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Design and Synthesis of Cobalt-Based Hollow Nanoparticles through the Liquid Metal Template

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Abstract: Co-based compounds have attracted much attention due to their competitive catalytic activities. To enhance their intrinsic electrocatalytic activity, morphology engineering is one of the effective strategies. Hollow structures have fascinating properties due to their low density and high loading capacity. In this work, we introduce a Ga-based liquid alloy as a reactive template for the synthesis of varying Co-based hollow nanoparticles. The fluidity character of the Ga-based liquid alloy facilitates the large-scale production of nanoparticles via a top-down shearing process. The pre-installed active species (here is Zn) in the liquid alloy serve as a sacrificial source to quantitatively reduce Co$^{2+}$ ions and form Co-based compounds. Well-structured Ga/CoOOH core-shell nanospheres are thus successfully prepared, and more varied Co-based hollow nanoparticles can be obtained by post-treatment and reaction. Hollow structures can offer enhanced interfacial area and increased active sites, benefiting the catalytic performance. Among the prepared Co-based catalysts, CoSe$_2$ hollow nanoparticles exhibited the best oxygen evolution reaction (OER) activity with an overpotential of 340 mV at the current density of 10 mA/cm$^2$. This work provides a novel strategy for the rational design and simple preparation of hollow nanoparticles.

Keywords: liquid metal; hollow structure; transition-metal compounds; electrocatalyst

1. Introduction

As a class of earth-abundant materials, Co-based compounds are widely used as electrocatalysts owing to their innate electrochemical activity and tunable properties [1–4]. To further improve the catalytic activities, many efforts have been devoted to designing unique morphologies to increase active sites and enhance charge transport capability. Among these morphologies, the hollow structures possess a large surface area, low density, and high loading capacity to promote the accessibility of active sites [5–7]. For example, Fan et al. prepared metal-organic framework derived hollow CoSe$_2$ microspheres and found the well-distributed hollow structures obtained via adjusting the annealing temperature exhibited outstanding electrochemical performance [8]. The template method, including soft, hard, and self-sacrifice templates, is an effective strategy to construct a hollow structure [5,9]. Conventionally, the templates for synthesizing hollow structures are commonly solid, such as SiO$_2$, PVP (polyvinylpyrrolidone), carbonaceous, and so on [8,10–12]. Inevitably, these approaches would involve multistep processes, including the preparation of the template and the following deposition of target materials; this increases the complexity of design and the risk of lacking uniformity and universality.

Room temperature Ga-based liquid metals (LMs) have attracted attention in many fields due to the ideal combination of metallic properties and fluidic properties [13–15]. Benefited from the richly surface chemical activity and good fluidity, Ga-based LMs can...
serve as novel soft templates for the preparation of low-dimensional materials. Through applying chemical reactions at the LM-solution interface, the preparation of various nanomaterials can also be achieved by changing the reactive surroundings [16–20]. For example, Ghasemian et al. prepared atomically thin hydrated MnO₂ using a galvanic replacement reaction between permanganate ions and Ga [21]. Meanwhile, based on the fluidity of LMs, the metal droplets can be easily sheared into nanoparticles and these nanoparticles simultaneously complete the construction of large-scale shell-core structures through interfacial deposition [22]. Nevertheless, the diversity of products is still limited if the related reaction is only between Ga and other species. For instance, it is kinetically slow for the reaction between Co²⁺ ions and Ga⁰ (which is actually thermodynamic favored), due to their redox potential difference being quite close [23]. It was found that eutectic metal elements inside the Ga-based LMs would undergo thermodynamically selective self-limiting surface oxidation at the LM-air interface, offering the successful synthesis of varying 2D oxides [24]. Similarly, it is believed that the higher reactive activity of Ga-based LMs can be tuned by adding more reactive metals inside the liquid matrix; more reactions with a greater variety of products can be achieved, such as the reduction of Co²⁺ ions.

In this work, we successfully synthesized varying Co-based hollow nanostructures by setting Ga-Zn liquid alloys as the soft templates. The experimental results showed that Ga-Zn alloys are more reactive and their uniformly distributed nanoparticles are easily obtained by ultrasound. It indicates that uniform templates can be collected and large-scale production can be achieved. As expected, through subsequent treatment of the precursor, the hollow nanoparticles are evenly distributed and possess good electrocatalytic performances. The obtained hollow CoSe₂ catalyst exhibited good OER activity in an alkaline solution.

