

Efficient oxygen evolution reaction catalyzed by low-density Ni-doped Co_3O_4 nanomaterials derived from metal-embedded graphitic C_3N_4 †

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A synthetic route to low-density porous Ni-doped Co_3O_4 nanomaterials that show stable and superior electrocatalytic activity for O_2 evolution reaction is reported. The materials are prepared via thermal treatment of 'pre-synthesized' metal ions-embedded graphitic C_3N_4 -based polymers.

Catalytic splitting of water into hydrogen and oxygen is one of the most important and yet challenging chemical energy conversion processes.¹ The water splitting reaction can be viewed by dividing it into two half reactions: the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). Of these two half-reactions, the OER is more complex because it involves a four-electron oxidation process and two water molecules to form one O_2 molecule.² Hence, finding good catalysts for OER is far more difficult than that for HER.

Over the past decade, several oxides based on transition metals such as Ru, Ir, Co, etc. have been investigated for OER. Although Ru and Ir oxides are particularly proven to be very active catalysts for OER,³ they are deemed not promising owing to the high-cost and scarcity of Ru and Ir. By comparison, cobalt oxides are preferable and more sustainable as OER catalyst because Co is relatively more earth-abundant.^{4–6} Hence, synthesis and fine structural optimization of cobalt oxide-based catalysts and a deep understanding of their structure–property relationships in OER have been actively pursued. In view of the fact that catalytic OER on metal oxides generally occurs on the surfaces of the materials, a more convenient strategy to enhance the catalytic activity of Co-based catalysts is preparing them in a nanostructured form in order to increase their surface area.^{7–7} This in turn provides them with higher density of surface reactive sites and greater contact area with reactants, and thereby better

catalytic activity towards OER. Moreover, the activity of OER catalysts in the nanostructured form can further be easily improved by modifying their surfaces (e.g., via surface heterostructuring)⁸ or tuning their composition (e.g., via elemental doping).⁹

However, the inherent tendency of nanomaterials to aggregate/agglomerate often limits the range of potential applications of many nanostructured catalysts. This is especially true for OER nanocatalysts, which are often used in thin film form, where aggregation/agglomeration of catalytic species can be more prominent. Thus, to make full use of an OER nanocatalyst, any possible aggregation/agglomeration of its nanocatalytic units during synthesis or operation should be avoided at all cost.

Herein we report a facile synthetic method to low-density, porous Ni-doped Co_3O_4 nanostructured materials that are stable against aggregation/agglomeration and also exhibit enhanced catalytic activity for OER, thanks to their 3D nano-network structure. This method (dubbed as Route A) involved controlled synthesis of Co(II) and Ni(II)-embedded graphitic C_3N_4 ($g\text{-C}_3\text{N}_4$) polymers as precursors, followed by simple thermal treatment of the latter in air to remove $g\text{-C}_3\text{N}_4$ as well as to form a metal oxide *in situ* (Fig. 1). This resulted in Ni-doped Co_3O_4 nanomaterials, denoted as Ni- Co_3O_4 -A. Besides forming multicomponent materials, the synthetic method allows ease of doping of Co_3O_4 with elements such as Ni to improve Co_3O_4 's catalytic activity towards OER. In particular, the Ni- Co_3O_4 -A sample with Ni:Co atomic ratio of 1:9 was found to have the most optimal activity for OER.

As shown in Fig. 1A, the first step in the synthesis of Ni- Co_3O_4 -A is the preparation of metal ions-doped $g\text{-C}_3\text{N}_4$ precursor. This is achieved in one-pot by mixing CoCl_2 and NiCl_2 (the sources of the metals) in different ratios with dicyandiamide (the monomer of the $g\text{-C}_3\text{N}_4$ polymer). When the mixture was thermally treated at elevated temperature (500 °C) under N_2 , the dicyandiamide was transformed into $g\text{-C}_3\text{N}_4$ while the metals were directly self-assembling with it. This resulted in metal-embedded $g\text{-C}_3\text{N}_4$, denoted as M- C_3N_4 , where M represents Co (and Ni). Calcination of the M- C_3N_4 precursor at 450 °C in air then led to formation of Ni- Co_3O_4 materials possessing a porous nano-network structure. For comparison, a classic polymer–metal complex synthetic route⁹ (Route-B, Fig. 1B) was applied to produce the corresponding Ni-doped Co_3O_4 ,

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