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Controlled synthesis of hexagonal annular Mn(OH)F for water oxidation

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ABSTRACT

Controlling the morphology and size of materials is very important for their chemical and physical properties. Herein, we synthesized a novel hexagonal annular Mn(OH)F by a simple hydrothermal method. We also investigated the growth process of the materials from hexagonal block to hexagonal ring via controlling the hydrothermal temperature and time. Comparing with the hexagonal block, the hexagonal rings showed enhanced electrocatalytic water oxidation performance in alkaline solutions. The observed catalytic performance of this novel Mn(OH)F is correlated to its unique structure. Furthermore, we expect that Mn(OH)F would be a new type of Mn-based water oxidation catalyst.

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1. Introduction

The synthesis of materials with special morphology has aroused a great deal of interest to researchers, due to their unique chemical and physical properties [1–3]. Various materials with different morphologies have been synthesized, such as nanotubes [4], nanorods [5,6], yolk-shell nanoboxes [7], hollow spheres [8]. Moreover, these materials have proven to be used in various fields such as sensing [9], catalysis [10–13], energy storage [14–18]. However, in these functionalized materials, it is still a challenge to synthesize uniform ring structures by a simple protocol. These ring-like materials may have unique properties due to their unique inner cavity [19]. It is reported that these rings have good applications in the field of electron-

ics and semiconductors [20,21]. In the past, the synthesis of annular materials was almost using templating technologies [22]. At present, many ring-like materials have been reported. Such as α -Fe₂O₃ [23], Sb₂Te₃ nanorings [1], ZnO [24], and Ni(OH)₂/Co(OH)₂ hollow nanohexagons [25] by microwave-assisted method [19], wet chemical method and hydrothermal method [24,25].

Recently, metal hydroxide, fluoride and hydroxyl fluoride have been widely used in water oxidation and energy storage [26–28]. Interestingly, we noticed that these metal hydroxides and hydroxyl fluoride materials tend to form hexagonal blocks, which can be converted into hexagonal rings. Dong and co-workers [29] reported the low-cost one pot production of Ni_{0.33}Co_{0.66}(OH)F hollow hexagons woven by multi-walled car-

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bon nanotubes. Due to the unique hollow structure of hexagons, the materials have good electrochemical performance [29]. In addition, we reported the formation mechanism of six-fold symmetrical β -Co(OH)₂/Co(OH)F hierarchical hexagons with good water oxidation property [30].

In this work, we synthesized a novel hexagonal annular Mn(OH)F by controlling the amounts of hydrazine and ammonium fluoride in a one-pot wet chemical reaction. We also investigated the formation process of this hexagonal annular Mn(OH)F. The hexagonal annular sample has better electrocatalytic performance when compared with the hexagonal block analogue.

2. Experimental

2.1. Materials

All chemicals were used as received without any further purification. Mn(NO₃)₂·4H₂O (98%) was purchased from the Alfa Aesar, NH₄F (98.0%) was purchased from the Energy Chemical, N₂H₄ (AR, 80%) was purchased from the Tianjin Fuyu Fine Chemical Co., Ltd.

2.2. Synthesis of hexagonal annular Mn(OH)F

In a typical synthesis, 1 mmol of Mn(NO₃)₂·4H₂O and 4 mmol of NH₄F were dissolved in 30 mL of distilled water, then 4 mmol of N₂H₄ was added into the prepared solution. The solution was stirred for 5 min at room temperature and then heated at 160 °C for 6 h in a sealed 50 mL Teflon-lined autoclave. After naturally cooling down to 25 °C, the obtained solid materials were collected and centrifuged, followed by washing with deionized water for several times before the drying in an oven at 60 °C.

2.3. Preparation of the electrocatalyst

Typically, 2 mg of the sample, 1 mg of carbon black and 20 μ L of Nafion solutions were dispersed in 0.5 mL water/ethanol (2:1) solution by 30 min of sonication. Then the catalyst ink (5 μ L) was dropped onto a GC working electrode with a working area of 0.07 cm². All electrochemical tests were performed on the CH Instruments Electrochemical Analyzer (CHI 660E). LSV was performed at a 5 mV/s in 1 mol/L KOH solutions. A platinum column was used as the counter electrode and a saturated Ag/AgCl as the reference electrode.

2.4. Physical characterization

Powder X-ray diffraction (XRD) patterns of as-prepared materials were measured with a X-ray diffractometer (Rigaku D/Max2550VB+/PC, Cu K α , λ = 1.5406 Å, 40 kV and 100 mA). The morphology of the as-prepared material was observed with scanning electron microscopy (SEM, Hitachi, SU8020) Fourier-transform infrared (FTIR) spectra were obtained using an IR spectrometer (Bruker, Tensor27) by making thin pellets with dried KBr powder. The X-ray photoelectron spectroscopy

(XPS) analysis of the materials was performed with a Kratos AXIS ULTRA XPS. Thermogravimetric analysis (TGA) was applied by heating the as-prepared sample at a rate of 10 °C min⁻¹ with N₂ and air from 20 to 1000 °C in a TA Instruments SDT Q600.

