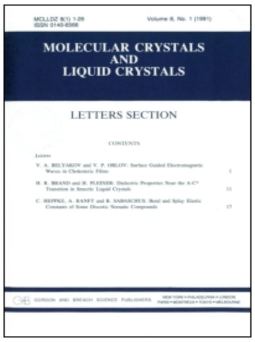


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

# Preparation and characterization of indium doped tin oxide (ITO) via a non-aqueous sol-gel

Anh Khuong Quoc Nguyen, Tai Thien Huynh & Van Thi Thanh Ho

**To cite this article:** Anh Khuong Quoc Nguyen, Tai Thien Huynh & Van Thi Thanh Ho (2016) Preparation and characterization of indium doped tin oxide (ITO) via a non-aqueous sol-gel, Molecular Crystals and Liquid Crystals, 635:1, 32-39, DOI: 10.1080/15421406.2016.1200920

**To link to this article:** http://dx.doi.org/10.1080/15421406.2016.1200920

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 635, 32–39
http://dx.doi.org/10.1080/15421406.2016.1200920

# Preparation and characterization of indium doped tin oxide (ITO) via a non-aqueous sol-gel

Anh Khuong Quoc Nguyen, Tai Thien Huynh, and Van Thi Thanh Ho

Hochiminh City University of Natural Resources and Environment (HCMUNRE), Viet Nam

**ABSTRACT**

Tin-doped indium oxide (ITO) nanoparticles (NPs) were conceived as promising materials using as noncarbon support for Pt NPs on the cathode side of Proton Exchange Membrane Fuel Cells (PEMFC). In this paper, ITO nanoparticles have been synthesized via a nonaqueous sol-gel process using indium acetylacetonate and tin bis(acetylacetonate)dichloride in oleyamine as starting materials. The ITO exhibits solid solution phase, relatively porous, good crystallinity with a uniform size of 15–20 nm, resulting in a high specific surface area and excellent conductivity. The effects of reaction temperature, calcination temperature on the specific surface area as well as the conductivity of ITO nanoparticles were studied in this paper. We found that the ITO nanoparticles synthesized at 235°C and calcination temperature at 500°C for 3 hours shows the excellent conductivity of 1.242 S/cm, was significantly ∼8-fold higher than that of commercial ITO produced by Sigma-Aldrich (0.15 S/cm). The results of this research suggested that the ITO synthesized by non-aqueous sol-gel process exhibits relatively good properties as well as can apply this process to prepare the others nanomaterial support based on $In_2O_3$-materials by doping different oxide into indium oxide.

**KEYWORDS**

ITO; Indium doped tin oxide; sol-gel; conductivity; nanoparticles

## 1. Introduction

In recent year, fuel cell, particularly the proton exchange membrane fuel cells (PEMFC), have attracted considerable interest as an environmentally friendly power source that convert directly chemical energy from fuels such as hydrogen into electricity with high power density, high efficiency, and low to zero emissions. However, fuel cell commercialization is still hampered as there are several problems, for example insufficient durability and high cost contributed substantially by PEMFC catalysts. With the current state of technology, Pt supported on carbon is still the most widely used electrocatalyst in proton exchange membrane fuel cell (PEMFC). However, the weak interaction between metal and carbon supports causes a severe sintering/agglomeration of catalytic metal nanoparticles and consequently falls off the active surface area, which leads to the degradation of performance under long-term operations. Besides, the stability of the carbon material itself is also an important concern[1–4]. To address these issues, a number of substitute noncarbon support materials have been explored and developed especially metal oxides[2, 5, 6].

