]. Therefore, it's a meaningful task to explore the catalysts with excellent activity toward HER. Many researches have been reported about this over the past few years, such as transition metal chalcogenides (TMCs) [8], phosphides

[9,10], oxides [11], selenides [12,13], among which MS<sub>2</sub> (M = Ni or Co) is a class of earth-abundant and inexpensive catalysts with high catalytic activity for HER [14].

Pretty extensive active sites and conductive properties are affirmed as two crucial factors during the HER electrocatalytic process [15]. The high-efficiency catalysts with richer active sites can be obtained from surface control, which is deemed to be one of the most potential methods to achieve great stability and activity [16,17]. Generally, surface control could build the unique architecture of the catalyst, thus offering improved and new functionality [18,19]. For instance, Xu et al. obtained core-shell Ni/NiO nanostructure exhibiting better activity by annealing Ni/NiO nanoparticle in air condition for HER [20]. Similarly, core-shell CoNi-alloy@CoNi-sulfide nanoarrays with excellent activity have been synthesized by Zhou et al. through hydrothermal treatment of CoNi alloy arrays for hydrazine electrooxidation [21]. Indeed, these reported catalysts with excellent catalytic properties are obtained through surface engineering, and the admirable activity is chiefly ascribed to the synergistic effect of the unique structure. However, the controllable surface preparation of TMCs with outstanding activity for HER in acidic solution based on synergistic effect has rarely been reported so far. As is well-known,

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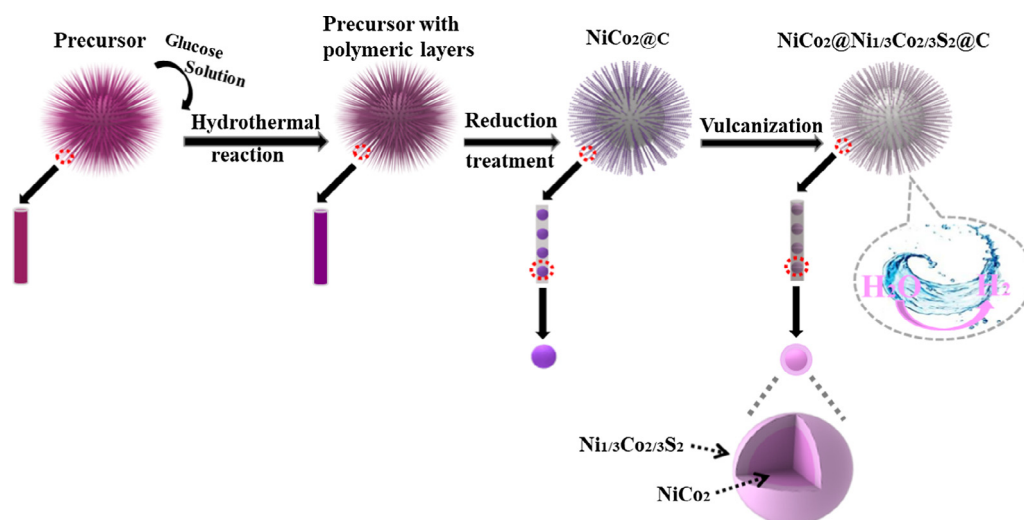
inexpensive and earth-abundant TMCs are regarded as potential catalyst toward HER [22], and compound catalysts are famous for synergistic effect [23], thus exhibiting that a whole catalytic effect of the compound TMCs in HER is greater than any part of it. Generally,  $MS_2$  ( $M = Ni$  or  $Co$ ) is one of the TMCs with high durability and activity, while metallic alloys are superior catalysts because of their benefit to electron transfer, respectively [8,24]. Therefore, it's meaningfully valuable to except that metallic alloys coated with  $MS_2$  ( $M = Ni$  or  $Co$ ) could actually show remarkable conductive properties and extensive active sites to enhance HER performances due to their synergistic effect. Besides, Wang and co-workers have reported that the stability of carbon-based nanomaterial would be improved due to its protective function for the nanostructure in HER [25,26]. In this regard, it is significant to explore the catalytic activity of compound TMCs encapsulated in carbon film in the acidic electrolyte.

Herein, considering these advantages above, we have prepared a novel three-dimensional (3D) hollow urchin-like catalyst, noted as  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$ , with excellent catalytic property in acidic medium. Such high activity of  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$  is primarily attributed to the interactive influence of the unique nanoparticles: the internal  $NiCo_2$  alloy core offers the available routes for electron transfer, and the external  $Ni_{1/3}Co_{2/3}S_2$  shell provides efficient active sites for hydrogen generation, respectively. Moreover, Density functional theory (DFT) calculations show that hydrogen separated activation energy of  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$  is obviously lower than that of  $Ni_{1/3}Co_{2/3}S_2@C$  and  $NiCo_2@C$  due to the introduction of  $Ni_{1/3}Co_{2/3}S_2$  shell on the surface of  $NiCo_2$  core, which further affirms the rational design of the  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$  structure for HER.