3. Results and discussion

The obtained materials were characterized by powder XRD. The Fig. 1(a) and (b) show the XRD patterns of the materials synthesized with different amounts of N₂H₄·H₂O and NH₄F at 120 °C for 6 h. The results indicate that the formation of Mn₃O₄ (JCPDS#18-0803) in the absence of NH₄F, whereas no precipitation was obtained without hydrazine hydrate. When the amount of N₂H₄·H₂O is 4 mmol, it can be clearly seen that pure Mn(OH)F is formed with the increase of NH₄F to 4 mmol [31]. We can conclude that pure Mn(OH)F can be obtained when the molar ratios of hydrazine hydrate and ammonium fluoride are relatively low. From Fig. S1, there is no phase change at different temperatures and time. As shown in Fig. S2, the C, O, Mn and F elements are present in the material and the atomic ratio of Mn to F is close to 1:1 according to the EDS spectrum, which further confirms the obtained sample is Mn(OH)F. The synthesized Mn(OH)F was further confirmed by the IR spectroscopy (Fig. 1(c)). The strong peak at 3463 cm⁻¹ is attributed to the O–H stretching mode. The shoulder peak at 3367 cm⁻¹ belongs to the interactions between the hydroxide and fluoride anions. A group of small peaks at $\approx$ 2924 cm⁻¹ is likely due to N–H vibrations of the surface-adsorbed NH₄⁺ or N₂H₄ species formed during the hydrothermal synthesis. The peaks at the 955 and 789 cm⁻¹ are attributed to the Mn–OH and Mn–F bending modes [28,32]. The obtained sample was identified by TGA and DTG curves, as shown in the Fig. 1(d). The weight loss of the sample before 300 °C indicates the loss of water produced via the sample resolving [31]. Furthermore, the XRD of the Mn(OH)F after calcination at 600 °C for 2 h in N₂ atmosphere demonstrate that the sample decomposed into MnF₂ and MnO (Fig. S3).

The morphology of the Mn(OH)F was investigated by SEM. From the Fig. S4, it is obvious that the morphology of the product can be controlled by adjusting the amount of N₂H₄ and NH₄F. A bulk sample with surface layers is observed without the addition of NH₄F (Fig. S4(a)). When the amount of NH₄F is 2 mmol, random sheets begin to form and stack together (Fig. S4(b)). Continuing to increase the amount of NH₄F to 4 mmol, the sheets become thicker and hexagonal rings can be observed. As the amount of NH₄F continues to increase to 6 mmol (Fig. S4(d)), 8 mmol (Fig. S4(e)) and 10 mmol (Fig. S4(f)), we can observe that the angle of the hexagonal blocks becomes less apparent and the products have morphology of a pile of columns formed by lots of sticks. As shown in Fig. S5, with the increasing of hydrazine hydrate at 4 mmol of NH₄F, the holes in the hexagonal blocks are getting smaller and the structure of hexagonal rings is gradually destroyed. So the formation of the hexagonal rings is due to the interaction of fluorine ions in the initial process and hydrazine hydrate provides an alkaline condition for providing hydroxide ions [23,28].

Fig. 1. (a) XRD patterns of the samples prepared with 4 mmol NH_4F and different amounts of hydrazine. (b) XRD patterns of the samples prepared with 4 mmol hydrazine and different amounts of NH_4F . The reactions were conducted at 120 °C for 6 h. IR (c) and TGA (black) and DTG (red) curves (d) of the sample from 4 mmol hydrazine and 4 mmol NH_4F at 160 °C for 6 h.

To obtain more detailed information about the growth process, experiments at different hydrothermal temperatures were conducted. Fig. S6 shows the SEM images of the products synthesized with different hydrothermal temperatures ranging from 100–160 °C. It can be seen that the solid hexagon has been synthesized when the reaction temperature is 100 °C with a size of about 4 μm . The surfaces are rough and are made up of layered slices. These pieces extend outward like petals along the hexagonal angles. It can be observed that the middle part of the hexagonal solid protruding upward. This may be due to the rise in temperature, which causes the decomposition of NH_4F to form HF. Thus, the F^- is adsorbed onto the surface of the hexagonal block to start etching the surface. As the temperature rises to 120 °C, these slices on the surface of hexagonal block grow outward along the hexagonal angles. With etching continues, the sample displayed special morphology that there is a round cake made up of small particles inside the center of the original hexagonal block. Moreover, there is a clear dividing line between the inner round cake and the outer hexagonal rings [29]. When the temperature continues to rise to 140 °C, the core-shell structure became uniform, and the center cake is etched to be looser and smaller. The core inside the hexagonal ring falls off from the hexagonal shell, leading to the formation

of the hexagonal rings when the temperature reaches to 160 °C. As the temperature continues to a higher temperature, the structure of the rings is destroyed. (Fig. S6(e).)

