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One-pot hydrothermal synthesis of MoS_2 nanosheets/C hybrid microspheres

Lin Ma [a,c,*], Wei-Xiang Chen [b], Li-Mei Xu [a,c], Xiao-Ping Zhou [a,c], Bei Jin [a,c]

[a] Chemistry Science and Technology School, Zhanjiang Normal University, Zhanjiang 524048, PR China
[b] Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China
[c] Development Center for New Materials Engineering & Technology in Universities of Guangdong, Zhanjiang 524048, PR China

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Abstract

Uniform MoS_2 nanosheets/C hybrid microspheres with mean diameter of 320 nm have been successfully synthesized via a facile one-pot hydrothermal route by sodium molybdate reacting with sulfocarbamide in D-glucose solutions. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). XRD patterns showed that the MoS_2 was kept as a two-dimensional nanosheet crystal and C was retained as amorphous even after their annealing treatment at 800 °C. TEM and SEM images indicated that the MoS_2 nanosheets were uniformly dispersed in the amorphous carbon. The experiment results also revealed that the appropriate amount of D-glucose had an obvious effect on the formation of uniform MoS_2 nanosheets/C hybrid microspheres. A possible formation process of MoS_2 nanosheets/C hybrid microspheres was preliminarily presented.

Keywords: A. Powders: chemical preparation; B. Nanocomposites; D. Carbon

1. Introduction

As one of the members of the transition metal sulfides (TMS), MoS_2 has a sandwich structure which consists of covalently bound S–Mo–S trilayers separated by a relatively large van der Waals gap [1]. Due to the distinctive layer structure and electronic properties, MoS_2 attracted considerable attention and has numerous applications as indispensable industrial catalysts for hydrodesulfurization of crude oil [2], potential hydrogen storage media [3], electrode materials for Li ion and Mg ion batteries [4,5] and solid superlubricants in high temperature and vacuum environments [6–9]. The weak interlayer interactions of MoS_2 also allow foreign atoms or molecules to be introduced between the layers through intercalation. Thus MoS_2 could be developed as an intercalation host to form new materials [10]. For example, the electrochemical intercalation of Li^+ into the MoS_2 and the electrochemical performance of MoS_2 for Li-ion batteries have been investigated, and the results showed that the particle size and morphology of materials have a great influence on their electrochemical properties [5,11,12].

Specific structural characteristics may correspond to distinct performance specialties. Due to the layered structures and novel properties of carbon nanomaterials such as carbon fullerenes [13] and carbon nanotubes [14], from this point, one would expect that the composite functional nanomaterials by combination of MoS_2 and carbon materials could bring unexpected novel properties and thus enable the materials to meet more of the needs of technology. We previously reported a mild hydrothermal method to successfully coated MoS_2 layers onto carbon nanotubes [15]. Wang and Li prepared MoS_2 overlayers supported on coaxial carbon nanotubes and found that this unique nanoarchitecture demonstrated highly reversible capacity (approaching 400 mAh/g) and excellent cyclability [16].

Carbonaceous materials could be prepared from saccharide starting materials by dehydration under hydrothermal conditions [17] and had been applied in Li-ion batteries electrode materials such as $LiFePO_4$/C, SnO_2@C and NiO–C because the carbonaceous materials not only had good lithium ion and electronic conductivity, but also could serve as a buffer and partly alleviate mechanical stress caused by the volume change

* Corresponding author at: Chemistry Science and Technology School, Zhanjiang Normal University, Zhanjiang 524048, PR China.
Tel.: +86 759 3183205; fax: +86 759 3183510.
E-mail address: ml_buct@126.com (L. Ma).

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of active phase during charge/discharge process [18–21]. In this paper, we report a facile one-pot hydrothermal route to prepare MoS_2 nanosheets/C hybrid microspheres with D-glucose as carbon precursors. The products were characterized by XRD, SEM and EDX. Our experiments showed that the as-prepared MoS_2 nanosheets/C hybrid microspheres had a uniform size with mean diameter of 320 nm and consisted of two-dimensional MoS_2 nanosheet crystals uniformly dispersed in the amorphous carbon even after their calcinations at 800 °C. The experiment results also revealed that this one-pot hydrothermal method and the appropriate D-glucose amount had an obvious effect on the formation of uniform MoS_2 nanosheets/C hybrid microspheres. A possible formation mechanism of MoS_2 nanosheets/C hybrid microspheres under hydrothermal conditions was preliminarily presented.