## 2. Results and discussion

The feasible synthesis strategy of  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$  catalyst mainly involves four steps as illustrated in Fig. 1. Firstly, the 3D urchin-like precursor with really vast hydroxyl (hydrated) groups was fabricated via a hydrothermal treatment. Then, the polymeric layers would increasingly form, after the mixed solution of the precursor and glucose (carbon source) conducted a hydrothermal reaction and the glucose was assimilated onto the surface of the

precursor by means of hydrogen bonding. Subsequently, the carbon film could be formed, once the polymeric layers were carbonized through calcination in  $N_2$  atmosphere. Meanwhile, the  $NiCo_2@C$  catalyst, solidly encapsulated in carbon film, was obtained by the reduction treatment, which includes the emancipation of gas substances and the decomposing of the hydrated precursor. Finally, the partial vulcanization, precisely controlling the reaction time, was carried out for synthesizing the final  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$  catalyst. It's noted that the  $NiCo_2@Ni_{1/3}Co_{2/3}S_2$  nanoparticle is constituted of  $NiCo_2$  core and  $Ni_{1/3}Co_{2/3}S_2$  shell. Fig. S1a displays the scanning electron microscopy (SEM) images of the uniform 3D urchin-like precursor, which had been synthesized with a large scale. Besides, Fig. S1b shows its X-ray diffraction (XRD). The XRD patterns of  $NiCo_2@C$ ,  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$ , and  $Ni_{1/3}Co_{2/3}S_2@C$  are presented in Fig. 2a. In the pattern, the  $NiCo_2@C$  with all typical peaks are matched to the Ni and Co of cubic phase displaying planes (1 1 1) and (2 0 0), and the interplanar value of plane (1 1 1) of Ni and Co is 2.04 Å and 2.05 Å, respectively [26]. In addition, the image of energy-dispersive spectrum (EDS) (Fig. S2) explicitly states that the chemical component (atomic ratio of Ni:Co) is approximately 1:2, which is the named origin of  $NiCo_2@C$ . In terms of the  $Ni_{1/3}Co_{2/3}S_2@C$  sample, all the dominant diffraction peaks definitely lie between the plane (2 1 1) of  $NiS_2$  (JCPDS No. 80-0377) with the interplanar value 2.28 Å and the plane (2 1 1) of  $CoS_2$  (JCPDS No. 41-1471) with the interplanar value 2.26 Å, respectively, thus proving the catalyst crystallized in solid solution phase. Besides, the EDS image of the  $Ni_{1/3}Co_{2/3}S_2@C$  catalyst is shown in Fig. S3. As for the  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$  catalyst, it's apparent that the conspicuous peaks are coordinately overlapped of  $NiCo_2@C$  phase and  $Ni_{1/3}Co_{2/3}S_2@C$  phase, guaranteeing that the catalyst was successfully synthesized through direct vulcanization of previous  $NiCo_2@C$ . Compared with the patterns of  $NiCo_2@C$  and  $Ni_{1/3}Co_{2/3}S_2@C$ , the main peak of  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$  is consistent with that of  $NiCo_2@C$ , and another peak at 32.2, corresponding to chalcogenides, is properly weak, indicating that a small amount of the interaction between  $NiCo_2@C$  and sulfur powder takes place in the vulcanization process. Fig. 2b is the enlarged image of XRD, in which the 2-theta is from 30 to 35, and it distinctly conveys that the foremost peak of the  $Ni_{1/3}Co_{2/3}S_2@C$  and  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$  is well distributed there. Meanwhile, the EDS spectroscopy (Fig. S4) assists us to further



**Fig. 1.** Schematic illustration for the synthetic procedure of the 3D urchin-like  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$  catalyst composed of 1D peapods, and the nanoparticles of the peapod possess a special nanostructure:  $NiCo_2$  as the core and  $Ni_{1/3}Co_{2/3}S_2$  as the shell. Firstly, the prepared precursor acted as sacrificial template. Then, the glucose played the role of green carbon source. Finally, the product of  $NiCo_2@Ni_{1/3}Co_{2/3}S_2@C$  catalyst was obtained through a hydrothermal polymerization,  $N_2$  calcination and vulcanization in sequence.

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