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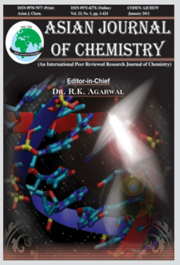

An Effective Fabrication of Sheet-Like Iron by Electrochemical Deposition

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The metal iron sheets were successfully fabricated with the help of cetyltrimethylammonium bromide (CTAB) combined with the electrochemical deposition technology. The sheet-like structures perpendicularly grew up on the foil and formed the array constructed by iron sheets. To the best of our knowledge, it is the first report on sheet-like iron. This method is very facile and effective to prepare the sheet-like structure with the uniform thickness. Especially, the addition of CTAB can not only effectively attribute to the formation of the sheet-like structure as shape-controller, but also prevent iron from oxidizing as the protective agent. The effects of the experimental parameters on the morphologies of the products were deeply discussed by scanning electron microscopy and the possible formation mechanism was proposed. And the size of iron sheets and the sheet intensity in the array can be controlled by adjusting the concentration of CTAB and the electric potential, respectively.

Key Words: Fabrication, Iron, Sheet-like structure, Electrochemical deposition.

INTRODUCTION

The development of novel nano-structured materials with controlled shapes and ordered morphology has stimulated great research interest for their unique optical, catalytic and electrochemical properties that are not conceivable in bulk micrometric structures[1-5]. Among them, two-dimensional (2D) nanomaterials, such as monolayers, plates, nanosheets and layered compounds, have been well investigated as building blocks of higher architectures[6-10]. Recently, extensive attention has been devoted to the fabrication of 2D metallic nano-materials, such as palladium[11,12], silicon[13], silver[14] and gold[15,16].

Metal iron nano-materials have been studied both experimentally and theoretically because of their outstanding properties and potential applications in catalysis, magnetism, electronics, biomedical and environmental engineering[17,18]. However, to the best of our knowledge, there is no report on the sheet-like iron. As far as the synthesis of iron nano-materials is concerned, several procedures have been reported which lead to partially or totally oxidized materials[19]. Therefore, there is a need to find a novel fabrication approach of metal iron, especially metal sheet-like iron with 2D structure.

In this paper, we reported a simple and facile method to successfully fabricate metal iron sheets assisted by cetyltrimethylammonium bromide (CTAB) combined with the electrochemical deposition technology. In our reaction system, iron chloride is used as iron source and CTAB as the shape-controller that could effectively adjust the morphologies of iron materials. The fabricated iron sheets were examined by scanning electron microscopy (SEM). Based on the experimental results, the possible formation mechanism was described.

EXPERIMENTAL

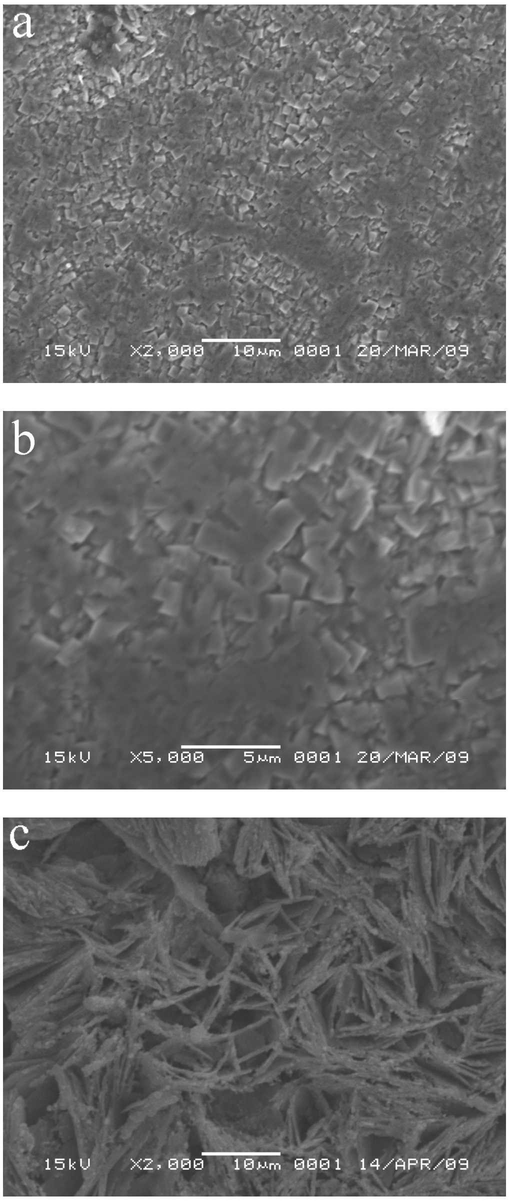
Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), boric acid (H_3BO_3) and cetyltrimethylammonium bromide (CTAB) were of analytical grade and purchased from Shanghai Chemical Reagents Company without further purification. Deionized water was used as the solvent in all experiments.