---

**CONTACT** Van Thi Thanh Ho ✉ httvan@hcmunre.edu.vn Hochiminh City University of Natural Resources and Environment (HCMUNRE), Vietnam.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

Conducting metal oxides are considered to be emerging candidates for catalyst support in fuel cell applications owing to effective metal support interactions resulting in improving significantly the stability and catalytic activities[7]. Tin-doped indium oxide (ITO) is a promising metal oxide support for Pt at cathode side of PEMFC. ITO is a solid solution of indium(III) oxide ($In_2O_3$) and tin(IV) oxide ($SnO_2$), constantly 90% $In_2O_3$, 10% $SnO_2$ by weight. Normally, ITO in the form of thin films is the most widely used in screen display techniques due to it exhibits transparent conducting films[8, 9]. The ideal for using ITO powders as noncarbon catalyst support for fuel cell applications is determined as a promising way due to ITO can connect the outstanding characteristics of both oxides, it can perform effectively the role as catalyst support. Ota et al. found that the interaction between platinum and tin oxide has an effect on the adsorption/desorption of oxygen on platinum[10].

As a consequence, the formation of platinum oxides suppressed and the morphology of the catalyst layer unchanged brought about the stability of Pt over a wide potential range[11, 12, 13]. As regards indium oxide, it is not only high conductivity material but also long-term durability in acid at ORR relevant potentials[14].

In this paper, ITO nanoparticles have been synthesized one step via a nonaqueous sol-gel process using indium acetylacetonate and tin bis(acetylacetonate)dichloride in oleyamine as starting materials. The structure, morphology, BET as well as conductivity of as- ITO are characterized in this work. The effects of reaction temperature, calcination temperature on the specific surface and the conductivity of ITO nanoparticles are also studied.

## 2. Experimental section

### Materials

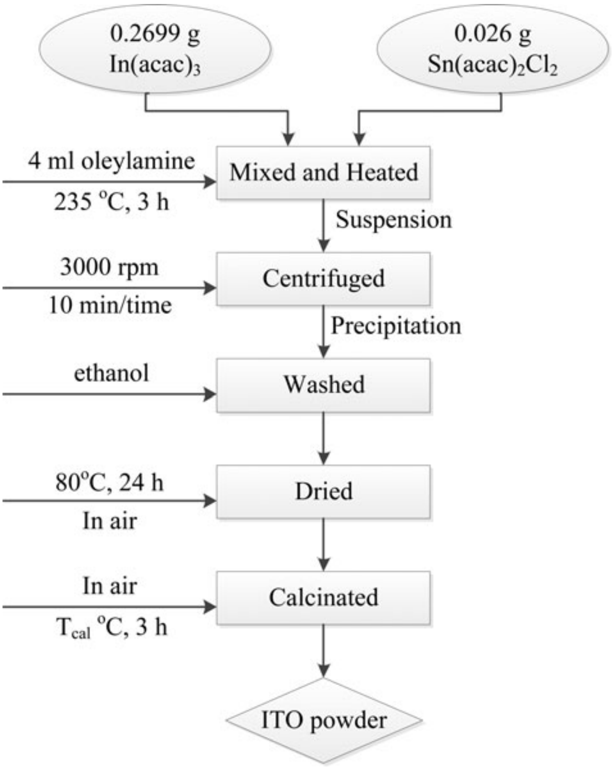
All reagents and solvents are commercially available and used without further purification. Indium(III) acetylacetonate ($In(acac)_3$, 99,99%), oleyamine (70%) were purchased from Acros - Belgium. Tin(IV) bis(acetylacetonate)dichloride (98%) were purchased from Sigma - Aldrich. Ethanol (99,7%) were obtained from Xilong - China.

### Preparation

A total of 0.2699 g of $In(acac)_3$ and 0.026 g of ($Sn(acac)_2Cl_2$) were combined with 4 ml of oleyamine in a three-neck flask connected with a condenser. This solution was stirred virgorously and heated at 235°C for 3h in air to produce a dark yellow suspension. The ITO particles were collected by centrifugation, washed many times with ethanol to remove residual oleyamine and dried at 80°C for 24 h in air. A gray powder of ITO NPs was obtained and calcinated in furnace at different temperatures values between 400°C and 600°C. The final products were yellow (see detail in Scheme 1).

### Characterization

The properties of catalyst are characterized by Powder X-ray diffraction (XRD), transmission electron microscopy (TEM), BET, and Conductivity measurements.



