Journal of Physics and Chemistry of Solids 72 (2011) 1397–1399

Contents lists available at SciVerse ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Facile synthesis of flower-like nickel nanocrystals and properties

DongEn Zhang [a,b,c,*], Wen Yang [a], MingYan Wang [a], XiaoBo Zhang [a], ShanZhong Li [a], GuiQuan Han [a], AiLing Ying [a], ZhiWei Tong [a,c,*]

[a] Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, People's Republic of China
[b] School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China
[c] SORST, Japan Science and Technology Agency (JST), Japan

ARTICLE INFO

Article history:
Received 11 February 2011
Received in revised form
21 July 2011
Accepted 2 August 2011
Available online 21 September 2011

Keywords:
A. Nanostructures
B. Crystal growth
D. Electrical properties
D. Magnetic properties

ABSTRACT

A solvo-hydrothermal synthesis approach for the preparation of a new type of flowerlike nickel nanostructure is reported. The as-synthesized flower-like nickel nanocrystallites were characterized by X-ray diffraction and scanning electron microscopy. The nickel flowers modified glassy carbon electrode can be prepared and used to detect methanol and ethanol in the solution. The results show that the nickel flowers give a very high activity for detecting the methanol and ethanol, which provide a new application of nickel flowers. Compared with that of bulk nickel, thus-prepared nickel flowers showed a much enhanced coercivity.

1. Introduction

Recently, nanostructured electrode materials have received extensive interest due to their potential use in electrode modification by enhancing the electrode conductivity, facilitating the electron transfer, and improving the analytical sensitivity and selectivity [1,2]. As a result of their strong structure-, size-, and shape dependent physical and chemical properties, it is generally understood that various nanomaterials modified electrodes have distinct electrochemical characteristics [3]. In the past few years, many investigations have been conducted on the nanomaterials modified electrode as chemical/biological sensors, such as platinum nanoparticle and carbon nanotube co modified electrode to be excellent sensors for H_2O_2 [4,5], gold nanoparticles modified electrode as arsenite analysis [6,7], etc. Hence, control over the dimension of the active electrode material is very important for manipulating its electrochemical behavior.

At the same time, three-dimensional (3D) nanomaterials are derived from low-dimensional nanowires, nanorods, and nanotubes have attracted increasing attention due to shape-dependent chemicophysical properties. In comparison to their low-dimensional counterparts, the hierarchical nanostructures exhibit not only high surface-to-volume ratios, but also excellent structural stabilities and spatial uniformity, which makes them strong candidates for wide applications in photonics, nanoelectronics, catalysts, biosensors, and so on [8]. The most promising and now extensively used method for achieving novel structures is self-assembly processes. Recently, much effort has been focused on the self-assembly of low dimensional building blocks into two- and three-dimensional (2D and 3D) hierarchical structures [9–15]. To date, many self assembly processes driven by chemical or physical principles have been developed for organizing curved structures, such as "dandelion" formations via a modified Kirkendall effect [16], triangular and Fibonacci number patterns driven by stress on core/shell microstructures [17], and colloidosomes formation using emulsion droplets as templates [18,19]. However, although major advances have been made in "building" the curved structures, developing facile and simple methods is still highly desired for fully understanding and exploiting the self-assembly process.

In this paper, metal nickel with 3D structure was successfully synthesized via solvo-hydrothermal route. It was found that the nickel flowers modified glassy carbon electrode can be prepared and used to detect methanol and ethanol in the solution. The results show that the nickel flowers give a very high activity for detecting the methanol and ethanol, which provide a new application of nickel flowers.

2. Experimental

In a typical experiment, $NiCl_2 \cdot 6H_2O \cdot$ (0.166 g) was dissolved in distilled water (25 mL) to give a green transparent solution. Then a heptane solution (6 mL) was added dropwise into the solution. Subsequently, $N_2H_4 \cdot H_2O$ (2.0 mL, 80 wt. %) containing

* Corresponding authors.
E-mail address: zdewxm@yahoo.com.cn (D. Zhang).

0022-3697/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2011.08.001

0.8 g NaOH (10 mL water) was added under continuous stirring. The mixture was stirred for 10 min and transferred into a Teflon-lined autoclave with a capacity of 50 mL. The autoclave was sealed, heated at 120 °C for 24 h, and then cooled naturally to room temperature. The resulting black powders were collected and washed, and finally dried in vacuum at 40 °C for 4 h.

The Ni/GC electrode was fabricated as follows: firstly, 1.0 mg Ni nanoparticles were dispersed into 4.0 mL doubly distilled water by 10 min ultrasonic agitation to give a homogeneous nano-Ni suspension. Then, the glassy carbon electrode (3 mm in diameter) was polished to a mirror-like surface with 1.0, 0.3, and 0.05 μm alumina slurry followed by rinsing thoroughly with doubly distilled water. The electrode was successively sonicated in ethanol and doubly distilled water, and allowed to dry with fluid stream of highly purified nitrogen gas at room temperature. Finally, the prepared GC electrode was coated with 2.5 μL of the Ni suspension and allowed to evaporate water under an infrared lamp. The freshly prepared Ni/GC electrode was rinsed twice with doubly distilled water; the Ni nanoparticle modified GC electrode was stored in air at room temperature after use.

