Chalcogenide Letters Vol. 12, No. 12, December 2015, p. 645 - 651

TRIBOLOGICAL BEHAVIORS OF ZnSe NANOPLATES AS LUBRICANT ADDITIVE

X. H. ZHANG[a], M. Q. XUE[b*], Z. D. HUANG[b], Z. P. WANG[b], F. YANG [b]
[a]*School of Mechanical Engineering, Jiangsu University of Technology, Changzhou, Jiangsu Province, 213001, P. R. China*
[b]*Changzhou Vocational Institute of Light Industry, Changzhou, Jiangsu Province,213164, P.R.China*

The ZnSe nanoplates were synthesized by a facile and effective hydrothermal method. The morphology and structure of the ZnSe nanoplates were characterized by powder X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results indicated that ZnSe nanoplates with diameters of 200-300 nm and average thickness of 100 nm. The performance of the ZnSe nanoplates as a base oil additive was investigated by employing a UMT-2 ball-on-disc tribotester. Under the determinate conditions, the friction coefficient of the base oil containing 1.5wt% ZnSe nanoplates was lower than that of the base oil. The improved tribological properties of ZnSe as additives could be attributed to the stable tribofilm on the rubbing surface.

(Received October 10, 2015; Accepted December 3, 2015)

Keywords: ZnSe; Nanoplates; Hydrothermal; Tribological behaviors; Tribofilm

1. Introduction

Over the last several decades, many investigations on metal chalcogenides have been conducted due to both their significance in theoretical research and their many potential applications in energy conversion and storage[1-2], electronics and optoelectronics [3-4], tribology [5-6] , surface protection[7], spectroscopy[8], oxygen reduction[9-10], photovoltaics[11-12] and catalysis fields [13-14].

To date, many different strategies including chemical vapor deposition [15], solution-based method [16], two-sourced evaporation [17], pulsed-laser deposition [18], vapor phase growth [19], molecular-beam epitaxy[20-21], solution-phase growth [22-23], atomic-layer deposition[24-25], hydrothermal or solvothermal methods[26-28], and so on have been adopted for preparing metal chalcogenides. As compared to the other methods, hydrothermal or solvothermal methods provide several distinct advantages: it can induce the formation of well crystallized products with mild synthetic conditions and simple manipulation, also it can control the phase, shape and size of the resultant products simply through adjusting the synthesis conditions such as composition of the solution, pH, temperature, duration, etc.

Zinc selenide (ZnSe), as an important metal selenide [29-31], in recent years, has garnered a respectable interest for its unusual combination properties and extensive applications in sensors[32-33],optical fibers [34],photoelectrochemical cell[35], photoluminescence devices [17], photocatalysis[36], lithium ion batteries [37-38], photodetector [39-40] and so forth. Therefore, it is extraordinarily important to synthesise ZnSe with well-controlled dimensionality, size, morphology, and crystal structure for industrial and high technology applications.

Nanoplates materials have been regarded as fascinating nanomaterials in the field of lithium storage [41,42], biosensing [43], supercapacitors [44], anode material [45,46] and so on. However, ZnSe nanoplates have rarely been reported, therefore, it is still a great challenge to develop a facile and effective process to fabricate ZnSe nanoplates. In addition, to the best of our knowledge, little work focused on the tribological properties of ZnSe as lubrication additive.

[*]Corresponding author: xuemaoq@163.com

In this work, the ZnSe nanoplates were successfully prepared by hydrothermal reaction Zinc acetate dihydrate, Polyvinyl pyrrolidone (PVP) and Se powder in ethylene glycol under mild conditions. The tribological properties of ZnSe nanoplates as additives in the 100SN base oil were also investigated. This study provides a simple and novel route for the hydrothermal preparation of ZnSe and will be useful for ZnSe practical application in the future.

2. Experimental

2.1 Synthesis of ZnSe nanoplates:

All chemical reagents were of analytic purity and applied directly without further purification. First, Zinc acetate dihydrate $C_4H_6O_4Zn\cdot 2H_2O$ (1.865 g), Polyvinyl pyrrolidone (PVP) (10 g), Se powder (0.671 g) were dissolved in 68 ml ethylene glycol under constant stirring. The final solution was transferred into a 100ml Teflon-lined stainless steel autoclave, which was sealed and treated at 200 °C for 48 h and cooled down to room temperature naturally. The resulting suspension were washed several times with distilled water and absolute ethanol, and dried in air at 70 °C for 12 h.