2. Materials and Methods

2.1. Chemicals

The Ga 99.99%, Zn 99.99%, Co(NO₃)₂·6H₂O 99.99%, selenium powder 99%, 200 meshes, ammonia solution (NH₃ 25~28%), and thiourea 99% are purchased from Aladdin Chemistry Co., Ltd. (China).

2.2. Preparation of Hollow CoSe₂ Nanospheres

Preparation of CoOOH/Ga: a 700 mg GaZn liquid alloy was added into a 30 mL ethylene glycol solution and ultrasonicated with a cell crusher for 20 min to obtain GaZn nanoparticles. The nanoparticles were collected by centrifugation at 1000 to 3000 rpm for particle size screening. The GaZn nanoparticles were added dropwise into the 10 mM Co solution and stand for 10 min. The samples were collected by washing with deionized water and centrifugation, then freeze-dried in a freeze dryer.

Preparation of Co(OH)₂: 200 µL ammonia water was diluted with 20 mL deionized (pH~11.3) water and stirred evenly; then, 20 mg CoOOH/Ga was put into the solution and left to stand for 36 h to obtain a powdery white precipitate. The samples were collected by centrifugation with deionized water and then freeze-dried in a freeze dryer.

Preparation of CoSe₂: the obtained 10 mg Co(OH)₂ powder was placed in the center of the tube furnace, and 50 mg of selenium powder was placed upstream of the tube furnace. Selenization annealing was carried out at 350 °C and 450 °C for 1 h to obtain the black powder, and the samples were collected.

Preparation of CoS₂: the obtained 10 mg Co(OH)₂ powder was placed in the center of the tube furnace, and 50 mg thiourea was placed upstream of the tube furnace. The sulfidation annealing temperature was maintained at 350 °C for 1 h.

2.3. Electrochemical Measurements

Electrochemical measurements are performed by an electrochemical workstation (CHI 660D, CH Instruments, Inc., China) in a 1M KOH (Aladdin Chemistry Co., Ltd., China) solution (pH~13.8); a typical three-electrode electrochemical cell consists of a reference
electrode (using Hg/HgO electrode), a counter electrode (carbon rod), and a working electrode. Convert the potential to a reversible hydrogen electrode (RHE) using a standard conversion formula with 95% iR compensation. The electrocatalytic OER performance was measured by linear sweep voltammetry (LSV) curves at a scan rate of 5 mV/s under ambient nanospheres. Electrochemical impedance spectroscopy was performed at an open-circuit voltage in the frequency range $10^0$–$10^6$ Hz. The electrochemical surface area was obtained by scanning CV with a voltage window of 1.532–1.567 V vs. RHE in a KOH solution at scan rates from 20 to 180 mV/s.

3. Results and Discussion

Figure 1 shows a schematic illustration for the synthesis of Co-based hollow nanoparticles. The prepared GaZn LM nanoparticles gained by ultrasonication are dropped into the solution containing Co$^{2+}$, and then the galvanic reaction happens at the interface of LM and aqueous solution. The redox reaction actually involved two species: one is the Co$^{2+}$ in the solution that can move to the LM interface; and the other is the internal Zn atoms, which can also move freely to the surface of LM due to the dynamical atomic arrangement inside LM. The main reason is that the Zn has a lower electrochemical potential ($E^{0}_0\text{Zn}/Zn^{2+} = -0.763$) than Ga ($E^{0}_0\text{Ga}/Ga^{3+} = -0.549$) and is more likely to react with Co ions ($E^{0}_0\text{Co}/Co^{2+} = -0.280$) [23]. The more reactive atoms tend to move to the surface and participate in redox reactions. Therefore, the Ga nanoparticles are retained in the core, while the Zn atoms in LM alloys undergo galvanic replacement reactions with Co ions to form solid products wrapped around the surface of Ga nanoparticles. Further, since Ga atoms can react with an alkaline solution to convert to Ga$^{3+}$, the inner Ga core can be removed to obtain Co-based hollow nanoparticles. By means of a following post-processing reaction, more diversity can be achieved; for instance, CoS$_2$ and CoSe$_2$ hollow nanoparticles can be obtained by the following sulfurization and selenization treatment.