Preparation of sheet-like iron: The electrodeposition solution consisted of $FeCl_3$ (0.1 mol L^{-1}), H_3BO_3 (0.1 mol L^{-1}), cetyltrimethylammonium bromide (4 g L^{-1}) and deionized water. Electrodeposition was carried out in a two-electrode electrochemical cell and both the anode and cathode electrode were composed of the copper foils with the diameter of 0.8 cm and the length of 1.5 cm. The two electrodes placed parallel to each other and perpendicularly inserted into the electrodeposition solution. The electrodepostion was carried out at the constant electric potential of 1.0 V without heating and stirring.

Sample characterization: After reacted for several minutes, the cathode as the working electrode was taken out and carefully rinsed with deionized water more than five times, then allowed to air dry before characterization. The samples for scanning electron microscopy were directly fixed to a SEM stub and were sputtered with a 5 nm layer of platinum. Images were obtained with a JEOL JSM-6360 LV SEM operating at an accelerating voltage of 15 kV or 20 kV. The copper foils deposited by specimens were directly placed on the sample stage for structural characterization. The results were performed by means of X-ray diffraction (XRD) using a D/Max-RA diffractometer with CuK$_\alpha$ radiation.

RESULTS AND DISCUSSION

Fig. 1 shows the scanning electron microscopy images of the samples assisted by no additive and by cetyltrimethylammonium bromide, respectively. As shown in Fig. 1a-b, the electrochemical deposition without cetyltrimethylammonium bromide in the electrolyte leads to the formation of the nubby structures. The magnification image in Fig. 1b shows that the ruleless nubby structures pile up each other and occupy the whole surface of copper foil. Fig. 1c-d show the SEM images of the product deposited with cetyltrimethylammonium bromide in the electrolyte. The sheet-like structures with the thickness of 200-500 nm perpendicularly grow up on the foil and interweave each other, forming the array constructed by sheets. Therefore, the addition of cetyltrimethylammonium bromide can attribute to the formation of sheet-like structures.



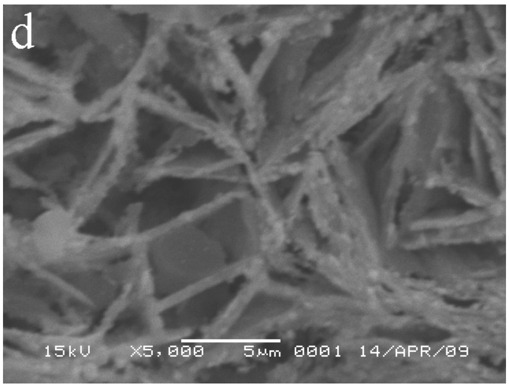


Fig. 1. SEM images of the products without CTAB (a and b) and with CTAB (c and d) in the electrolyte at the electric potential of 1.0 V for 10 min

Fig. 2 shows the X-ray diffraction (XRD) patterns of the samples fabricated without cetyltrimethylammonium bromide and with cetyltrimethylammonium bromide, respectively. The diffraction peaks at about 43.2º and 50.4º can be attributed to the face-centered cubic (fcc) directions of Cu (111) and (200) (JCPDS file No. 04-0836) from the copper foils in Fig. 2. The diffraction peak at about 28.2º can be indexed as the primitive hexagonal direction of Fe (102) in good agreement with JCPDS file No. 34-0529. The appearance of other peaks at the range of 10-50º in Fig. 2a indicates the presence of iron oxide. However, in addition to the peaks of metal iron and copper, no peaks is found in Fig. 2b, suggesting that the assisted growth by cetyltrimethylammonium bromide could effectively prevent iron from oxidizing. Therefore, the addition of cetyltrimethylammonium bromide in the electrolyte can not only be helpful for the formation of sheet-like structure, but also contribute to the growth of metal iron.