2.2 Characterisation of ZnSe samples:

The phase and crystallinity of the as-synthesized products were characterized by X-ray diffraction with a D8 advance (Bruker-AXS) diffractometer employing CuKα radiation operated at 40Kv and 20mA, data analysis with Jade software. The composition was characterised by energy-dispersive spectroscopy (EDS). The morphologies and structures of the samples were investigated by scanning electron microscopy (SEM, JEOL JSM-7001F) equipped with single crystal W cathode, and transmission electron microscope (TEM, JEOL JEM-2100) equipped with LaB_6 cathode using an accelerating voltage of 200 kV. The samples for the SEM and EDS studies were prepared by placing the ZnSe powders on to a copper disk with conducting resin followed by metal spraying. The samples for the TEM studies were prepared by dispersing the powders in ethanol through ultra-sonication and drop casting the dispersion onto a carbon coated copper grid.

2.3. Tribological behaviors of ZnSe nanoplates as a lubrication additive:

The as-prepared ZnSe nanoplates were distributed into the 100SN base oil via 60 min ultrasonication without any active reagent. The friction and antiwear properties of the oil with ZnSe samples were examined on a UMT-2 ball-on-disc friction and wear tester at ambient conditions. The testing of the friction reduction and wear resistance was conducted at a slidinging speed of 0.167m/s and a load of 10–30 N for 800 s. The material of the upper sample was a 440C stainless-steel ball with a diameter of 10 mm, a hardness of 62 HRC and the counterpart is a 45 steel disc of Ø30 mm × 5 mm in size. The friction coefficient was recorded automatically and the wear scars widths were measured by a conventional optical microscope. Morphologies of wear scars were examined using a JSM-5600LV scanning electron microscope (SEM). The elements of the friction surface were analyzed using energy-dispersive X-ray spectroscopy (EDS).

3. Results and discussion

3.1. Characterization of ZnSe nanoplates:

The crystallinity, structure, and phase purity of the prepared samples were confirmed by XRD and EDS. Fig. 1(a) shows the XRD pattern of the ZnSe sample fabricated by the hydrothermal reaction $C_4H_6O_4Zn\cdot 2H_2O$, PVP and Se powder in ethylene glycol at 200 °C for 48 h. All peaks in the XRD pattern can be readily indexed to the hexagonal ($P6_3/mmc$ space group) ZnSe phase, with lattice constants a=3.996Å, c=6.550Å, which are in good agreement with the reported values (JCPDS card no.15-0105). No characteristic peaks from other impurities are observed in the XRD pattern, indicating the high purity of the ZnSe samples. The XRD peaks are a little broad and this suggests that the as-prepared products are somewhat amorphous during the hydrothermal process. Energy-dispersive X-ray spectrometer (EDS) result as shown in Fig. 1(b) reveals that the sample consisted of element Zn and Se, no other element is observed.

