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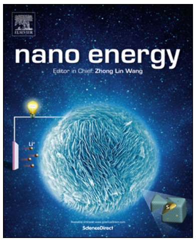

FULL PAPER

Synergistic effects in biphasic nanostructured electrocatalyst: Crystalline core versus amorphous shell

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Abstract
The recent study on active amorphous catalytic materials provokes rethinking of the previous research on atomic and electronic structures in the crystalline catalyst. Is there any active catalyst with biphasic structure, in particular the integration of crystalline and amorphous components? Inspired by this question, a crystalline-amorphous biphasic quaternary oxide catalyst is novelly fabricated via one-step solvothermal method in this work. The as-prepared catalyst displays a well-designed core-shell architecture composed of crystalline $Co(Zn_xNi_{2-x})O_4$ nanorod (core) and amorphous NiO nanosheet (shell). This heterogeneous core-shell catalyst exhibited high activity in the oxygen evolution reaction by demonstrating a low over-potential of 1.57 V vs RHE, a high half-wave potential (0.89 V vs RHE), and long-term electrochemical stability for 25 h. It was found that the synergistic effects from the amorphization of the shell on the one hand, and the atomic/electronic structure of the crystalline core on the other hand, could significantly facilitate the catalytic activity both at the surface and in the bulk volume of the solid oxides. Therefore, this new developed crystalline-amorphous biphasic catalyst could provide instructive roles in the future design of new catalysts for O_2 evolution and other catalytic reactions.

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Introduction

The conflict between the global environment crisis and the increasing demand of the fossil fuels raises concerns about the exploitation of renewable clean energy and the effective energy conservation. In this respect, photocatalytic water splitting by directly converting the solar energy to the chemical fuel (hydrogen) has been considered as a straightforward and green way to collect and store the solar energy in the chemical bonds of molecules [1,2]. Besides, electrocatalysis has been commonly used to study the activity of catalysts in the water-splitting process because it is seen as an efficient and environment-friendly technology for the energy conversion and storage [3-5]. What's more, electrocatalytic oxygen evolving reaction (OER) and oxygen reduction reaction (ORR) are at the key processes in some of the energy-related technologies, such as metal-air batteries and fuel cells. However, the efficiency of OER and ORR is generally limited by the slow reaction kinetics because of the involved four-electron transfer process [6,7]. To accelerate these reactions, the active electrocatalysts are required in order to reduce the overpotential for the OER and ORR. The noble metals, such as Pt, Pd and its alloys, have shown promising catalytic effects for OER and ORR, but their high cost and rarity limit their use in the large-scale application. Although different kinds of organic molecules and inorganic materials have been widely developed and investigated, the complexity of the synthesis and/or the instability of the catalysts promote the need of stable and efficient catalysts for both OER and ORR [8-12].

In the past few years, great efforts have been devoted to develop highly active OER electrocatalysts containing earth abundant elements, such as the transition metal based mixed metal oxides and spinels [13-17]. Polynary oxides that contain of more than two transition metals such as ternary, quaternary, quinary oxides, have shown the greatly improved OER activity than the corresponding binary metal oxides [18-20]. The structure of active phases and the oxidation state of transition metal centers have been systematically studied in order to understand the functions of these polynary oxides catalysts [21-23]. In the recent studies it is revealed that the crystalline materials, such as transition metal oxides of Fe, Ni, Co, and Mn, or their alloys, exhibited the inferior oxygen-evolving catalytic activities and the instability under the ambient conditions [24-26].

Some recent reports demonstrated that the amorphous catalysts exhibited superior performance than the corresponding crystalline ones in terms of the Tafel slope, overpotential and stable operation in neutral or slightly basic aqueous solutions [27-29]. Nocera and coworkers for the first time reported the amorphous cobalt oxide/hydroxide film electrodeposited via simple anodic electrode polarization in a neutral phosphate solution of Co^{2+} [27]; Shao-Horn group proposed the surface amorphization of perovskite oxide catalysts may change and affect the OER activity [28]. Thereafter, great efforts have been devoted to the preparation of different amorphous catalytic films such as Co-, Ni-, and Mn-based metal oxides by the surface reconstruction. For example, amorphous heterobimetallic Co-Fe oxide system showed outstanding OER activity, surpassing that of its crystalline form [29]. Besides, amorphous $Mn^{III/IV}$ oxide transformed from the inactive nanocrystalline MnO exhibited superior catalytic activity for OER [30]. The obtained prominent behavior of the molecular catalysts was believed to correlate to their structure amorphization [31].

The fact that the emerging amorphous catalysts exhibiting promising catalytic properties could promote great challenge on the previous studies that the direct influences of atomic and electronic structures in crystalline materials are significant for the efficient OER. The recent perspective work by Diego González-Flores and collaborators [32] addressed the bewilderment in the relationship between material structure and the activity for OER catalysis. By systematically investigating crystalline cobalt phosphate, they concluded that both surface catalysis and bulk-volume catalysis need to be taken into account for the catalytic process. In detail, the catalyst showed high-TOF (turnover frequency) surface activity in crystallites of pakhomovskyite ($Co_3(PO_4)_2 \bullet 8H_2O$, Pak), while its volume activity was dominated by its amorphization. Therefore, it is speculated that the heterogeneous catalysts with both crystalline bulk-volume catalysis and amorphous surface catalysis would be desirable for highly efficient electrocatalytic reactions. Inspired by the conclusion above, one practical question awaiting clarification is in front of us: Is there any active heterogeneous catalyst which can be directly grown with a biphasic structure, in particular the integration of crystalline and amorphous components? Under the guidance of this query, in this work, bifunctional catalysts containing both crystalline and amorphous building blocks were novelly prepared, and their catalytic effects in OER were investigated in details.

In the present work, quaternary oxide catalyst (dual-doped Co_3O_4 nanostructure) with crystalline core and amorphous shell was successfully fabricated via a facile solvothermal method. Instead of tedious strategies used for amorphous film deposition, such as electrodeposition, sputtering, electron beam vaporization, photodegradation, photochemical metal organic deposition (PMOD) [33-36], the employment of one-step solvothermal method ensures the high possibility of large area synthesis and application of the materials with low cost. The one-step fabrication of crystalline-mesoporous biphasic structure, to our best knowledge, has not been reported before. The as-prepared catalyst displayed well-designed core-shell architecture with crystalline $Co(Zn_xNi_{2-x})O_4$ core and amorphous NiO shell. The synergistic effects of the core and shell promote excellent electrocatalytic OER and ORR performance by catalyzing both at the surface and within the bulk volume of the structure. In view of the fact that electrocatalytic reaction on metal oxides generally occurs on the surfaces of the materials, the catalysts prepared in nanostructured form with higher density of surface reactive sites and greater contact area with reactants, are promising in order to enhance the catalytic activity towards OER and ORR. In this respect, shape-tailored nanostructures with controllable core-shell construction was achieved by regulating the solvent and precursors. Ascertaining structure-property relationships remains a central challenge in the field of heterogeneous catalysis and comprises an important strategy for the development of superior electrocatalysts. Herein, we provide detailed insight into the correlation between the catalytic performance and the crystalline-

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