To get an insight into the formation mechanism of sheet-like iron assisted by CTAB, we need to investigate the effect of the electrochemical deposition time on the morphologies of the products by SEM analysis. At the beginning of the electrochemical deposition, the sheet-like structures with the thickness of about 200 nm grew up and sparsely arranged on the foil in Fig. 3a. When the reaction time reached to 5 min, the sheet-like iron with the almost unchanged thickness became more bushy (Fig. 3b). With the increasing reaction time, the sheet-like structures of the products further developed in number and interwove each other, forming the array constructed by sheets (Fig. 1c and Fig. 3c). After reacted for 30 min, the interwoven iron sheets gradually formed the aggregates of the plates randomly covering the copper foil (Fig. 3d). The above experimental results clearly indicate that the presence of CTAB in the electrolyte attributes to the different growth rates in orientations, which promotes the formation of the sheet-like iron. Therefore, at first the sheet-like iron perpendicularly grew up on the foil and formed the array constructed by sheets and the thickness of sheet-like structures protected by CTAB hardly

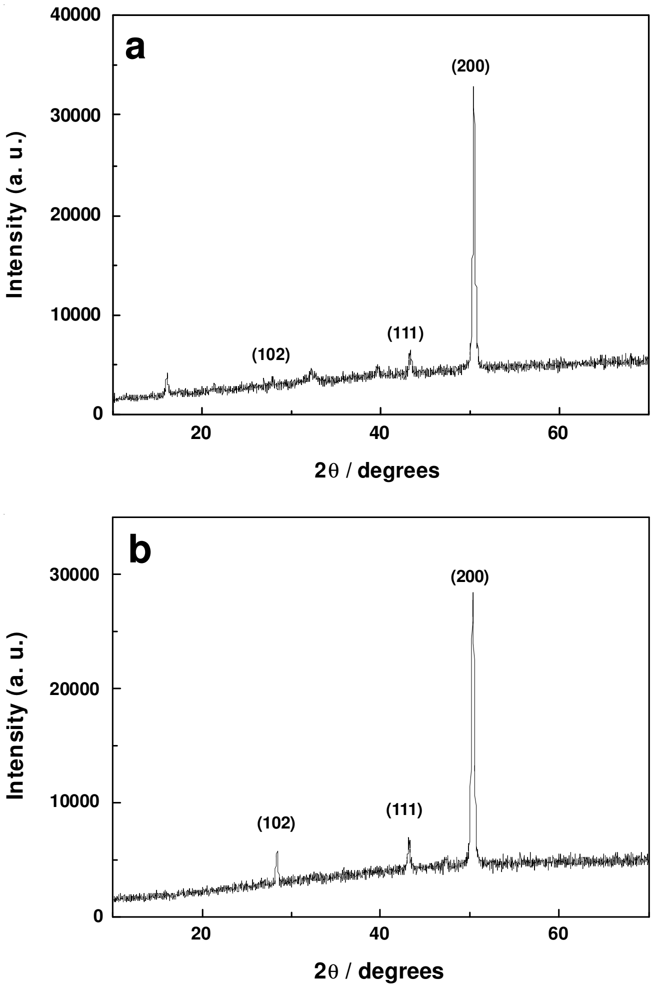
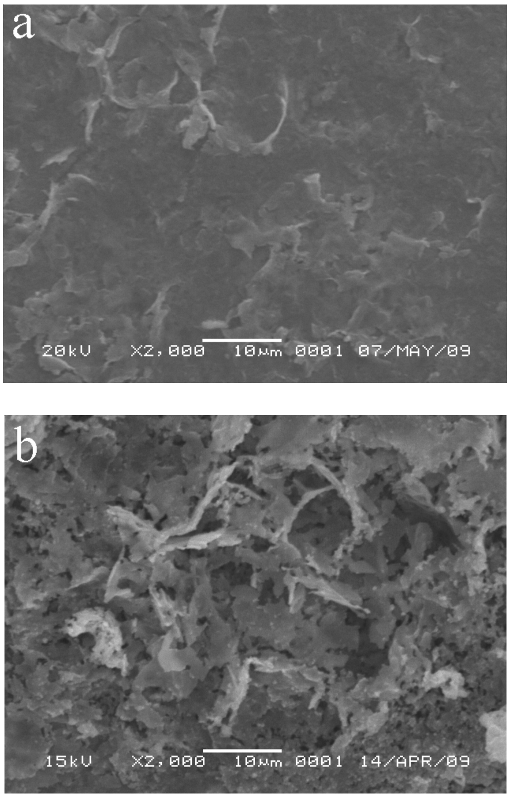


Fig. 2. XRD patterns of the products without CTAB (a) and with CTAB (b) in the electrolyte at the electric potential of 1.0 V for 10 min