**Scheme 1.** ITO NPs synthesis process via a nonaqueous sol-gel method.

## 3. Results and discussion

Figure 1 displays the experimental XRD patterns of tin-doped indium oxide nanoparticles (ITO NPs) without calcination process and with varying calcination temperature. All the diffractograms match very well the cubic bixbyite structure of indium oxide pattern (JCPDS 06–0416) at $2\theta$ positions 21.5°, 30.6°, 35.5°, 45.7°, 51.0°, 60.7$^0$ with no secondary phases, suggesting the formation of solid solutions rather than the mixture of indium oxide and tin

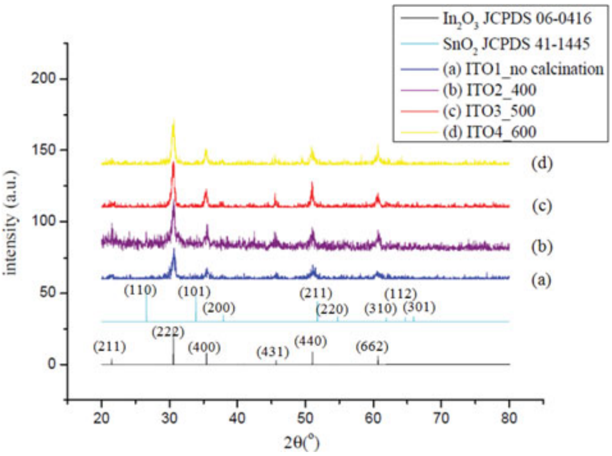


**Figure 1.** XRD patterns of tin-doped indium oxide (ITO) NPs without calcination process and with varying calcination temperature.

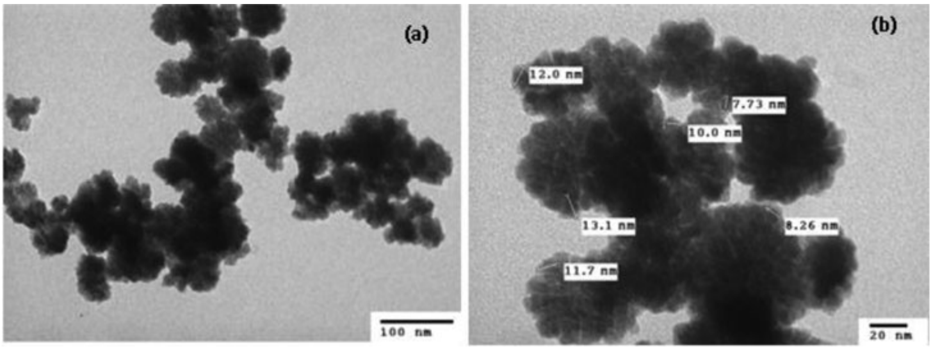


**Figure 2.** TEM micrographs of ITO1 sample (without using calcination process): (a) the overview of ITO distribution and (b) high resolution of ITO NPs.

oxide. The (222) peak of ITO is shifted to the higher $2\theta$ values comparing to pure $In_2O_3$ on account of the differences in ionic radii of $Sn^{4+}$ (~0.71Å) and $In^{3+}$ (~0.8 Å), proving that the smaller Sn ions incorporate into $In_2O_3$ causing the shrink of the crystal lattice. Furthermore, heat treatment temperature also affected to the ITO crystalline structure formation. For example, heat-treated ITO samples (ITO2, ITO3, ITO4) are more highly crystalline than unheated sample (ITO1), indicating the high crystallinity of ITO have been obtained when using calcination process. This is concluded that crystalline phases can be obtained by further heat-treatment at higher temperatures, however surface area of ITO are also optimized for support materials.

Figure 2 shows TEM micrographs of ITO1 sample without using calcination process. Interestingly, Fig. 2a exhibits the overview of ITO distribution is formed as flowerlike cluster and some agglomerates. An average size of nanoparticles within the cluster distributing ranging from 7 nm to 14 nm can be observed (Fig. 2b). The morphology of ITO1 could be explained by the Limited Ligand Protection (LLP), resulting in 3D nanoflowers formation. When nanocrystals are not sufficiently protected by organic ligands, aggregation seemed to be a reasonable pathway for minimizing the surface energy of nanocrystals[15, 16].