![Figure 1. Schematic illustration of the formation for the Co-based compounds.](image)

The morphologies of the samples after a galvanic reaction were characterized by SEM images, as shown in Figures 2a and S1b. It was observed that the GaZn alloy nanoparticles were obtained by ultrasound in ethylene glycol solution. The nanoparticles are uniformly dispersed and have a smooth surface. The surrounding ethylene glycol can prevent the formation of a surface Ga-oxides shell. Figure S1a plots the particle size distributions of
nanoparticles obtained in Figure 1 between 200 and 400 nm. After reacting with the Co ion solution, the nanosheets are found to wrap on the spherical surface of nanoparticles, forming core-shell nanostructures (Figures 2b and S1c). For comparison, pure Ga nanoparticles without Zn contents were also injected into a Co ion solution. The obtained products exhibit a smooth surface, as demonstrated in the SEM image in Figure S2; this indicates that no obvious reaction happened between the Ga and Co ions. This clear difference claims that the introduction of the Zn element in the LM matrix triggered the reaction and the formation of a uniform shell with sheet-like nanostructures. This also means quantitative deposition of the Co-based compound as the shell can be achieved by setting a specific amount of Zn inside the Ga LM matrix. The crystal structure of the material was further analyzed by XRD. Figure 2d shows that the core-shell structures obtained by the replacement reaction of a GaZn alloy with Co ions correspond to the peaks of CoOOH [25]. Considering the Ga LM nanoparticles are amorphous, the CoOOH should correspond to the outer shell. Here, due to the relatively high reactivity of Zn element, the Co ions can be reduced by Zn atoms in solution [26]. In the presence of oxygen and OH⁻ in solution, the Co²⁺ can release electrons under the applied bias to form CoOOH [27].

Figure 2. SEM images of (a) GaZn nanoparticles; (b) CoOOH/Ga; (c) Co(OH)₂; and (d) the XRD patterns of CoOOH/Ga and Co(OH)₂.

The Ga/CoOOH core-shell nanoparticles remain stable in a neutral solution, while after the alkaline solution treatment, Ga would be oxidized to cationic into the solution and removed from the inner core. Thus, Co-based hollow nanoparticles can be obtained after Ga is completely removed, as evidenced in Figures 2c and S1d. The XRD pattern in Figure 2d illustrated that the hollow nanoparticles in Figure 2c correspond to the peaks of Co(OH)₂. It indicates that the outer CoOOH shell was converted to Co(OH)₂ through dissolution-crystallization processes in ammonia solution [28]. It should be noted that different mass ratios of CoOOH/Ga will affect the sample morphology and the consumption of the Ga core in an ammonia solution. Figure S3a,b show the SEM images of Co(OH)₂/Ga-40 (Figure S3a) and Co(OH)₂/Ga-60 (Figure S3b) obtained by adding 40 mg and 60 mg of CoOOH/Ga into a 20 mL ammonia solution with pH = 11.3, respectively. It was observed that the hollow structure cannot be maintained and large-sized residual Ga nanoparticles remained. It seems Ga cannot be completely consumed due to the increase in the mass of the precursor. The different pH of the alkaline solution also affects the morphology of the
sample after removing the LM templates. When the pH is~12.3, the morphology of the samples is partly kept hollow and partly transformed into flakes (Figure S4a,b). Moreover, the strong alkaline solution would result in the construction of hollow structures during the removal process of the Ga template. The samples obtained by soaking the CoOOH/Ga precursor in a NaOH solution with pH~11.3 are sheet-like structures (Figure S4c,d). It is believed that the rapid depletion of Ga atoms in the strong alkaline solution could increase the surface tension and induce the rupture of the outer shell.

The obtained hollow Co(OH)$_2$ nanoparticles can be used as good templates for the preparation of other Co-based materials. Here, serving as representative examples, hollow CoS$_2$ and CoSe$_2$ nanostructures were successfully synthesized via further sulfurization and selenization treatments, respectively. As shown in Figures 3a and S5a, the morphology of CoS$_2$ after 350 °C sulfurization still maintains a good hollow nanostructure, being composed of uniformed thin nanosheets. The XRD (X-ray Diffraction) analysis in Figure 3b claimed that the as-prepared product corresponds to CoS$_2$ (standard card PDF #65-3322). Hollow CoSe$_2$ nanoparticles (Figures 3c and S5b) can be also obtained by selenizing the hollow Co(OH)$_2$ nanoparticles at 350 °C. The XRD result of the sample also confirms its crystalline structure is CoSe$_2$ (standard card PDF #53-0449, Figure 3d). Note, it is better to use mild condition for further treatment. For example, when the selenization temperature was raised to 450 °C, the hollow structures collapsed into fragmented nanosheets (Figure S6).