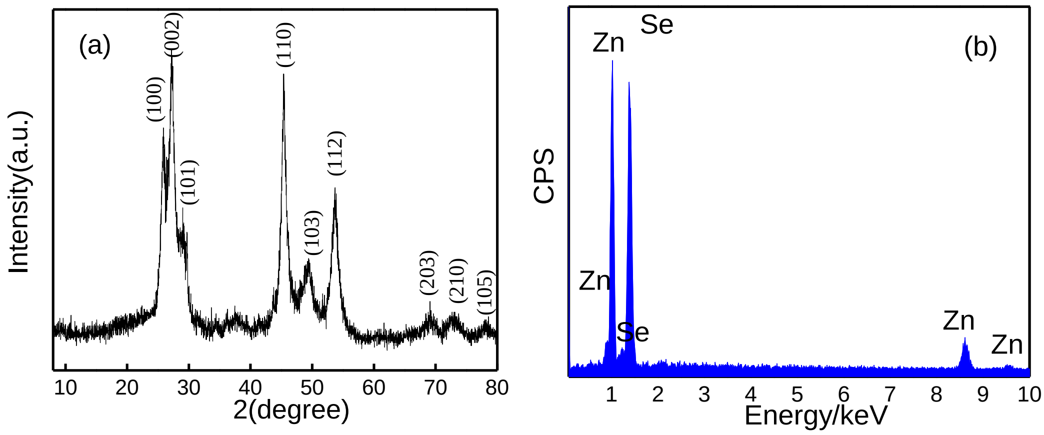

Fig.1. (a) XRD pattern and (b) EDS spectrum of the as-prepared ZnSe nanoplates.

The morphology of the obtained ZnSe products was investigated by SEM (Fig. 2a and 2b) TEM (Fig. 2c) and HRTEM (Fig. 2d). Fig. 2(a) displayed the low magnification SEM images of ZnSe nanomaterials architecture, and these nanomaterials composed of many nanoplates. An enlarged SEM image apparently showed that the obtained samples have thickness about 100 nm and diameters of 200-300 nm, as shown in Fig. 2(b). Further insight into the morphology and microstructure of ZnSe nanomaterials was gained by TEM. As shown in Fig. 2(c), the low-magnification TEM imaged shows that the as-synthesized ZnSe nanomaterials assembled of many plates with diameters of 200-300 nm, the results are consistent with the above SEM observation. The high- magnification TEM image, as shown in Fig. 2(d), indicates that the lattice fringe spacing between two adjacent crystal planes of the nanoplates was determined to be 0.1818 nm.

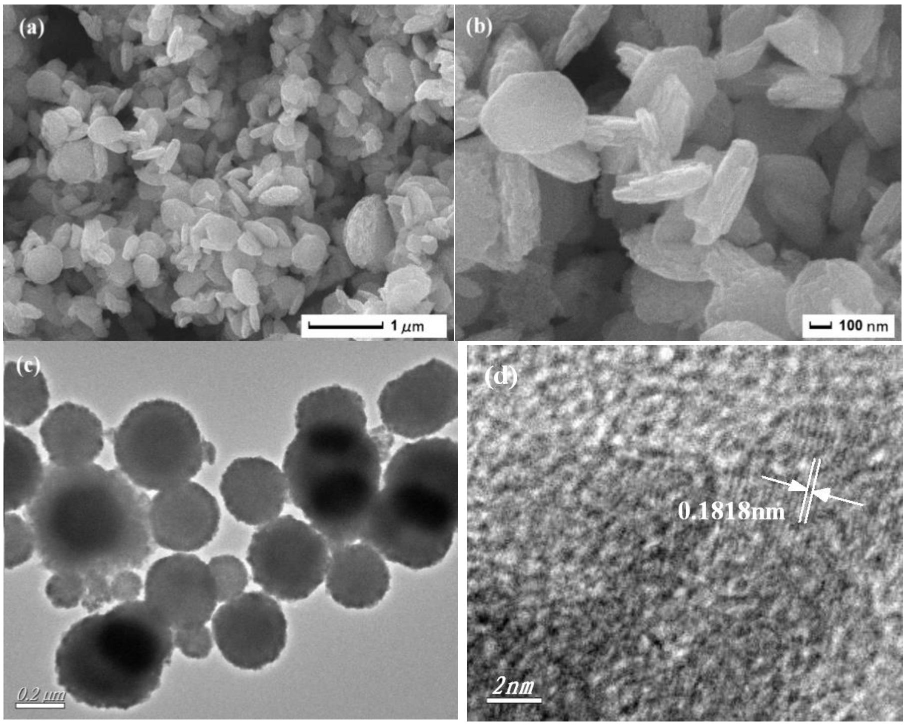

Fig.2. SEM (a, b), TEM (c) and HRTEM (d) image of the ZnSe nanoplates.