When ITO sample was calcinated at 500°C (denote ITO3 sample), (Figure 3) the ITO3 shows a spherical morphology with better dispersibility and the uniformity of the grains. Furthermore, the particle size distribution is uniform in the range of 15–20 nm. This could

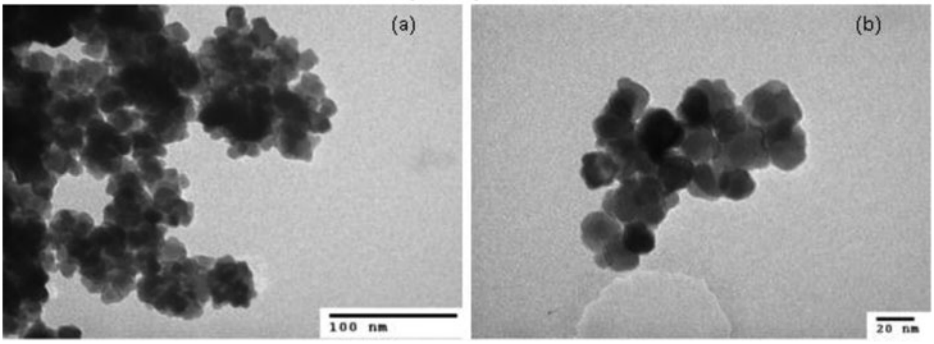


**Figure 3.** TEM micrographs of ITO3 sample (with calcination temperature about 500°C): (a) the overview of ITO distribution and (b) high resolution of ITO powder.

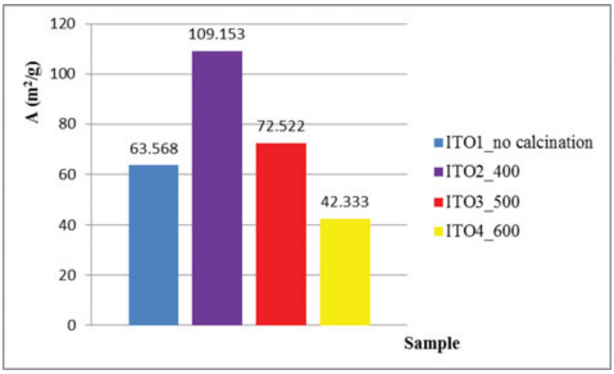
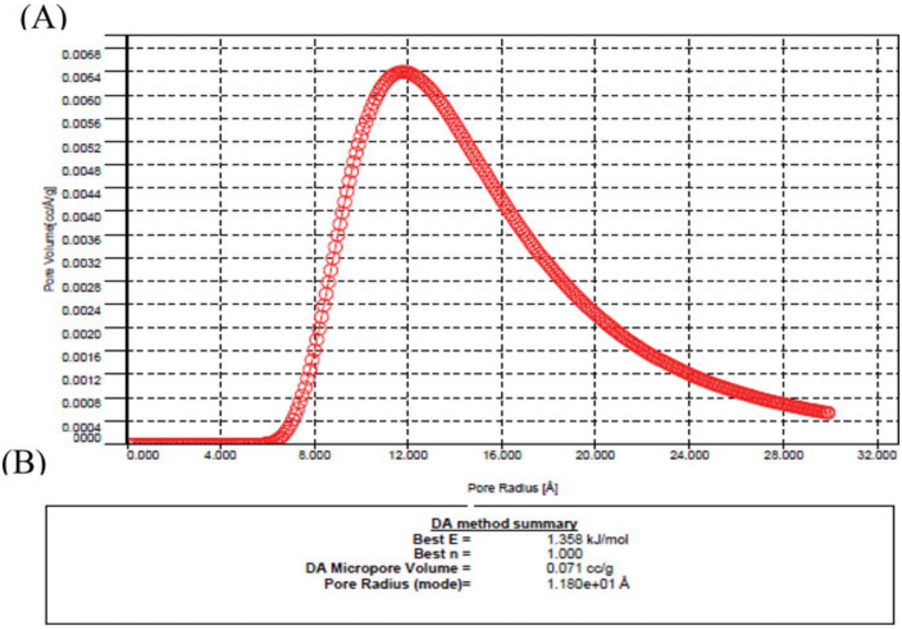


**Figure 4.** BET measurement data for ITO sample without and with various calcination temperatures.

be explained due to the removing of organic ligand covered particle surface when burning off at 500°C in a pure-oxygen environment, resulting in the change of ITO morphology. ITO3 sample was measured the composition by ICP measurement. The results show the ratio of In:Sn = 91.54%: 8.46%, which is closed to the beginning of In:Sn = 90%: 10%.