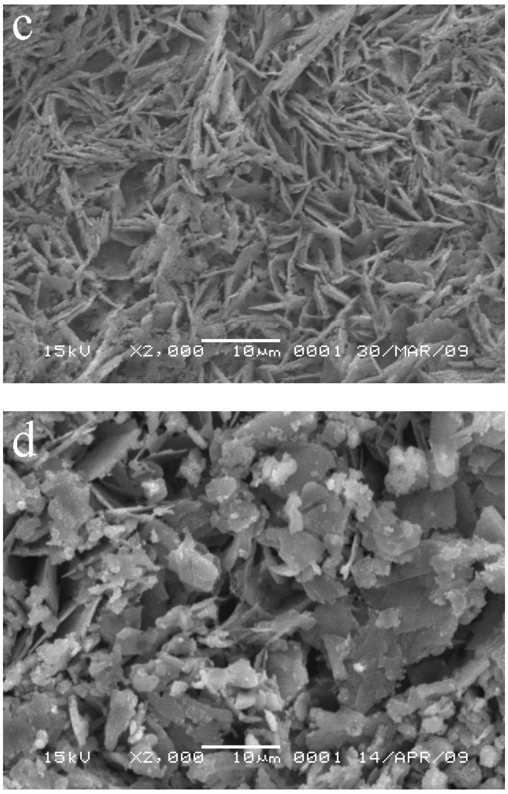
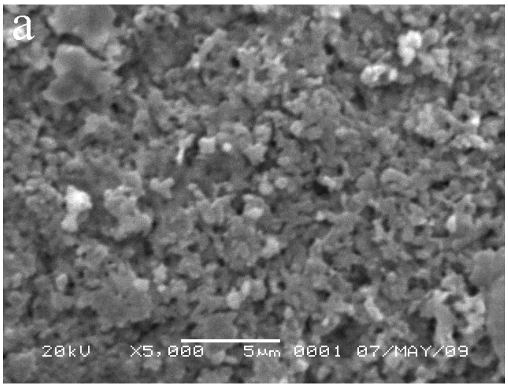


Fig. 3. SEM images of the products with CTAB at the electric potential of 1.0 V for the different deposition times: (a) 1 min, (b) 5 min, (c) 20 min and 30 min (d)

changed with the increasing reaction time. Then the iron sheets further grew up and interwove, which destroyed the array of sheets and finally made the formation of the aggregates of the plates.

Based on the experiments, it is found that CTAB plays an important role in the formation process of iron sheets. Therefore, we lay a strong emphasis on the effect of the concentration of CTAB on the morphologies of the products in Fig. 4. The SEM images in Fig. 4 indicates that at the lower concentration of CTAB than 2.0 g L^{-1} only particles are fabricated (Fig. 4a) and the higher concentration of CTAB than 4 g L^{-1} can effectively promote the formation of iron sheets (Fig. 1c). Also the size of iron sheets with the unchanged thickness gradually decreases with the increasing concentrations of CTAB. It is suggested that the affluent CTAB could effectively ensure the formation of iron sheets, but prevent the iron sheets from further growing in other directions.



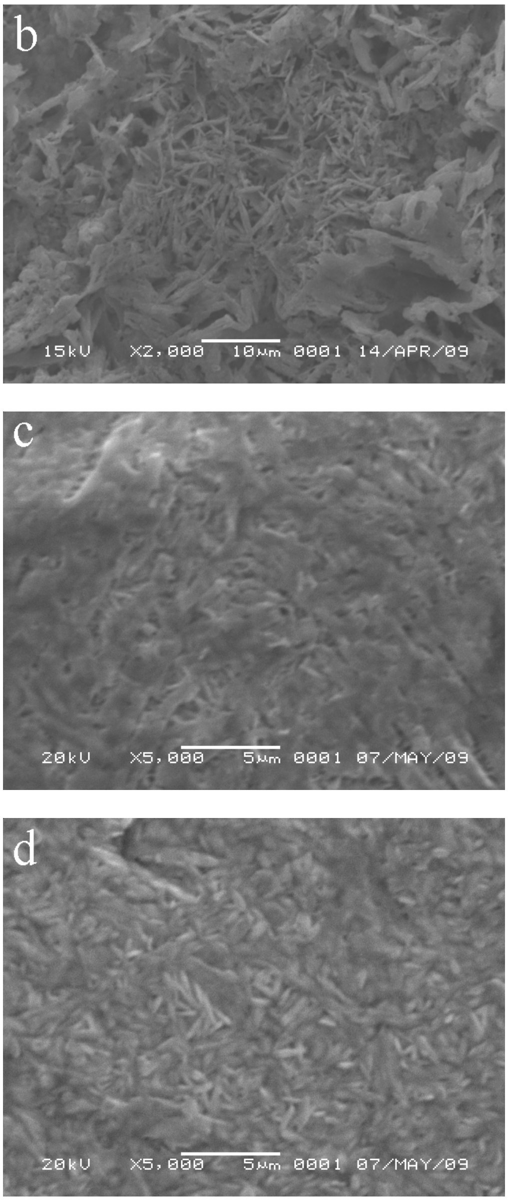


Fig. 4. SEM images of the products fabricated in the electric potential of 1.0 V for 10 min at the different concentrations of CTAB: (a) 2 g L^{-1}, (b) 8 g L^{-1}, (c) 12 g L^{-1} and (d) 20 g L^{-1}