In order to further understand the growth process of the hexagonal rings, the time-dependent experiment was done. As shown in Fig. S7(a), the SEM images show the morphologies of the sample obtained at 160 °C with different reaction times. The solid hexagonal block with sheets on the surface was obtained after 1 h. The morphology is similar to the material shown in Fig. S6(a) obtained at 100 °C for 6 h. By extending the reaction time to 2 h, it can be clearly observed that the hexagonal center was etched into loose small particles and these small particles are protruding slightly (Fig. S7(b)). With even longer reaction time, the core-shell structure begins to form, and the core in the middle of the hexagonal ring could be observed clearly (Fig. S7(c)). As the reaction time prolonging, the hexagonal rings can be obtained after 6 h (Fig. S7(d)). By prolonging the reaction time to 10 h, the hexagonal rings have been destroyed (Fig. S7(e)).

Fig. 2(a–d) shows the morphologies of the hexagonal rings. It can be observed that the hexagonal rings are uniformly distributed in the synthesized material. The outer size of the hexagonal rings is about 4–5 μm , the inner ring is about 3.3 μm and

Fig. 2. SEM (a–d) and EDX elemental mapping (f–h) images of the hexagonal annular Mn(OH)F.

Fig. 3. The formation process of the hexagonal Mn(OH)F ring.

the thickness of the ring is $\sim 0.9 \mu\text{m}$. The energy-dispersive X-ray (EDX) elemental mapping images of the Mn(OH)F hexagonal rings are shown in Fig. 2(f–h), indicating the uniformity of Mn, F and O elements in the hexagonal ring.

Based on the above results, the main reason for the formation of the hexagonal annular Mn(OH)F is the corrosion of the F^- . Besides, the formation of the structure is related to temperature and time. So the growth process of the hexagonal Mn(OH)F ring can be illustrated in Fig. 3. First, the reactant ions form a homogeneous solution before the hydrothermal reaction was carried out at 160°C . Then, a hexagonal block was obtained at 1 h. As the reaction time increases to 2 h, the inner parts of the solid hexagonal begin to be loose due to the corrosion of the F^- and the gas released by the decomposition of hydrazine hydrate [29]. A center cake is formed inside the hexagonal rings by etching for 4 h. Finally, the inner core was etched away, leading to the formation of the ring-shaped Mn(OH)F. This process of the formation for hexagonal Mn(OH)F ring can be illustrated by the following equations.

Fig. 4. (a) The modeling morphology of the Mn(OH)F. (b) The structure of the (110) facet of Mn(OH)F.

The possible mechanism of the formation of hexagonal rings can also be explained by the theoretical models [33]. As shown in Fig. 4(a), the Mn(OH)F tends to form hexagonal morphology as calculated with the Materials Studio based on the Bravais-Friedel Donnay-Harker (BFDH) method [34]. According to the BFDH model, the growth rate of the crystal face (rhkl) is negative proportional to the distance of the crystal plane (dhkl). Therefore, the crystal face (110) has the largest surface area due to the slow growth rate (Fig. 4(a), Table S1). In contrast, the faces (011) and (101) grow relatively fast and lead to small surface area. The face (020) may disappear due to the fast growth rate during the crystal growth process [35]. The calculated morphology is consistent with the morphology of the sample observed in the experiment (Fig. S7(a)). Moreover, the amount of Mn atoms is quite high as shown from the crystal structure of the top surface (110) of Mn(OH)F crystal (Fig. 4(b)) [31], indicating that fluoride ions are easier to be adsorbed on the (110) surface [36]. Therefore, the (110) surface of the hexagonal crystal is etched by the HF. Finally, the hexagonal ring is formed.

The surface physical information of the sample is studied by XPS. As shown in Fig. 5a, the position of the F 1s peak at 684.8 eV is attributed to metal hydroxyfluoride [37,38]. It is cleared that there are two peaks for O 1s in the XPS spectrum (Fig. 5(b)). The peak at 531.6 eV could be assigned to the metal hydroxides and another peak (533.6 eV) belongs to C–O–H [39]. The valence states of manganese are usually determined by the relative position of Mn $2p_{1/2}$ satellite structure ($\Delta E 2p_{1/2}$) and the splitting of Mn 3s ($\Delta E 3s$) [40,41]. $\Delta E 2p_{1/2}$ (Fig. 5(c)) and $\Delta E 3s$ (Fig. 5(d)) are 6.48 and 6.2 eV, respectively, which correspond to Mn(II).

