Mg Doping Induced Effects on Structural, Optical, and Electrical Properties as Well as Cytotoxicity of CeO₂ Nanostructures

JAVED IQBAL, TARIQ JAN, M.S. AWAN, SAJJAD HAIDER NAQVI,
NOOR BADSHAH, ASMAT ULLAH, and FAZZAL ABBAS

Here, Mg_xCe_{1-x}O₂ (where $x = 0, 0.01, 0.02, 0.03, 0.04$, and 0.05) nanostructures have been successfully synthesized by using a simple, easy, and cost-effective soft chemical method. X-ray diffraction (XRD) patterns substantiate the single-phase formation of a CeO₂ cubic fluorite structure for all samples. Infrared spectroscopy results depict the presence of peaks only related to Ce-O bonding, which confirms the XRD results. It has been observed *via* ultraviolet (UV)-visible spectroscopy that Mg doping has tuned the optical band gap of CeO₂ significantly. The electrical conductivity of CeO₂ nanostructures has been found to increase with Mg doping, which is attributed to enhancement in carrier concentration due to the different valance states of dopant and host ions. Selective cytotoxic behavior of Mg_xCe_{1-x}O₂ nanostructures has been determined for neuroblastoma (SH-SY5Y) cancerous and HEK-293 healthy cells. Both doped and undoped CeO₂ nanostructures have been found to be toxic for cancer cells and safe toward healthy cells. This selective toxic behavior of the synthesized nanostructures has been assigned to the different levels of reactive oxygen species (ROS) generation in different types of cells. This makes the synthesized nanostructures a potential option for cancer therapy in the near future.

DOI: 10.1007/s11663-015-0560-2

© The Minerals, Metals & Materials Society and ASM International 2016

I. INTRODUCTION

RARE earth oxide nanostructures have extraordinary physiochemical characteristics such as optical, magnetic, and electronic properties because of their unfilled 4f electronic structure.^[1] CeO₂ is an important rare earth oxide having a wide band gap and stable cubic fluorite structure. It is a highly reactive rare earth metal oxide that is used in various fields such as catalysis, polishing materials, luminescence, optical additive, ultraviolet (UV)-adsorbents, hydrogen storage materials, oxygen sensors, solid oxide fuel cells,^[2–11] ionic conduction, and as counterelectrodes for electrochromic devices. CeO₂ nanostructures have received much attention due to their changed and enhanced characteristics as compared to their bulk counterparts.^[12–15] In recent years, several synthetic methods have been used to explore CeO₂ nanostructures fabrication such as the surfactant-assisted approach,^[16] micro-emulsion,^[17] spray

pyrolysis, pyrolysis (low temperature or spray),^[18] thermodecomposition,^[19] reflex method,^[20] hexamethylenetetramine,^[21] microwave-assisted heating,^[22] chemical co-precipitation,^[23] organometallic decomposition,^[20] solution and solid combustion methods,^[24] sol-gel methods,^[25] flow method,^[26] hydrothermal synthesis,^[27] microwave heating,^[28] and gas and sonochemical methods.^[29] The chemical co-precipitation technique has several advantages, such as low cost, high reproducibility, versatility, and control over particle sizes and shapes.^[30] Furthermore, it has been reported that several properties of CeO₂ and its photocatalytic activity can be tuned *via* selective chemical doping.^[31] Magnesium (Mg), having a lower valency than Ce, can stabilize and tune various properties of CeO₂ nanostructures. In this article, a series of CeO₂ nanostructures doped with different concentrations of Mg ions have been synthesized by a simple, wet chemical co-precipitation technique at a comparatively low temperature. The influence of Mg content on the structural, optical, and dielectric characteristics of CeO₂ nanostructures has been studied in detail. Moreover, the cytotoxicity of the synthesized Mg_xCe_{1-x}O₂ nanostructures toward cancerous and healthy cells has been investigated in detail.

II. MATERIALS AND METHODS

A. Synthesis of Undoped and Mg Doped CeO₂

For synthesis of Mg_xCe_{1-x}O₂ nanostructures, chemicals like cerium nitrate (Ce(NO₃)₃·6H₂O) and magnesium sulfate (MgSO₄·7H₂O) were used as precursor materials.