![Figure 3](image)

Figure 3. The SEM images of (a) CoS$_2$ and (c) CoSe$_2$; the XRD patterns of (b) CoS$_2$ and (d) CoSe$_2$.

The OER activity of the as-prepared samples was tested through a typical three-electrode system in 1M KOH, and the performances of different Co-based hollow nanoparticles were evaluated. The LSV curves show that the hollow-structured CoSe$_2$ nanoparticles exhibit the best OER performance. Its overpotential corresponds to a voltage of 340 mV at a current density of 10 mA/cm$^2$, which outperforms those of CoS$_2$ (370 mV) and Co(OH)$_2$ (402 mV). Figure 4b reveals the Tafel slopes of CoSe$_2$ (80.0 mV/dec), CoS$_2$ (71.6 mV/dec), and Co(OH)$_2$ (86.4 mV/dec), respectively. CoS$_2$ exhibited the smallest Tafel slope, which indicates that it had the fastest reaction kinetics. To characterize the electrode kinetics, electrochemical impedance spectroscopy was tested in Figure 4c. To characterize the electrode kinetics, electrochemical impedance spectroscopy was tested in Figure 4c. The charge
transfer resistance \( (R_{ct}) \) is obtained from the high frequency region. The semi-circular diameter of \( \text{CoSe}_2 \) and \( \text{CoS}_2 \) is much smaller than that of \( \text{Co(OH)}_2 \); thus, they have a smaller \( R_{ct} \) and faster electron transport. Figure 4d tests the stability of the samples by comparing the polarization curves before and after CV (Cyclic Voltammetry, CHI 660D, CH Instruments, Inc., China) 2000 cycles of \( \text{CoSe}_2 \). It is found that the two polarization curves almost overlap, indicating the good stability of the as-prepared \( \text{CoSe}_2 \) as electrocatalysts.

The OER activity of the as-prepared samples was tested through a typical three-electrode system in 1M KOH, and the performances of different Co-based hollow nanoparticles, \( \text{CoOOH/Ga nanoparticles} \) were calculated according to the CV curves, in which \( \text{CoS}_2 \) potential; thus, it is easy to undergo a redox reaction for the reduction of Co ions. Taking advantage of this strategy, the Ga/CoOOH core-shell nanostructure was successfully prepared; in addition, the \( \text{Co(OH)}_2 \) hollow nanostructure can be obtained by gently and effectively removing the Ga nanoparticles template. Furthermore, a series of other Co-based catalysts.

Figure 4. (a) OER polarization curves of \( \text{Co(OH)}_2 \), \( \text{CoS}_2 \), and \( \text{CoSe}_2 \); (b) Tafel plots; (c) Nyquist plots; (d) polarization curves of \( \text{CoSe}_2 \) before and after 2000 cycles.

The electrochemical surface area (ECSA) was measured by electrochemical double-layer capacitance \( (C_{dl}) \). Figure S7a–c tested the cyclic voltammetry curves of \( \text{Co(OH)}_2 \), \( \text{CoS}_2 \), and \( \text{CoSe}_2 \) at different scan rates. In Figure S7d, the \( C_{dl} \) values of different samples were calculated according to the CV curves, in which \( \text{CoS}_2 \) (9.1 mF/cm\(^2\)) has more electrochemically active sites than \( \text{CoSe}_2 \) (6.0 mF/cm\(^2\)) and \( \text{Co(OH)}_2 \) (5.6 mF/cm\(^2\)). Figure S8 shows the OER performance of \( \text{CoSe}_2 \) at different annealing temperatures. Compared with the hollow structure, the sheet-like structure exhibits higher overpotential (400 mV) in Figure S8a and a larger Tafel slope (93.7 mV/dec) in Figure S8b. In addition, Figure S9 shows that the morphology and residual Ga particles affect the OER performance of the samples. The performances of \( \text{CoOOH/Ga nanoparticles} \) of different quality placed in alkaline solution were compared. Figure S9a measured the LSV curves of the added 20, 40, and 60 mg \( \text{CoOOH/Ga nanoparticles} \). The overpotentials of the three samples were 402 mV \( (\text{Co(OH)}_2) \), 430 mV \( (\text{Co(OH)}_2/\text{Ga-40}) \), and 470 mV \( (\text{Co(OH)}_2/\text{Ga-60}) \) at 10 mA/cm\(^2\), respectively. As the Ga nanoparticles content increases, the Tafel slope of the samples also increases as shown in Figure S9b. The results show that the more remaining Ga particles will reduce the OER performance.