3. Results and discussion

The phase and purity of the as-prepared product was determined by X-ray diffraction (XRD), as shown in Fig. 1. All the diffraction peaks could be indexed as face centered cubic (fcc) nickel (JCPDS 01–1260). No characteristic peaks due to the impurities of nickel oxides or hydroxides were detected, indicating that pure crystalline nickel was fabricated under such conditions.

Scanning electron microscopy (SEM) was used to examine the morphology and structure of the as-obtained product. Fig. 2a shows the low magnification image of the as-prepared sample, which indicates that the sample is composed of a large number of flower-like structures. The high magnification SEM image further reveals that the flower is made up of many thin flakes, the thickness of which is ca. 20 nm (shown in Fig. 2b). Sonication for 10 min did not break this nanostructure into discrete particles, indicating that the nanoflowers were actually integrated, and were not only aggregations of flake like particles.

The electrocatalytic properties of Ni nanoparticles to methanol and ethanol were studied using cyclic voltammograms, the scan rate is 100 mV/s. As shown in Fig. 3a, the oxidation peak potential of methanol is shifted to more negative potential and an obvious enhancement of anodic peak current is produced at the Ni flowers modified electrode. The same phenomenon was observed in the ethanol electrocatalysis experiment, as shown in Fig. 3b. It is well known that the increase of the redox peak current and the decrease of the over potential are typically indicative of an electrocatalytic reaction. So Ni nanoparticles material plays an important role in improving the electrochemical performance of the modified electrode.

Nickel is widely used as magnetic material, whose magnetic properties were greatly affected by the sample size, shape, crystallinity, etc. Fig. 4 gave the magnetic hysteresis loop of the resultant nickel flowers measured at 25 °C in an applied field of 10,000 Oe, showing a coercivity (Hc), saturation magnetism (Ms) and remnant magnetism (Mr) of ca. 198.1 Oe, 48.5 emu g^{-1} and of 14.9 emu g^{-1}, respectively. Relative to that of the bulk nickel (100 Oe, 55 emu g^{-1}, 2.7 emu g^{-1}), a much enhanced coercivtiy was shown, probably for its nanosized subunits [20]. But the coercivity value was lower than that of the one-dimensional (1D) nickel nanoneeds (264 Oe) with high anisotropy [21]. Such a decrease could be ascribed to its special 3D assembled structure, which has an integral crystallite possessing low anisotropy. When subjected to an external magnetic field, those isolated 1D nanocrystals could all be aligned in the same direction, while only one column of our flower could be arranged along the direction of the external magnetic field; thus a relatively lower Hc was exhibited [22].

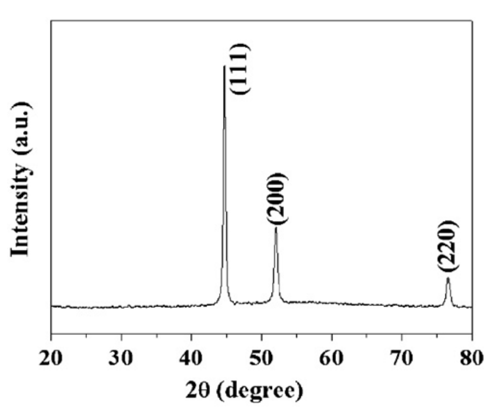

Fig. 1. XRD pattern of as-prepared nickel crystals.

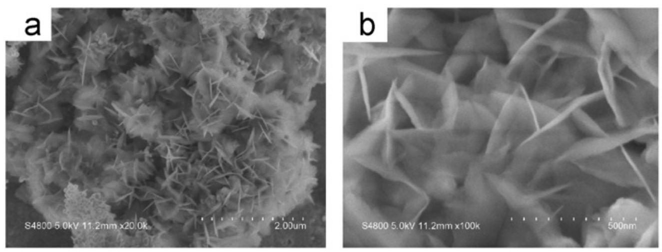

Fig. 2. SEM images of nickel flowers: (a) low-magnification and (b) high magnification.

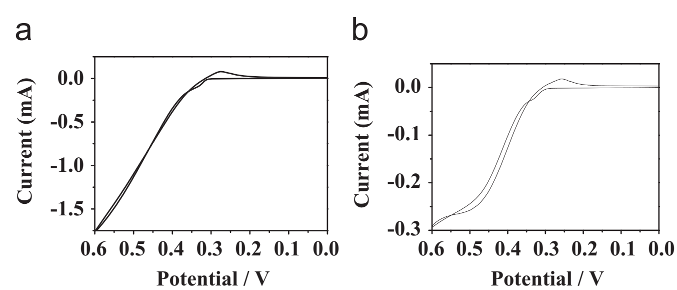

Fig. 3. Cyclic voltammograms of nickel flowers modified glassy carbon in NaOH: (a) with methanol and (b) with ethanol.