2. Experimental procedure

2.1. One-pot synthesis of MoS_2 nanosheets/C hybrid microspheres

All chemical reagents used in this experiment were analytical grade. The detailed synthesis procedures will be described in the following. Sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$, 0.3 g) and sulfocarbamide (NH_2CSNH_2, 0.4 g) were dissolved in 60 ml deionized water, then 3.3 g of D-glucose was added into the solution and stirred for 20 min. The resulting solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and sealed tightly. Hydrothermal reactions were carried out at 240 °C for 24 h. After that, the autoclave was allowed to cool down naturally. The black precipitates were collected, and washed with deionized water and absolute ethanol for at least three times. Finally, the product was dried in a vacuum at 60 °C for 6 h.

2.2. Calcination treatment of MoS_2 nanosheets/C hybrid microspheres

Calcination treatment of the as-synthesized MoS_2 nanosheets/C samples was carried out in a conventional tube furnace at 800 °C for 2 h with the nitrogen flow rate of about 200 sccm and the hydrogen flow rate of about 20 sccm (standard cubic centimeter per minute). Before the samples were heated, the tube was evacuated and purged to ensure the gas in the tube was normally pure nitrogen.

2.3. Characterization of MoS_2 nanosheets/C hybrid microspheres

X-ray diffraction (XRD) analysis was performed on a D/Max-2550 X-ray diffractometer with monochromatized CuKα radiation (λ = 0.1540562 nm). TEM was recorded on a transmission electron microscopy (TEM, JEOL JEM-200CX). Samples for TEM were obtained by dispersing the products in ethanol with 15 min ultrasonicating, and then dropping a few drops of the resulted suspension onto a copper grid precoated with amorphous carbon and allowing them to dry naturally. Scanning electron microscopy (SEM) images were taken with FEI SIRION-100 field-emission scanning electron microscope and the energy dispersive X-ray analysis (EDX) was carried out on the SEM equipped with energy-dispersive spectrometer (GENENIS-4000). The electronic conductivities of the samples were measured by a four-electrode method.

3. Results and discussion

The crystal structure and phase purity of the samples have been characterized by XRD. Fig. 1A shows the XRD patterns of the MoS_2 products prepared by hydrothermal route without D-glucose, which can be readily indexed to the hexagonal phase of MoS_2 consistent with the standard powder diffraction file of MoS_2 (JCPDS 37-1492). Fig. 1B shows the XRD patterns of the MoS_2 nanosheets/C composites obtained via one-pot hydrothermal route by adding 3.3 g D-glucose. It can be seen that only two unconspicuous XRD peaks at $2\theta = 32.9^\circ$ and 58.3° are found, which are attributed to (1 0 0) and (1 1 0) planes of MoS_2 (JCPDS 37-1492). However, the diffraction peak of (0 0 2) plane of MoS_2 is not detected. The absence of (0 0 2) reflection of MoS_2 indicates that the stacking of the single layers did not take place [22]. The fact indicates that MoS_2 is a two-dimensional nanosheet crystal [23,24]. In addition, there are no obvious diffraction peaks attributed to carbon in Fig. 1B, which could indicate that the carbonaceous material produced by hydrothermal carbonization of D-glucose was colloidal [25]. Fig. 1C shows the XRD patterns of the MoS_2 nanosheets/C composites obtained from the annealing treatment at 800 °C for 2 h in the atmosphere of nitrogen and hydrogen. It can be seen that the intensities of the diffraction peaks of MoS_2 have been improved to a certain extent after annealing treatment. It is worth noticing that the appearance of a broadened diffraction peak at $2\theta = 25.1^\circ$ is attributed to the (0 0 2) plane of graphite (JCPDS 75-1621). The fact indicates that the carbonaceous material is amorphous in the annealed MoS_2 nanosheets/C composites. Further EDX analysis reveals that the annealed MoS_2 nanosheets/C composites consist of C, Mo, S and a small