The effect of calcination temperature of ITO sample on the surface area (BET) is also studied in this work. (Figure 4) Interestingly, it is found that the ITO1 sample without using heat treatment shows the low BET surface area of 63.568 m$^2$/g. This data could be understood due to the covering of organic ligand on the surface of ITO nano particle led to the decrease surface area of this sample. However, when ITO sample is treated by heat treatment at 400°C in air, the BET surface area of ITO2 sample is increased significantly up to 109.153 m$^2$/g. This is indicating that the organic ligand cover on the ITO NPs is removed by heat treatment at 400°C in the air. Besides, the ITO2 sample also exhibits the porous structure (pore radius about 1.2 nm and the pore volume about 0.07cc/g) (Figure 5), so that the BET surface area



DA method summary
Best E = 1.358 kJ/mol
Best n = 1.000
DA Micropore Volume = 0.071 cc/g
Pore Radius (mode)= 1.180e+01 Å

**Figure 5.** (A) Pore radius and Pore volume data for ITO2 sample and (B) for ITO1.

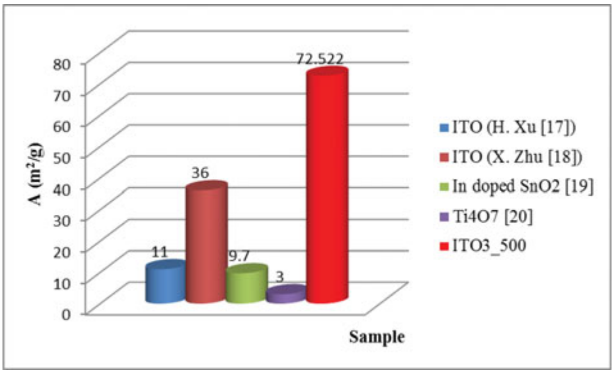


**Figure 6.** Comparison of the surface area between ITO3_500 in this work and ITO in others works as well as others noncarbon supports.

increases. The pore volume of ITO1 sample also was measured for comparison. The ITO1 exhibited the conductivity is about 0.061 cc/g for unheated sample that was lower than the value of ITO2 sample calcinated at 4000C (0.07 cc/g). However, when further increasing the heat treatment to 500°C and 600°C, the surface area decrease evidently from 72.522 drop down 42.33 $m^2/g$. This result is obvious thing as the growth of the particles generated by thermally induced crystallization leads to the reduction of surface area.

The ITO NPs synthesized in this work are compared with ITO prepared by different methods in similar calcination condition, The ITO sample prepared in this work shows larger surface area than those of ITO prepared by other methods in previous work (Figure 6). In addition, the surface area of ITO3 powder (72.522 $m^2/g$) is much higher than that of some noncarbon support such as $Ti_4O_7$ (3 $m^2/g$), In doped $SnO_2$ (9.7 $m^2/g$). Evidentially, ITO material meets the requirement for surface area to become new support for Pt in PEMFCs[21].