In order to explore the relationship between morphology and the electrocatalytic performance, the oxygen evolution reaction (OER) of the hexagonal Mn(OH)F rings and hexagonal blocks were conducted in 1 M KOH solutions by LSV at 5 mV/s. The OER of the carbon black was also conducted in the same conditions (Fig. S8). As shown in Fig. 6(a), the onset potential of the rings is 1.53 V and the block is 1.58 V, so the hexagonal rings show smaller onset potential and higher normalized current density than the hexagonal blocks. This may be due to that the ring material exposed the inner cavity, resulting in more active sites for water oxidation [42]. The Tafel slope of the

Fig. 5. The F 1s (a), O 1s (b), Mn 2p (c) and Mn 3s (d) XPS spectra of the Mn(OH)F.

Fig. 6. LSVs (a) and Tafel plots (b) of the sample with different morphologies. The red line is the hexagonal Mn(OH)F rings obtained at 6 h, and the black line is the hexagonal Mn(OH)F blocks obtained at 1 h.

hexagonal Mn(OH)F rings is 184 mV/dec, and the value for the hexagonal blocks is much higher at 293 mV/dec (Fig. 6(b)). The lower Tafel slope of the Mn(OH)F rings demonstrates that the mass diffusion is relatively more efficient, as induced by the cavities [43,44].

4. Conclusions

In summary, unusual hexagonal Mn(OH)F rings were syn-

thesized by a fine-tuned hydrothermal method. We explored the formation process of the hexagonal rings, which are generated by the etching of fluoride anions. The hexagonal Mn(OH)F rings have better electrochemical performance than the hexagonal blocks for OER due to the cavities in the unique structure. This protocol for the synthesis of unique ring-structures might be useful in the area of catalysis, which requires unusual facets for fast kinetics and open voids for efficient mass diffusion.

Graphical Abstract

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Controlled synthesis of hexagonal annular Mn(OH)F for water oxidation

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The hexagonal rings of Mn(OH)F shows higher electrochemical OER performance than the hexagonal solid sample in 1 mol/L KOH solutions.

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六元环状羟基氟化锰的可控合成及水氧化性能

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摘要: 含特殊结构的材料, 尤其具有内腔的环状材料, 因其独特的物理和化学性质而引起了人们的极大兴趣. 目前已经合成了许多环状材料, 广泛应用于催化, 传感, 生物医学, 环境保护, 储能等领域. 然而, 这些环状材料的合成方法大多比较复杂和困难. 如早期的模板技术, 以及用微波辅助法和湿化学法合成 α -Fe₂O₃, Sb₂Te₃纳米线, ZnO和Ni(OH)₂/Co(OH)₂空心纳米六元环等. 因此, 通过简单的方法来合成功能均匀的环状结构材料仍然是一个巨大的挑战. 近期的研究表明, 金属氢氧化物, 氟化物以及羟基氟化物被广泛应用于水氧化和储能等领域. 本文通过简单的水热法合成了一种新型的六元环状的羟基氟化锰, 它具有良好的水氧化催化性能.

粉末X射线衍射结果显示, 当水合肼用量为4 mmol时, 在不添加氟化铵的条件下得到的样品是Mn₃O₄; 随着氟化铵用量增加到4 mmol时为羟基氟化锰, 并得到红外、热重分析、能谱、X射线光电子能谱等表征的证实. 为了探究六元环状的羟基氟化锰的生长过程, 我们控制水热反应的温度和时间, 通过扫描电子显微镜表征了样品在不同的温度和时间条件下的形貌. 发现在较低的温度和较短的反应时间下得到的是表面粗糙的六角形的块状材料; 随着温度和反应时间的增加, 氟化铵和水合肼分解, 氟离子在材料的表面不断刻蚀, 形成了核壳结构的形貌; 当于160 °C反应6 h时形成了环状的羟基氟化锰. 随后通过理论模型解释了这种环状材料的生长机理. 为了探究结构和性能之间的关系, 在1 mol/L KOH溶液中对160 °C反应1 h得到的六元块状形貌的氟化羟基锰和反应6 h得到的六元环状氟化羟基锰的电催化水氧化性能进行了研究. 结果表明, 环状的氟化羟基锰的起峰电位是1.53 V, 块状的为1.58 V, 可见前者具有较低的起峰电位, 更高的电流密度. 塔菲尔测试结果显示了环状的塔菲尔斜率(184 mV/dec)比块状(293 mV/dec)的小, 表明环状材料的质量扩散的效率相对较高. 这可能由于环状结构的材料暴露了内腔, 暴露出更多的水氧化活性位点.

关键词: 水氧化; 电催化; 羟基氟化锰; 六元环状材料; 析氧反应

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