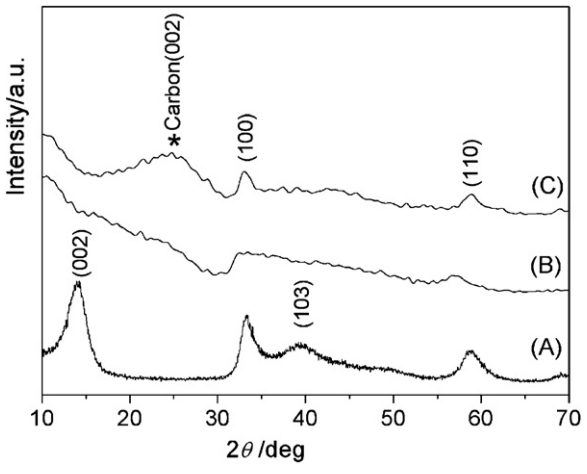

Fig. 1. XRD patterns of (A) MoS_2; (B) MoS_2 nanosheets/C samples prepared by hydrothermal route and (C) annealed MoS_2 nanosheets/C sample at 800 °C.

number of O. The content of carbon is 60.2 wt.% for the annealed MoS_2 nanosheets/C composites prepared by adding 3.3 g D-glucose. EDX analysis also confirms that the atomic ratios of Mo:S are 1:1.9–1:2.0, which agreed with the element composition of MoS_2.

The sizes and structures of the MoS_2 nanosheets/C samples were examined by TEM and SEM techniques. Fig. 2A shows the typical TEM image of the unannealed MoS_2 nanosheets/C samples, from which it can be seen that the as-prepared MoS_2 nanosheets/C samples have uniform spherical morphologies with mean diameter of 320 nm and the surfaces of each microsphere are covered with many nanosheets. A TEM image with the higher magnification is shown in Fig. 2B, which offers a clearer view of the surface structure of each microsphere. Fig. 2B reveals that many curled nanosheets are uniformly dispersed on the surfaces of the microspheres and stretched out towards the edges. Fig. 2C shows the typical SEM image of the MoS_2 nanosheets/C samples, from which it can be seen that the as-prepared products are actually uniform microsphere and the yield of the MoS_2 nanosheets/C composite microspheres is close to 100%. Moreover, these microspheres are not completely separate from each other but often coupled together. Fig. 2D (inset of Fig. 2C) clearly displays the surface structure of the single microsphere, which shows that many interlaced nanosheets growing in all directions appear on the surface of the microsphere. The SEM results agree well with the TEM observation. Fig. 2E displays the morphologies of the annealed MoS_2 nanosheets/C composite microspheres. It is noted that the annealed MoS_2 nanosheets/C products basically remained their fathers' morphologies, which indicated that these MoS_2 nanosheets/C products were stable and they did not be broken even after high temperature annealing treatment.

Parallel experiments were carried out to investigate the effects of the amount of D-glucose on the structures of the MoS_2 nanosheets/C samples. Fig. 3 shows the SEM image of the MoS_2 nanosheets/C samples prepared by one-pot hydrothermal process under the same conditions with different amounts of D-glucose. When 0.5 g of D-glucose was used, the obtained hydrothermal products were particles with irregular sizes and morphologies (Fig. 3A). With the amount of D-glucose increasing from 1.0 g to 2.0 g, the spherical shapes of the MoS_2 nanosheets/C samples gradually became clear and the sizes became larger (Fig. 3B and C). If excessive amount of D-glucose was used (e.g., 6.0 g), it was found that the obtained MoS_2 nanosheets/C microspheres had less uniform morphologies and at the same time some naked carbon spheres appeared (Fig. 3D). The experimental results indicate that appropriate amount of D-glucose has an important effect on the formation of uniform MoS_2 nanosheets/C composite microspheres.

Another two control experiments were implemented to further investigate the influence of D-glucose on the formation of MoS_2 nanosheets/C hybrid microspheres in the hydrothermal conditions. When no D-glucose was added to the reaction system, we could only obtain irregular MoS_2 nanosheets (Fig. 4A). This result further confirms that the nanosheets dispersed on the surfaces of the as-prepared MoS_2 nanosheets/C hybrid microspheres are MoS_2. To compare with one-pot hydrothermal synthetic route, we tried to adopt another hydrothermal approach called two-pot hydrothermal method to prepare MoS_2 nanosheets/C hybrid microspheres. The two-pot method is described as follows. First, carbonaceous