Besides the BET surface area is one of the major properties for support materials, electrical conductivity is also the important requirement for this kind of support materials. Figure 7 shows the impact of electrical conductivity for ITO sample without and with various calcination temperatures. It can be clearly observed that the electrical conductivity is lowest for the ITO1 sample without using heat treatment due to the covering of organic ligand as well

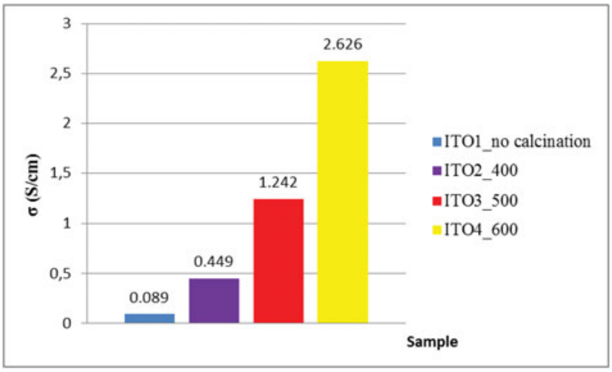


**Figure 7.** Electrical conductivity measurement data for ITO sample without and with various calcination temperatures.

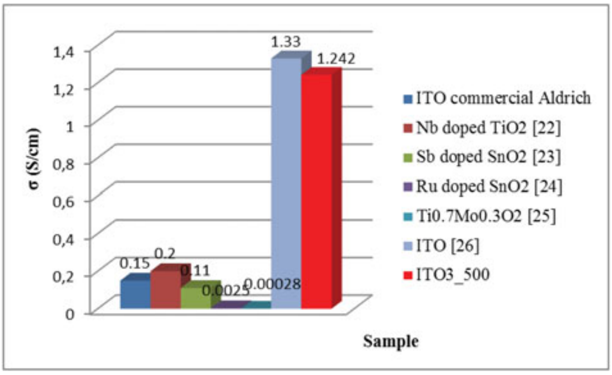


**Figure 8.** Comparison of the electrical conductivity between ITO3_500 in this work and ITO commercial Aldrich as well as others noncarbon supports.

as the low crystallinity of obtained ITO sample. This is accordance in the XRD (Fig. 1) and TEM (Fig. 2) data has been shown in previously. However, when increasing the calcination temperature from 400°C to 600°C, the electrical conductivity increases significantly 5-fold from 0.5 to 2.6 S/cm. This data could be indicated that for the semiconductors, when thermally activated process, electrons in the valance band are promoted into the conduction band, hence the concentration of charge carrier's increase. We also compare the electrical conductivity of our ITO's sample with and other non-carbon supports based on $TiO_2$ materials in previous research and commercial ITO powder to further understanding the properties of our material. (Figure 8).

Figure 8 shows that ITO3 prepared via a nonaqueous sol-gel and heated at 500°C exhibits a conductivity of 1.242 S/cm that is over ~8-fold higher than that of commercial available ITO powders (Aldrich, 10 wt% $SnO_2$, 25 – 45 nm mean particle size), with 0.15 S/cm and is similar with the ITO nanomaterials (1.33 S/cm) from the previous research [26] Furthermore, from the Figure 8 it is clear the conductivity of our ITO sample is the highest among compared non-carbon supports. This is suggesting that the impressive conductivity of ITO material is important factor for requirement of support materials so that the as-ITO prepared in this work could be become the advanced nanostructure supports to replace traditional carbon support for PEMFCs.

## 4. Conclusions

In summary, ITO nanoparticles have been synthesized successfully via a nonaqueous sol-gel process using indium acetylacetonate and tin bis(acetylacetonate)dichloride in oleyamine as starting materials. The ITO exhibits solid solution phase, relatively porous, good crystallinity with a uniform size of 15–20 nm, resulting in a high specific surface area and excellent conductivity. We found that the calcination temperature at 500°C for 3 hours that prepared the ITO with the excellent conductivity of 1.242 S/cm, was significantly ~8-fold higher than those of commercial ITO produced by Sigma-Aldrich (0.15 S/cm) as well as other support materials in previous research. Finally, the results of this research suggested that the ITO synthesized by non-aqueous sol-gel process exhibits relatively good properties as well as can apply this process to prepare the others nanomaterial support based on $In_2O_3$-materials by doping different oxide into indium oxide.

## Acknowledgments

We are grateful for finacial support from The National Foundation for Science and Technology Development (NAFOSTED) given under a special program for Basic Research Projects in Natural Science 2014 (Grants No. 104.03–2014.92), Dr. Bach Long Giang, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam supported for this work.