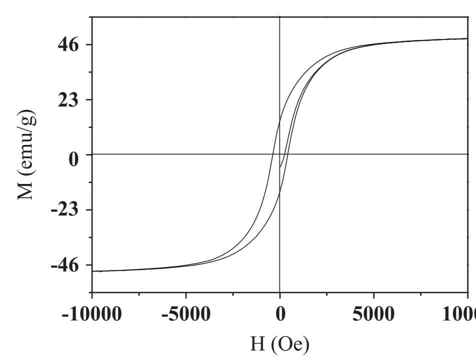

Fig. 4. Magnetic hysteresis loop of the resultant nickel flowers.

4. Conclusion

In summary, a novel new type of flower-shaped nickel nanostructure was prepared using a solvo-hydrothermal synthesis approach. It was found that the nickel flowers modified glassy carbon electrode can be prepared and used to detect methanol and ethanol in the solution. The results show that the nickel flowers give a very high activity for detecting the methanol and ethanol, which provide a new application of nickel flowers. As-prepared peculiar nickel flowers are expected to find applications in the fields of magnetism, catalysis, conduction, and other fields.

Acknowledgment

This work was supported by Grant-in-aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS), the CREST program of the Japan Science and Technology Agency (JST), the National Natural Science Foundation of China (50873042, 21001048), the Natural Science Foundation of Jiangsu Province (BK2009650, BK2009651), the High School Science Research Key Project of Jiangsu Province (11KJA430008), the High School Science Research Project of Jiangsu Province (no.11KJB150002) and “Qing Lan Project” of the universities and colleges in Jiangsu Province. We are also grateful to the electron microscope and X-ray diffraction facilities of University of Science and Technology of China for assistance in XRD and SEM measurement.

References

[1] J. Breen, P.R. Burch, H.M. Coleman, Appl. Catal., B 39 (2002) 65.
[2] F. Aupretre, C. Descorme, D. Duprez, Catal. Commun. 3 (2002) 267.
[3] S. Freni, S. Cavallaro, N. Mondello, L. Spadaro, F. Frusteri, Catal. Commun. 4 (2003) 259.
[4] F. Frusteri, S. Freni, L. Spadaro, V. Chiodo, G. Bonura, S. Donato, S. Cavallaro, Catal. Commun. 5 (2004) 611.
[5] V. Fierro, V. Klouz, O. Akdim, C. Mirodatos, Catal. Today 75 (2002) 141.
[6] F. Marino, G. Baronetti, M. Jobbagy, M. Laborde, Appl. Catal., A 238 (2003) 41.
[7] X.J. Zhang, G.F. Wang, X.W. Liu, H.Q. Wu, B. Fang, Cryst. Growth Des. 8 (2008) 1430.
[8] P.W. Li, N. Wang, R.M. Wang, Eur. J. Inorg. Chem. (2010) 2261.
[9] S. Park, J.H. Lim, S.W. Chung, C.A. Mirkin, Science 303 (2004) 348.
[10] J. Hu, Y. Bando, J. Zhan, D. Golberg, Adv. Mater. 17 (2005) 1964.
[11] X.J. Feng, J. Zhai, L. Jiang, Angew. Chem. Int. Ed. 44 (2005) 5115.
[12] S. Aggarwal, A.P. Monga, S.R. Perusse, R. Ramesh, V. Ballarotto, E.D. Williams, B.R. Chalamala, Y. Wei, R.H. Reuss, Science 287 (2000) 2235.
[13] P.D. Yang, Nature 425 (2003) 243.
[14] J. Schoiswohl, S. Surnev, M.G. Sock, M. Ramsey, G.P. Kresse, F. Netzer, Angew. Chem. Int. Ed. 43 (2004) 5546.
[15] M.H. Cao, T.F. Liu, S. Gao, G.B. Sun, X.L. Wu, C.W. Hu, Z.L. Wang, Angew. Chem. Int. Ed. 44 (2005) 4197.
[16] C.L. Yan, D.F. Xue, J. Phys. Chem. B. 110 (2006) 7102.
[17] C.R. Li, X.N. Zhang, Z.X. Cao, Science 309 (2005) 909.
[18] A.D. Dinsmore, M.F. Hsu, M.G. Nikolaides, M. Marquez, A.R. Bausch, D.A. Weitz1, Science 298 (2002) 1006.
[19] M.H. Cao, X.Y. He, Hu C.W. Chen., Cryst. Growth Des. 7 (2007) 171.
[20] K.V.P.M. Shaf, A. Gedanken, R. Prozorov, J. Balogh, Chem. Mater. 10 (1998) 3445.
[21] D.E. Zhang, X.M. Ni, H.G. Zheng, Y. Li, X.J. Zhang, Z.P. Yang, Mater. Let 59 (2005) 2011.
[22] X.M. Ni, Q.B. Zhao, D.E. Zhang, X.J. Zhang, H.G. Zheng, J. Phys. Chem. C 111 (2007) 601.