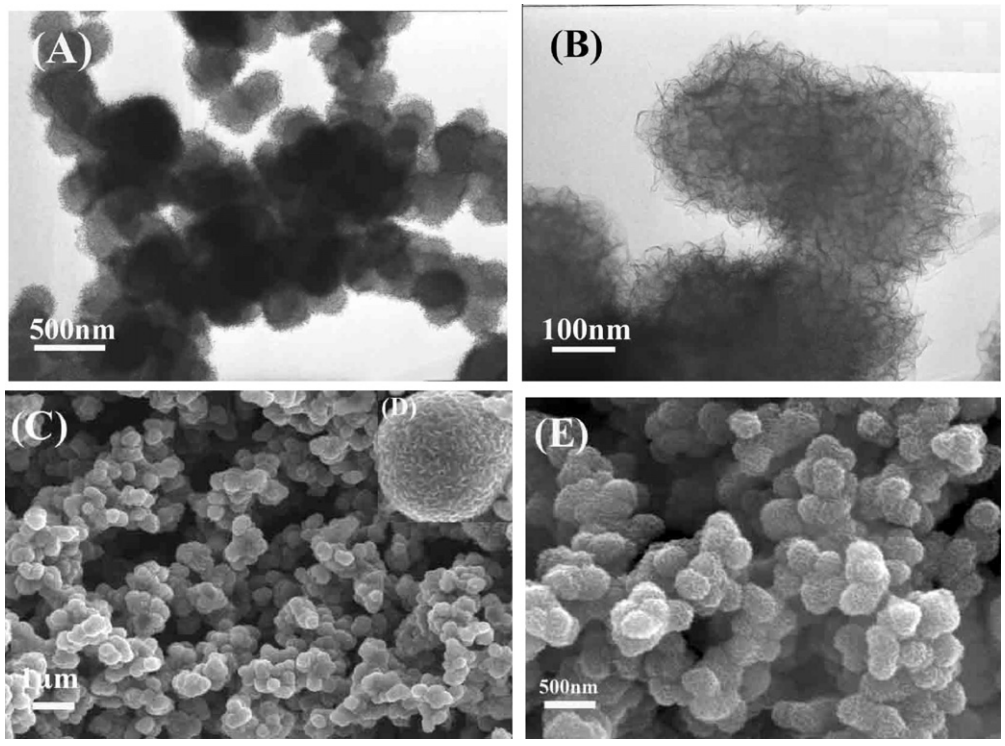

Fig. 2. TEM and SEM images of as-prepared MoS_2 nanosheets/C samples by adding 3.3 g D-glucose. (A)–(D) before and (E) after annealing treatment.