3.2. Tribological properties of ZnSe:

In order to investigate the variations of the friction coefficients with the different concentrations of various additives, the tribological performance of the base oil adding different contents of ZnSe were tested under a load of 20 N for 800s, respectively. Fig.3 (a) shows the evolution of the friction coefficient of the base oil with different concentration of ZnSe. It can be found that the base oil with 0.4% and 1.5% content of ZnSe additive gives lower friction coefficient than others from the start of the experiment and remains more stable throughout the test. This is not the case with the 3% and 5% content of ZnSe additive. With regards to the 3% content of ZnSe, at the beginning of the test and up to 200 seconds, the friction coefficient is low (~0.11) and fairly stable, then it progressively increases to 0.13 along with the sliding time. The oil formulated with 5% ZnSe shows different time dependence to that of with other content of ZnSe, and with somewhat higher and unstable friction coefficient. When the concentration of synthesized ZnSe is 1.5wt%, the best friction coefficient-reducing property is obtained.

Fig.3 (b) shows the wear scar width (WSW) of the lower steel disc of lubricant with different content of ZnSe with 20 N load and 0.167 m/s sliding speed. It can be seen that the WSW of the base oil is 0.403 mm, while the WSW of the base oil with 1.5wt% synthesized ZnSe is 0.163 mm. However, the WSWs of the base oil containing 3 and 5wt% synthesized ZnSe are increased, which is in good accordance with the friction coefficient value in Fig.3 (a). The results can be explained by the fact that too much higher concentration of the nanoparticles exhibited extensive agglomeration, could not enter the contact area easily [47], also could destroy the stability of the colloid system of the base oil [48]. Therefore, the optimum concentration of the synthesized ZnSe as an additive in base oil is suggested to be 1.5wt%.

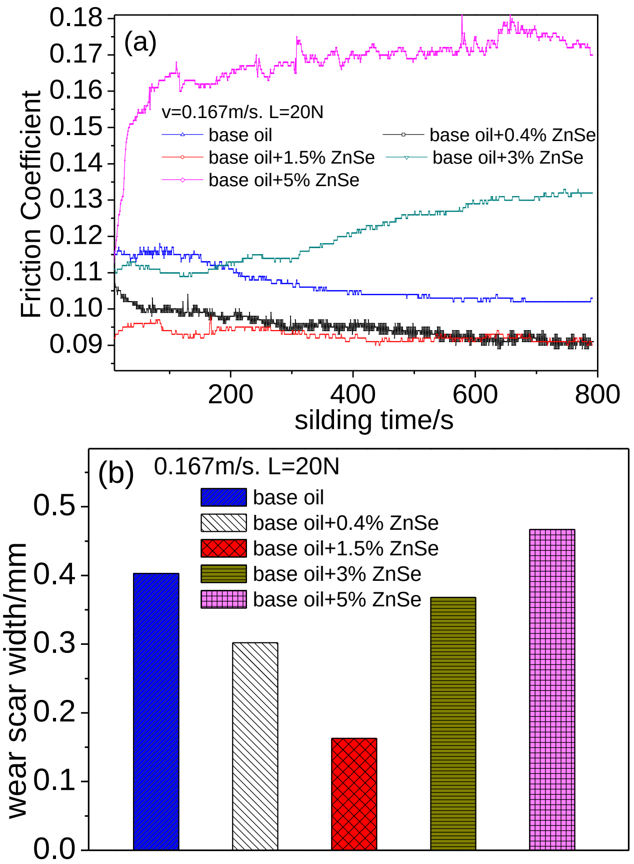

Fig. 3 (a) Friction coefficient as a function of sliding time, (b) wear scar width on disc specimens lubricated with different concentrations ZnSe nanoplates in base oil

The friction coefficients of base oil with 1.5% synthesized ZnSe nanoplates at different loads are shown in Fig.4. It can be seen that after an slightly running-in stage, the friction coefficient progressively increases along with the sliding time at the load of 10N.When the load is 20N, the friction coefficient of base oil with ZnSe nanoplates is stable and almost remain constant at about 0.092. When the load is higher to 30N, the friction coefficient remain constant at about 0.163 up to 660 seconds, then abruptly increases to 0.216.