In addition, the electric potential also plays an important role in the formation of the sheet-like iron (Fig. 5). The experimental results show that in the lower electric potential than 0.5 V the irregular lamellae pile up on the foil and increase in thickness and decreased in size with the increasing electric potential (Fig. 5a-b). When the electric potential is higher than 1.0 V, the sheet-like iron with the unchanged thickness perpendicularly grows up on the foil and becomes more dense with the increasing electric potential (Fig. 5c-d). It is indicated that the high electric potential could contribute to the quick growth of iron sheets.

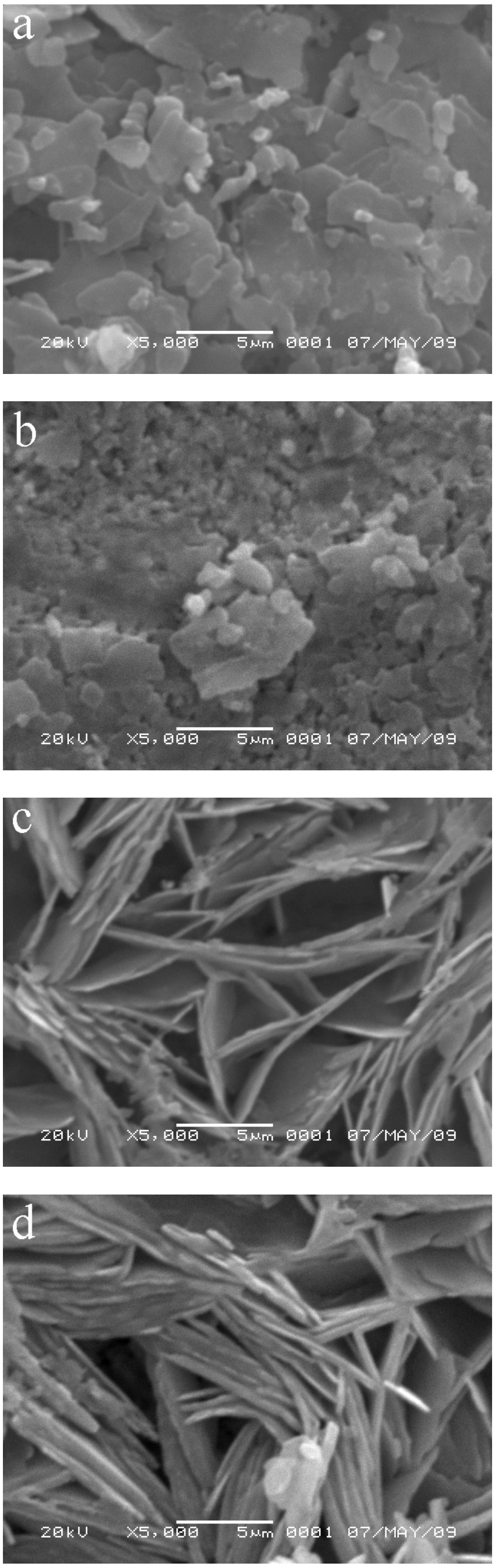


Fig. 5. SEM images of the products with CTAB at the different electric potentials for 10 min: (a) 0.1 V, (b) 0.5 V, (c) 1.5 V and (d) 2.0 V

Conclusion

The sheet-like iron has been successfully fabricated by the electrochemical deposition under the assistance of CTAB, reported here for the first time. The effects of the experimental parameters on the formation of iron sheets assisted by CTAB were studied by SEM analysis and the possible formation mechanism was suggested. The experimental results showed that the addition of CTAB could not only attribute to the formation of sheet-like structures, but also effectively prevent iron from oxidizing. The electrochemical deposition method of metal iron array assembled by sheets is simple, novel and facile. The iron sheets with the uniform thickness could perpendicularly grow up and construct the iron array on the foil, which would attribute to potential applications in electronic, optical, mechanical, magnetic and catalytic fields.

ACKNOWLEDGEMENTS

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