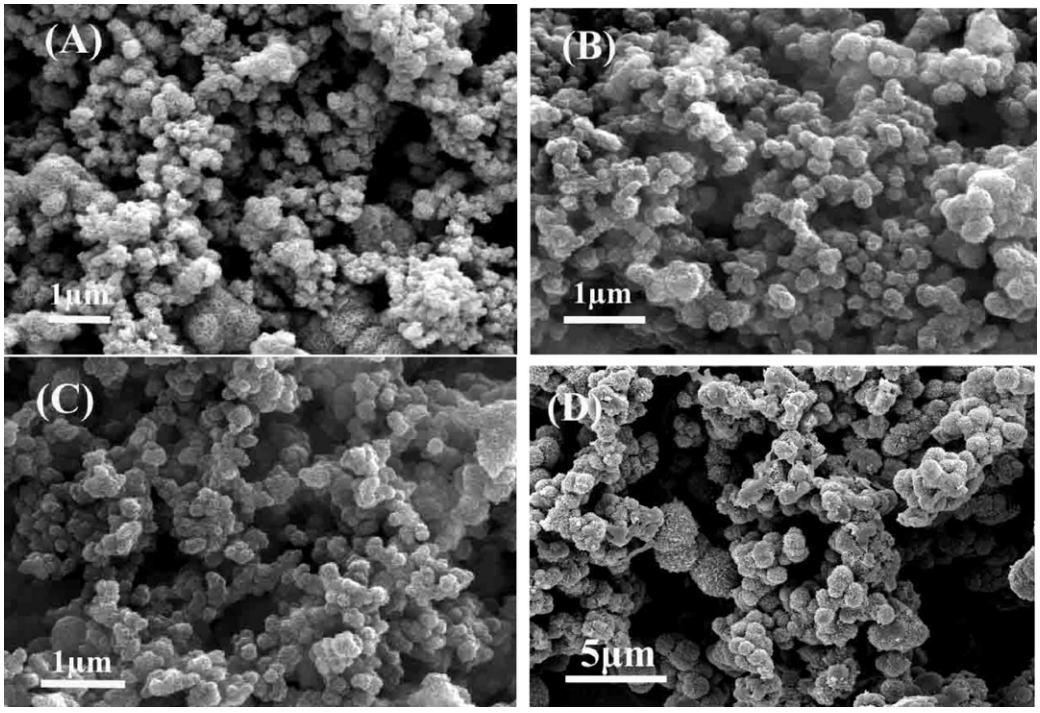

Fig. 3. SEM images of as-prepared MoS_2 nanosheets/C samples by adding different amounts of D-glucoses. (A) 0.5 g; (B) 1 g; (C) 2 g and (D) 6 g.

microspheres were synthesized in hydrothermal condition by use of D-glucose according to previous report [25]. Second, appropriate amount of the as-prepared carbonaceous microspheres were uniformly dispersed in the solution including sodium molybdate and sulfocarbamide and reacted in the same hydrothermal condition. The morphology of the obtained products is shown in Fig. 4B. It can be seen that there are many naked microspheres with smooth surfaces, which should be the carbonaceous microspheres produced by dehydration of glucose under hydrothermal conditions in the first step [25]. Simultaneously, it was found that some irregular MoS_2 nanosheets produced in the second step incompletely clung to surfaces of the carbonaceous microspheres. The experimental result indicates that the carbonaceous microspheres and MoS_2 nanosheets could not effectively form uniform MoS_2 nanosheets/C hybrid microspheres via the two-pot hydrothermal method.

Based on our experimental results, the possible formation process of the MoS_2 nanosheets/C hybrid microspheres under one-pot hydrothermal conditions could be explained as follows. On one hand, MoS_2 nanosheets could be produced by hydrothermal reaction between Na_2MoO_4 and NH_2CSNH_2. On the other hand, the chemical reactions of the glucose under hydrothermal conditions were rather complex and generally included polymerization and carbonization process according to Li's report [25]. Firstly, glucose could be dehydrated and polymerized to form oligosaccharides under hydrothermal conditions [25]. It was previously reported that polymers could be inserted in the van der Waals interlaminar spaces of MoS_2 matrix [26,27]. It was speculated that a number of oligosaccharide molecules might insert into the interlaminar spaces of MoS_2 during hydrothermal process. Secondly, the oligosaccharides were further involved in intermolecular dehydration, cross-linking and carbonization to form colloidal carbonaceous

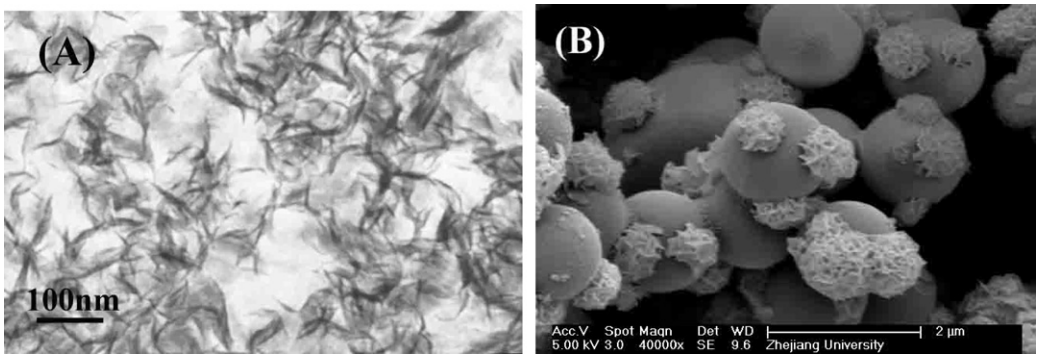

Fig. 4. (A) TEM image of as-prepared MoS_2 samples prepared by hydrothermal route without D-glucose and (B) SEM image of as-prepared MoS_2/C samples via a two-pot hydrothermal method.