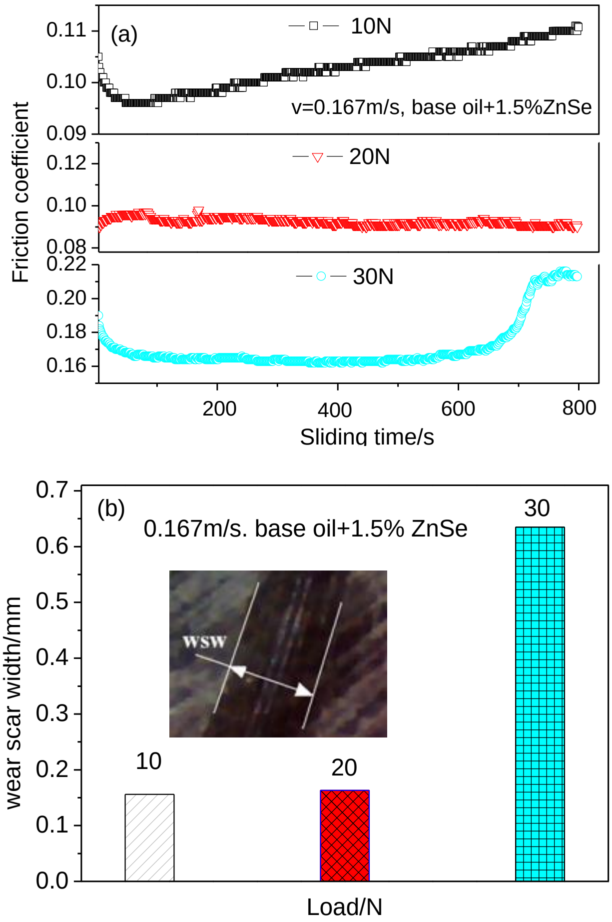

Fig.4 Friction coefficient of base oil mixed with 1.5wt% ZnSe additive under different loads.

Fig.4 (b) shows the wear scar width (WSW) of base oil containing 1.5wt% ZnSe nanoplates at different loads under a speed of 0.167m/s. for 800s. It can be observed that the WSW at the load of 30N is about 0.635 mm, more than four times of that at the load of 10N and 20N. With appropriate content of ZnSe additive, the lubricating oil may form a tribofilm in the friction process, however, a continuous tribofilm only begins to be formed under an optimal load. The protective film at the contact zone became unstable and easily damaged at high loads, result in a high wear scar width, and fluctuant friction coefficient.

Fig. 5(a) displays morphologies of the worn surfaces lubricated with the base oil containing 1.5wt% ZnSe at 20 N. The worn surfaces are smooth and show small pits and shallow furrows, suggesting that a compact and intact tribofilm formed on the friction surface, which results in a lower friction and lower wear scar width. In order to confirm the formation of the tribofilm and its composition, the corresponding EDS analysis of the worn surface was carried out. As shown in Fig. 10(b), besides high content of O, C and Fe, a small quantity of Zn and Se is found on the worn surface. It is believed that the smooth surface lubricated by composites results from the deposition of tribofilm on the friction surface.

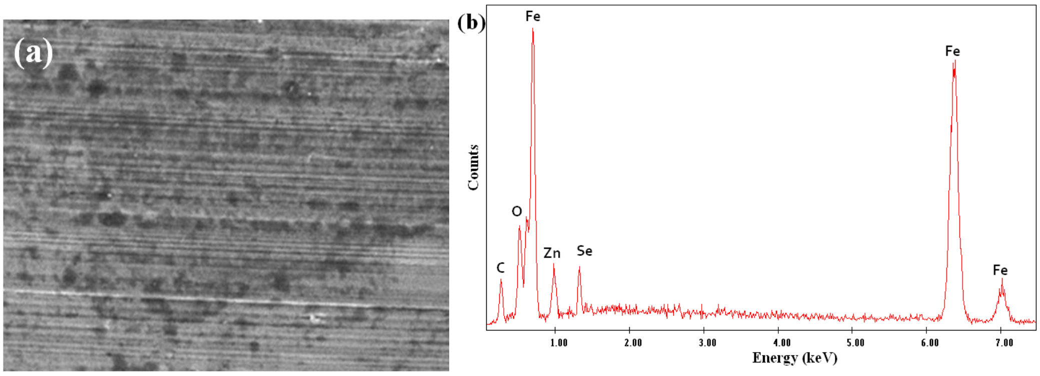

Fig.5 (a) SEM images, and (b) EDS spectrum of the worn surfaces lubricated with the base oil containing 1.5wt% ZnSe (20 N, 0.167 m/s, 800s)

4. Conclusion

In summary, novel ZnSe nanoplates with mean thickness of 100 nm and diameters of 200-300 nm were successfully prepared through hydrothermal reaction method. The experimental results show that the as-prepared ZnSe nanoplates were able to improve the tribological properties of the base oil as a lubricant additive under the optimum concentration (1.5 wt%). Tribological experiments indicated that the compact and stable tribofilm on the rubbing surface could be benefit to reducing friction.