4. Conclusions

In conclusion, the Zn species in the GaZn alloy nanoparticles have a lower redox potential; thus, it is easy to undergo a redox reaction for the reduction of Co ions. Taking advantage of this strategy, the Ga/CoOOH core-shell nanostructure was successfully prepared; in addition, the \( \text{Co(OH)}_2 \) hollow nanostructure can be obtained by gently and effectively removing the Ga nanoparticles template.
compounds can be obtained by subsequent processing. Such hollow nanostructures are able to enhance the catalytic active site and mass transport for Co-based electrocatalysts. Among the as-prepared samples, the CoSe$_2$ hollow nanostructure exhibits a high catalytic activity of 340 mV at 10 mA/cm$^2$ with a Tafel slope of 80.0 mV/dec. This work extends the utilization of Ga-based LMs as soft templates. This methodology can achieve the deposition of target products only relying on the electrochemical driving force. It offers the possibility to explore other hollow compounds in future research and is expected to be applied in sensing, electronics, and other fields. The unique properties of liquid metals provide a facile method for the preparation of hollow materials.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/mi13081292/s1, Figure S1: (a) The particle size distributions obtained from Figure 1; the larger magnification SEM images of (b) GaZn nanoparticles; (c) CoOOH/Ga; (d) Co(OH)$_2$; Figure S2: The SEM image of pure Ga nanoparticles reacting with Co solution; Figure S3: The SEM images of different quality CoOOH/Ga nanoparticles placed in ammonia solution with pH~11.3: (a) Co(OH)$_2$/Ga-40; (b) Co(OH)$_2$/Ga-60; Figure S4: The SEM images of (a,b) the sample of CoOOH/Ga template was cleaned by ammonia solution with pH~12.3; (c,d) the samples of CoOOH/Ga were cleaned by NaOH solution with pH~11.3; Figure S5: the larger magnification SEM images of (a) CoSe$_2$ and (b) CoS$_2$; Figure S6: SEM image of CoSe$_2$-450; Figure S7: Electrochemical capacitance measurements with different scan rates from 60 to 180 mV/s in a 1 M KOH solution of: (a) Co(OH)$_2$; (b) CoS$_2$; (c) CoSe$_2$; (d) the double layer capacitance ($C_{dl}$) results for all the samples; Figure S8: (a) The OER polarization curves; and (b) Tafel plots of CoSe$_2$ and CoSe$_2$-450; Figure S9: (a) The OER polarization curves; and (b) Tafel plots of Co(OH)$_2$, Co(OH)$_2$/Ga-40, and Co(OH)$_2$/Ga-60.

**Author Contributions:** Conceptualization, L.R., Z.L. and Y.L.; validation, Y.J., X.W. and L.R.; investigation, Y.J., X.W.; writing—original draft preparation, Y.J. and X.W.; writing—review and editing, Z.L., Y.L. and L.R.; visualization, Y.J. and X.W.; supervision, L.R. and Y.L.; project administration, Z.L., Y.L. and L.R.; funding acquisition, Z.L., Y.L. and L.R. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the National Natural Science Foundation of China (no. 82160353; 12004321), the Australian Research Council (ARC) (LP180100722), the Fundamental Research Funds for the Central Universities (WUT: 2022IVA006), and the QianKeHe talent-development platform [2018] (No. 5772-016).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors acknowledge the use of the facilities at Ningbo Jansen NMR Technology Co., Ltd. (Ningbo, China) under the financial support from the Australian Research Council (ARC) (LP180100722).

**Conflicts of Interest:** There are no conflict to declare.

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