## References

[1] Kou, R., Shao, Y., Mei, D., Nie, Z., Wang, D., Wang, C., Viswanathan, V. V., Park, S., Aksay, A. I., Lin, Y., Wang, Y., & Liu, J. (2011). *J. Am. Chem. Soc.*, *133*, 2541.
[2] Shao, Y. Y., Yin, G. P., & Gao, Y. Z. (2007). *J. Power Sources.*, *171*, 558.
[3] Borup, R. (2007). *Chem. Rev.*, *107*, 3904.
[4] Shao-Horn, Y., Sheng, W., Chen, S., Ferreira, P., Holby, E., & Morgan, D. (2007). *Top. Catal.*, *46*, 285.
[5] Stevens, D. A., Hicks, M. T., Haugen, G. M., & Dahn, J. R. (2005). *J. Electrochem. Soc.*, *152*, A2309.
[6] Shao, Y., Liu, J., Wang, Y., & Lin, Y. (2009). *J. Mater. Chem.*, *19*, 46.
[7] Wang, J. Y., Wilkinson, P. D., & Zhang, J. (2011). *Chem. Rev.*, *111*, 7625.
[8] Li, F. G., Liu, D. P., & Deng, P. (1999). *Rare Met. Cemented Carbides.*, *138*, 15.
[9] Wang, R., & Lee, C. C. (1999). *Society of Vacuum Coaters.*, 246.
[10] Nakada, M., Ishihara, A., Mitsushima, S., Kamiya, N., & Ota, K.-i. (2007). *Electrochem. Solid-State Lett.*, *10*, F1.
[11] Lei, B., Xue, J., Jin, D., Ni, S., & Sun, H. (2008). *Rare Metals.*, *27*, 445.
[12] Darling, R. M., & Meyers, J. P. (2003). *J. Electrochem. Soc.*, *150*, A1523.
[13] Darling, R. M., & Meyers, J. P. (2005). *J. Electrochem. Soc.*, *152*, A242.
[14] Koller, K. B., & Hawkridge, F. M. (1988). *J. Electroanal. Chem. Interfac.*, *239*, 291.
[15] Mullin, J. W. (1993). *Crystallization*, Butterworth-Heinemann: Oxford, UK.
[16] Narayanaswamy, A., Xu, H., Pradhan, N., Kim, M., & Peng, X. (2006). *J. Am. Chem. Soc.*, *128*, 10310.
[17] Xu, H., Zhu, G., Zhou, H., & Yu, A. (2005). *J. Am. Ceram. Soc.*, *88*, 986.
[18] Fang, Z., Assaaoudi, H., Guthrie, R. I. L., & Kozinski, J. A. (2007). *J. Am. Ceram. Soc.*, *90*, 2367.
[19] Park, I. S., Lee, E., & Manthiram, A. (2010). *J. Electrochem. Soc.*, *157*, B251.
[20] Slavcheva, E., Nikolova, V., Petkova, T., Lefterova, E., Dragieva, I., Vitanov, T., & Budevski, E. (2005). *Electrochim. Acta.*, *50*, 5444.
[21] Krawiec, P., & Kaskel, S. (2006). *J. Solid State Chem.*, *179*, 2281.
[22] García, B. L., Fuentes, R., & Weidner, J. W. (2007). *Electrochem. Solid-State Lett.*, *10*, B108.
[23] Saraidarov, T., Reisfeld, R., Zigansky, E. E., Saschiuk, A., & Lifshitz, E. (2008). *Opt. Appl.*, *38*, 109.
[24] Pang, H. L, Zhang, X.H, Zhong, X.X, Liu, B, Wei, X.G, Kuang, Y.F, & Chen, J.H. (2008). *J. Colloid Interface Sci.*, *319*, 193–198.
[25] Ho, V.T.T, Pan, C-J, Rick, J, Su, W-N, & Hwang, B-J. J. (2011). *Am. Chem. Soc.*, *133*, 11716–11724.
[26] Jianhua, B., Dina, F. R., Armin, F., Torsten, B., Igor, D., Michael, W., & Markus, N. (2006). *Chem. Mater.*, *18*, 2848.