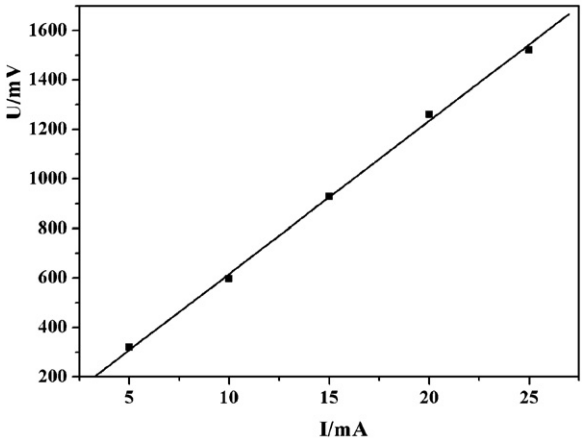

Fig. 5. Voltage–current test plot of the MoS_2/C samples prepared by adding 3.3 g glucose in the hydrothermal reaction and annealing at 800 °C for 2 h.

spheres [25]. The MoS_2 nanosheets could be well dispersed in the network of the colloidal carbonaceous materials in the course of carbonization to form MoS_2 nanosheets/colloid C hybrid microspheres. The carbonaceous materials in the composites might prevent the MoS_2 layers from stacking. The colloidal carbonaceous materials in the MoS_2 nanosheets/C samples would be further carbonized after their calcination at 800 °C, and retain the amorphous structures because the calcination temperature is much lower than graphitizing temperature (about 3000 °C). Therefore, the MoS_2 was a 2D nanosheet crystal and carbon was amorphous after their calcination. The precise mechanism still needs to be further explored.

The electrical conductivity of MoS_2/C composite annealed at 800 °C was also initially investigated by voltage–current test as shown in Fig. 5. The electronic conductivity of the annealed MoS_2/C samples was calculated to be approximately 4.60×10^{-1} S/cm larger than that of MoS_2 (about 3.30×10^{-5} S/cm). The reason of the improvement of the electronic conductivity of the composite is that the amorphous carbon structures could offer the electronic transport channels in the composites.

4. Conclusions

In summary, uniform MoS_2 nanosheets/C hybrid microspheres with mean diameter of 320 nm have been successfully synthesized via a facile one-pot hydrothermal route. Our experimental results indicate that the MoS_2 was a two-dimensional nanosheet crystal and C was amorphous even after their calcinations at 800 °C. TEM and SEM images showed that the MoS_2 was highly dispersed in the amorphous carbon. It is pointed out that the amount of D-glucose and the use of the one-pot hydrothermal method have a significant effect on the formation of uniform MoS_2 nanosheets/C hybrid microspheres. The possible formation process has been initially investigated. Amorphous carbon adding improves the electronic conductivity of MoS_2. The as-prepared MoS_2 nanosheets/C hybrid microspheres might have a potential application in electrode materials for Li ion batteries and super solid lubricants.