Acknowledgments

This work was supported by the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (14KJB460012), the Changzhou Sci&Tech Program(CJ20159048), the Natural Science Foundation of Jiangsu University of Technology (KYY14003) and Scientific and Technological Innovation Plan of Jiangsu Province (CXLX12_0636).

References

[1] M. R. Gao, Y. F. Xu, Jiang, J. and S. H. Yu, Chem. Soc. Rev. **42,** 7 (2013).
[2] A. Bahari, M. Adeli andS. M. Hosseini, Nano **6,** 04 (2011).
[3] T. Heine. Acc. Chem. Res. **48,** 1 (2014).
[4] S. J.Oh, N. E. Berry, J. H. Choi, E. A. Gaulding, T. Paik, S. H. Hong and C. R. Kagan, ACS nano, **7,** 3 (2013).
[5] J. F. Yang, B. Parakash, J. Hardell and Q. F. Fang, Front Mater. Sci. **6,** 2 (2012).
[6] Z. Li, X. Tao, Z. Wu, P. Zhang and Z. Zhang, Ultrason. Sonochem. **16,** 2 (2009).
[7] G. Chatzitheodorou, S. Fiechter, M. Kunst, J. Luck and H. Tributsch, Mater. Res. Bull. **23,** 9 (1988).
[8] L. D. DeLoach, R. H. Page, G. D. Wilke, S. Payne and W. F. Krupke, IEEE J. Quantum Electron. **32,** 6 (1996).
[9] N. Mahmood, C. Zhang, J. Jiang, F. Liu and Y. Hou, Chem.-Eur. J. **19,** 16 (2013).
[10] M. R. Gao, J. Jiang and S. H. Yu, Small **8,** 1 (2012).
[11] M. Graetzel, R. A. Janssen, D. B. Mitzi and E. H. Sargent, Nature **488,** 7411 (2012).
[12] Y. Y. Sun, M. L. Agiorgousis, P. Zhang and S. Zhang, Nano let. **15,** 1 (2015).
[13] Z. Bin and L. Hui, NANO 9, 08 (2014).
[14] M. R. Gao, X. Cao, Q. Gao, Y. F. Xu, Y. R. Zheng, J. Jiang and S. H. Yu, ACS nano **8,** 4 (2014).

