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Transition metal oxide/hydroxide is intensively studied for the oxygen evolution reaction (OER). Herein, the graphene-induced growth of Co3O4 nanoplates with modulable oxygen vacancies via a hydrothermal treatment is reported. With the increase of reaction time before the formation of Co(OH)2, the oxygen vacancies and conductivity of Co3O4 nanoplates continued to increase resulting in dramatically enhanced OER performances. An ultralow overpotential of 354 mV at a current density of 100 mA cm⁻² and a Tafel slope as low as 63.24 mV dec⁻¹ in 1 M KOH solution were obtained, superior to those of most reported oxides and RuO2.

Introduction

Owing to the depletion of fossil fuels and the increase of the greenhouse gases, energy conversion processes and storage devices, such as regenerative fuel cells, electrolysis cells, and metal-air batteries, have attracted great attention in the past decades.¹⁻³ Among them, water splitting via photoelectrocatalysis or electrocatalytic reaction is promising for producing reliable clean energy.⁴⁻⁶ The water splitting process consists of two parts: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). However, the OER often has a sluggish kinetics thus requiring high overpotentials, which will result in high energy consumption.⁵⁻⁷⁹¹¹ One of the challenges is to develop excellent electrocatalysts using earth-abundant materials, with high stability and prominent catalytic activity. At present, noble-metal oxides (such as IrO2 and RuO2) are commercially used as OER catalysts, but their scarcity and high cost limit their applications. In recent decades, transition metal oxide/hydroxide has attracted great interests for the OER.

Transition metal-based compounds, such as sulfides, hydroxides, oxides, and phosphides, have been reported for the OER owing to their tunable electronic structures and abundant active sites. For example, Co3O4, an inexpensive earth-abundant material, has been considered to be promising for the OER process because of its high electrical conductivity, adjustable structure, and oxygen defects.¹²⁻¹⁶ Generally, oxygen defects (such as oxygen vacancies and interstitials) are found to be vitally affecting the material properties such as electronic structure,¹⁷ conductivity,¹⁰ and intrinsic catalytic activity.¹⁸¹⁹ Graphene has been intensively and extensively studied due to its excellent conductivity. It can also be used as a template to form two dimensional nanomaterials. Herein, we report the graphene-induced growth of Co3O4 nanoplates (denoted as g-Co3O4) via a hydrothermal reaction. The OER activity was evaluated over the as-obtained g-Co3O4 electrocatalysts. And oxygen defects and conductivity were analyzed with respect to the HT time.

Results and discussion

Fig. 1 shows the schematic diagram of the formation of g-Co3O4 nanoplates via a facile hydrothermal reaction. The morphology and particle size distribution diagram with respect to different reaction times were characterized by scanning electron microscopy (SEM). As shown in Fig. 2a and S1,⁸ pristine Co3O4 has sphere-like morphology with an average size of 60 nm. The SEM images of g-Co3O4 are shown in Fig. 2b–e. The TEM image (Fig. S2†) of the home-made graphene shows clear wrinkles indicating an ultrathin film. When the HT time was 3 h, triangular nanoplates formed with an average lamellar size of ca. 0.17 μm and were uniformly coated by gauze-like graphene. Fig. 2c shows...
a further change of the material morphology as the reaction proceeded. Hexagonal nanoplates formed after 6 h, where graphene behaved like glue between the nanoplates. It can be clearly observed that the lamellar size increased fivefold to ca. 0.82 μm. After 6 h, the morphology of hexagonal nanoplates did not change much but its size gradually increased. As control experiments, the pristine Co₃O₄ samples were treated by the HT process without graphene, as shown in Fig. S3–S6,† which exhibited bulky materials instead of any nanoplate morphology. Therefore, we can come to a short conclusion that as a template, graphene assisted the formation of Co₃O₄ nanoplates.

The as-obtained samples of g-Co₃O₄ were characterized by XRD, as shown in Fig. 3a. The peaks at 19.00, 31.28, 36.88, 44.88, 55.68 and 59.38° can be attributed to the (111), (220), (311), (400), (422), (511) and (440) planes of Co₃O₄ (PDF no. 43-1003). It can be found that the pristine Co₃O₄ has a cubic crystal structure, and its cell parameters are: \( a = b = c = 8.084 \). As for g-Co₃O₄ 3 h and 6 h, it could be clearly observed that the characteristic peak intensity of Co₃O₄ decreased significantly. This proved that the crystal structure of the material had started to transition from a cubic structure of Co₃O₄ to a hexagonal structure of Co(OH)₂. In other words, oxygen vacancies appeared in g-Co₃O₄ after 3 h due to reduction reaction. As for the sample of g-Co₃O₄ 12 h, the diffraction peak of the material is consistent with that of Co(OH)₂ with a hexagonal structure. And the cell parameters are \( a = b = 3.183, c = 4.652 \). So, g-Co₃O₄ 12 h is considered as Co(OH)₂, and the remaining samples are Co₃O₄ with adjustable oxygen vacancies. Note that there is no obvious graphene signal in the catalyst, suggesting that the graphene content is very low. The existence of oxygen vacancies over the as-obtained samples were further confirmed by X-ray photoelectron spectroscopy (XPS). The pristine Co₃O₄ exhibits two subpeaks. The one at 529.8 eV corresponds to lattice O arising from the Co–O bond, and the other at 531.4 eV corresponds to oxygen vacancies. As the HT time increased until 9 h, the peak intensities and areas of the oxygen vacancies increased. From 9 h to 12 h, the formation of Co(OH)₂ made the oxygen defects disappear, corroborated by the Co 2p spectra as shown in Fig. S7.† The peaks at 779.8 eV and 781.3 eV for Co₃O₄, g-Co₃O₄ 3 h and g-Co₃O₄ 6 h correspond to Co³⁺ and Co²⁺, respectively. As the HT reaction time proceeded to 9 h and 12 h, only Co²⁺ was observed.

OER performances over pristine Co₃O₄ and g-Co₃O₄ were evaluated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Fig. S8 and S9† show the CV curves of the g-Co₃O₄ and control experiments, as well as the LSV curves of the control experiments. It is proved that the active species was CoO(OH). By contrast, the onset potential to form CoOOH decreased from 0.308 V to 0.272 V, and the overpotential decreased by 20 mV at a current density of 100 mA cm⁻² over the g-Co₃O₄ 6 h electrocatalyst. Fig. 4 shows that the onset potentials to form CoOOH were only 0.256 V.
Co₃O₄ exhibited an Rct value as low as 0.84. The electrochemical surface area (ECSA) increased. Combining with the above-mentioned double layer capacitance test further demonstrates that as the HT time increased, the electrochemical surface area of the as-prepared catalysts.

Conclusions

In summary, the graphene-induced growth of Co₃O₄ nanoplates with modulable oxygen vacancies via a hydrothermal treatment was reported. With the increase of the hydrothermal reaction time before the formation of Co(OH)₂, the oxygen vacancies and conductivity of Co₃O₄ increased, which resulted in greatly improved OER performances. An ultralow overpotential of 354 mV at a current density of 100 mA cm⁻² and a Tafel slope as low as 95.1 mV dec⁻¹ in 1 M KOH solution were obtained, superior to those of most reported oxides and RuO₂. The enhanced activity can be attributed to the nanoplate morphology, abundant oxygen vacancies and improved conductivity. Our strategy for the rational design of non-precious metal catalysts with superior OER activity can be applied to other systems, which may find ways for practical applications.

Conflicts of interest

There are no conflicts to declare.

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