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References

[1] R. Tenne, Doped and heteroatom-containing fullerene-like structures and nanotubes, Adv. Mater. 7 (12) (1995) 965–995.
[2] P.T. Asudevan, J.L.G. Fierro, A review of deep hydrodesulfurization catalysis, Catal. Rev. 38 (1996) 161–188.
[3] J. Chen, N. Kuriyama, H.T. Yuan, H.T. Takeshita, T. Sakai, Electrochemical hydrogen storage in MoS_2 nanotubes, J. Am. Chem. Soc. 123 (2001) 11813–11814.
[4] X.L. Li, Y.D. Li, MoS_2 nanostructures: synthesis and electrochemical Mg^{2+} intercalation, J. Phys. Chem. B 108 (2004) 13893–13900.
[5] R. Dominko, D. Arcon, A. Mrzel, A. Zorko, P. Cevc, P. Venturini, M. Gaberscek, M. Remakarand, D. Mihailovic, Dichalcogenide nanotube electrodes for Li-ion batteries, Adv. Mater. 14 (21) (2002) 1531–1534.
[6] L. Rapoport, Y. Bilik, Y. Feldman, M. Homyonfer, S.R. Cohen, R. Tenne, Hollow nanoparticles of WS_2 as potential solid-state lubricants, Nature 387 (1997) 791–793.
[7] M. Chhowalla, G.A.J. Amaratunga, Thin films of fullerene-like MoS_2 nanoparticles with ultra-low friction and wear, Nature 407 (2000) 164–167.
[8] L. Rapoport, M. Lvovsky, I. Lapsker, W. Leshchinsky, Y. Volovik, Y. Feldman, R. Tenne, Friction and wear of bronze powder composites including fullerene-like WS_2 nanoparticles, Wear 249 (2001) 149–156.
[9] W.X. Chen, J.P. Tu, Z.D. Xu, R. Tenne, R. Rosenstveig, W.L. Chen, H.Y. Gan, Wear and friction of Ni–P electroless composite coating including inorganic fullerene–WS_2 nanoparticles, Adv. Eng. Mater. 4 (9) (2002) 686–690.
[10] W.M.R. Divigalpitiya, R.F. Frindt, S.R. Morrison, Inclusion systems of organic molecules in restacked single-layer molybdenum disulfide, Science 246 (1989) 369–371.
[11] G.X. Wang, S. Bewlay, J. Yao, H.K. Liu, S.X. Dou, Tungsten disulfide nanotubes for lithium storage, Electrochem. Solid-State Lett. 7 (2004) A321–A323.
[12] C.Q. Feng, J. Ma, H. Li, R. Zeng, Z.P. Guo, H.K. Liu, Synthesis of molybdenum disulfide (MoS_2) for lithium ion battery applications, Mater. Res. Bull. 44 (2009) 1811–1815.
[13] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, C60: Buckminsterfullerene, Nature 318 (1985) 162–163.
[14] S. Iijima, Helical microtubules of graphitic carbon, Nature 354 (1991) 56–58.
[15] L. Ma, W.X. Chen, Z.D. Xu, J.B. Xia, X. Li, Carbon nanotubes coated with tubular MoS_2 layers prepared by hydrothermal reaction, Nanotechnology 17 (2006) 571–574.
[16] Q. Wang, J.H. Li, Facilitated lithium storage in MoS_2 overlayers supported on coaxial carbon nanotubes, J. Phys. Chem. C 111 (2007) 1675–1682.
[17] X.M. Sun, J.F. Liu, Y.D. Li, Oxides@C core–shell nanostructures: one-pot synthesis, rational conversion, and Li storage property, Chem. Mater. 18 (2006) 3486–3494.
[18] A. Vadivel Murugan, T. Muraliganth, A. Manthiram, One-pot microwave-hydrothermal synthesis and characterization of carbon-coated $LiMPO_4$ (M = Mn, Fe, and Co) cathodes, J. Electrochem. Soc. 156 (2009) A79–A83.
[19] R. Yang, W. Zhao, J. Zheng, X.Z. Zhang, X.G. Li, One-step synthesis of carbon-coated tin dioxide nanoparticles for high lithium storage, J. Phys. Chem. C 114 (2010) 20272–20276.

[20] X.H. Huang, J.P. Tu, C.Q. Zhang, X.T. Chen, Y.F. Yuan, H.M. Wu, Spherical NiO–C composite for anode material of lithium ion batteries, Electrochim. Acta 52 (2007) 4177–4181.
[21] J. Hassoun, S. Panero, P. Simon, P.L. Taberna, B. Scrosati, High-rate, long-life Ni–Sn nanostructured electrodes for lithium-ion batteries, Adv. Mater. 19 (12) (2007) 1632–1635.
[22] K.S. Liang, R.R. Chianelli, F.Z. Chien, S.C. Moss, Structure of poorly crystalline MoS_2 – a modeling study, J. Non-Cryst. Solids 79 (1986) 251–273.
[23] J.W. Seo, Y.W. Jun, S.W. Park, H. Nah, T. Moon, B. Park, Two-dimensional nanosheet crystals, Angew. Chem. Int. Ed. 46 (46) (2007) 8828–8831.
[24] R.A. Gordon, D. Yang, E.D. Crozier, D.T. Jiang, R.E. Frindt, Structures of exfoliated single layers of WS_2, MoS_2, and $MoSe_2$ in aqueous suspension, Phys. Rev. B 65 (2002) 125407–125415.
[25] X.M. Sun, Y.D. Li, Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles, Angew. Chem. 116 (2004) 607–611.
[26] E. Benavente, M.A. Santa Ana, F. Mendizábal, G. González, Intercalation chemistry of molybdenum disulfide, Coord. Chem. Rev. 224 (2002) 87–109.
[27] R. Bissessur, D. Gallant, R. Brüning, Novel nanocomposite material consisting of poly[oxymethylene-(oxyethylene)] and molybdenum disulfide, Mater. Chem. Phys. 82 (2003) 316–320.