[15] C. Li, L. Huang, G. P. Snigdha, Y. Yu and L. Cao, ACS nano **6,** 10 (2012).
[16] H. Wei, Y. Su, S. Chen, Y. Liu, Y. Lin and Y. Zhang, Mater. Lett. **67,** 1 (2012).
[17] J. Wei, K. Li, J. Chen, J. Zhang and R. Wu, J. Alloys Compd. **531,** (2012).
[18] L. Chen, J. S. Lai, X. N. Fu, J. Sun, Z. F. Ying, J. D. Wu and N. Xu, Thin Solid Films **529** (2013).
[19] J. S. Lee, S. Brittman, D. Yu and H. Park, J. Amer. Chem. Soc. **130,** 19 (2008).
[20] X. Yuan, L. Tang, S. Liu, P. Wang, Z. G. Chen, C. Zhang and F. Xiu, Nano Lett. **15,** 5 (2015).
[21] R. Yue, A. T. Barton, H. Zhu, A. Azcatl, L. F. Pena, J. Wang and C. L. Hinkle, ACS nano **9,** 1 (2014).
[22] X. Huang, Z. Zeng, S. Bao, M. Wang, X. Qi, Z. Fan and H. Zhang, Nat. Comm. **4,** (2013).
[23] W. Jung, S. Lee, D. Yoo, S. Jeong, P. Miró, A. Kuc and J. Cheon, J. Amer. Chem. Soc. **137,** 23 (2015).
[24] S. J. Oh, N. E. Berry, J. H. Choi, E. A. Gaulding, H. Lin, T. Paik and C. R. Kagan, Nano Lett. **14,** 3 (2014).
[25] E. Thimsen, S. C. Riha, S. V. Baryshev, A. B. Martinson, J. W. Elam and M. J. Pellin, Chem. Mater. **24,** 16 (2012).
[26] Z. Ma, F. Weng, Q. Wang, Q. Tang, G. Zhang, C. Zheng and F. Huang, RSC Adv. **4,** 55 (2014).
[27] Q. Peng, Y. Dong and Y. Li, Angew. Chem. Int. Ed. **42,** 26 (2003).
[28] W. Yao, S. H. Yu, X. Y. Huang, J. Jiang, L. Q. Zhao, L. Pan and J. Li, Adv. Mater. **17,** 23 (2005).
[29] M. Durand, A. Houard, K. Lim, A. Durécu, O. Vasseur and M. Richardson, Opt. Express **22,** 5 (2014).
[30] J. Han, S. Xue, W. Zhou, S. Wu, P. Xie and R. Zou, J. Colloid Interface Sci. **430**, (2014).
[31] J. Wang, C. Yang, Z. Huang, M. G. Humphrey, D. Jia, T. You and C. Zhang, J. Mater. Chem. **22,** 19 (2012).
[32] J. Wang and T. J. Mountziaris, Biosens. Bioelectron. **41,** (2013).
[33] X. Gao, G. Tang and X. Su, Biosens. Bioelectron. **36,** 1 (2012).
[34] J. R. Sparks, R. He, N. Healy, M. Krishnamurthi, A. C. Peacock, P. J. Sazio, J. V. Badding, Adv. Mater. **23,** 14 (2011).
[35] G. M. Lohar, S. T. Jadhav, M. V. Takale, R. A. Patil, Y. R. Ma, M. C. Rath and V. J. Fulari, J. Colloid Interface Sci. **458,** (2015).
[36] L. Chen, W. Zhang, C. Feng, Z. Yang and Y. Yang, Ind. Eng. Chem. Res. **51,** 11 (2012).
[37] Z. Zhang, Y. Fu, X. Yang, Y. Qu and Q. Li, Electrochim. Acta **168,** (2015).
[38] H. T. Kwon and C. M. Park, J. Power Sources **251,** (2014).
[39] Z. Wang, J. Jie, F. Li, L. Wang, T. Yan, L. Luo and C. Wu, Chem. Plus.Chem. **77,** 6 (2012).
[40] B. Nie, L. B. Luo, J. J. Chen, J. G. Hu, C. Y. Wu, L. Wang and J. S. Jie, Nanotechnol **24,** 9 (2013).
[41] L. Zhang, G. Zhang, H. B. Wu, L. Yu and X. W. D. Lou, Adv. Mater. **25,** 18 (2013).
[42] C. Zhu, X. Mu, P. A. Van Aken, Y. Yu and J. Maier, Angew. Chem. Int. Ed. **53,** 8 (2014).
[43] C. Gao, Z. Lu, Y. Liu, Q. Zhang, M. Chi, Q. Cheng and Y. Yin, Angew. Chem. Int. Ed. **51,** 23 (2012).
[44] Y. S. Yun, S. Y. Cho, J. Shim, B. H. Kim, S. J. Chang, S. J. Baek and H. J. Jin, Adv. Mater. **25,** 14 (2013).
[45] W. Tang, L. Liu, S. Tian, L. Li, Y. Yue, Y. Wu and K. Zhu, Chem. Commun. **47,** 36 (2011).
[46] H. Hwang, H. Kim and J. Cho, Nano Let. **11,** 11 (2011).
[47] X. Zhang, M. Xue, X. Yang, G. Luo and F. Yang, Micro & Nano Lett. **10,**7 (2015).
[48] G. Zhao, Q. Zhao, W. Li, X. Wang and W. Liu, Lubr. Sci. **26,** 1 (2014).