JAVED IQBAL, Assistant Professor, TARIQ JAN, Research Scholar, ASMAT ULLAH, Master Student, and FAZZAL ABBAS, Ph.D. Scholar, are with the Laboratory of Nanoscience and Technology, International Islamic University, Islamabad, Pakistan. Contact e-mail: javed.saggu@iiu.edu.pk M.S. AWAN, Principal Scientist, is with the Ibn-e-Sina Institute of Technology (ISIT), H-11/4 Islamabad, Pakistan. SAJJAD HAIDER NAQVI, Assistant Professor, is with the Department of Biochemistry, University of Karachi, Karachi, Pakistan. NOOR BADSHAH, Assistant Professor, is with the Department of Basic Science, University of Engineering and Technology, Peshawar, Pakistan.

Manuscript submitted April 20, 2015.

Article published online January 29, 2016.

The synthesis was done *via* a simple co-precipitation technique by using distilled water as a solvent. A total of 2.17-g powder of $(\text{CeNO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 2-g granular NaOH were dissolved in 50-mL distilled water separately to obtain 0.1- and 1-M solutions, respectively. Furthermore, 2 mL of acetic acid was added to the precursor solution as a surfactant to control the particle size. Then the NaOH solution was added to this solution dropwise until a pH value of 10 was reached and was further stirred for 1 hour to complete the reaction. Finally, precipitates were washed several times with distilled water and collected *via* centrifugation. For Mg doping, a similar practice was followed whereby $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was added to $(\text{CeNO}_3)_3 \cdot 6\text{H}_2\text{O}$ with various molar ratios of 1, 2, 3, 4, and 5 pct Mg. The collected precipitates were dried in an electric oven for 12 hours at 353 K (80 °C) and then grinded to acquire the powder. For decomposition of the precipitates, samples were heated in an electric oven for 2 hours at 453 K (180 °C) and annealed at 573 K (300 °C).

The structural properties of the prepared samples were characterized by X-ray diffraction (XRD) technique in the 2θ range of 20 to 80 deg using a PANalytical X-ray diffractometer (Model: 3040/60 X'Pert PRO made in The Netherlands), which uses $\text{CuK}\alpha$ X-rays with a wavelength of 1.54 Å. Surface morphologies were investigated by using scanning electron microscopy (SEM) (JEOL, SEM, Model JSM6490LA). The surface chemistry was analyzed by Fourier transform infrared spectroscopy (FTIR) (NICOLET 6700 FTIR spectrometer made by THERMO SCIENTIFIC, USA) with the KBr technique. Pellets of the synthesized nanostructure and KBr were made *via* a hydraulic presser, and for background corrections, FTIR spectra of only the KBr pellets was recorded. UV-visible absorption spectroscopy was used to investigate the optical characteristics of the synthesized nanostructures. The powder samples were dispersed in distilled water in a certain amount, and their absorption spectra were recorded by using a PerkinElmer Lambda 200 UV/VIS/NIR absorption spectrometer. For electrical characteristics analysis, pellets of $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures were made with the help of a hydraulic presser. These pellets were then sintered in an electric oven at 453 K (180 °C) for 2 hours. For electrical contacts, silver paste was coated on these pellets. The AC measurements were carried out by using a Wayne Kerr 6500 B Impedance analyzer at room temperature in the frequency range of 1 kHz to 5 MHz. The dielectric constant (ϵ') was calculated from the following equation:

$$\epsilon' = (t \times C_p) / (A \times \epsilon_0)$$

where t is the thickness of the pellets, C_p is the equivalent parallel capacitance obtained experimentally, A is the area of the pellets, and ϵ_0 is the permittivity of the vacuum. The dielectric loss (ϵ'') was calculated from the multiplication of ϵ' with the dissipation factor D obtained experimentally. Finally, the AC conductivity was calculated from the following equation:

$$\sigma_{ac} = 2\pi f \epsilon_0 \epsilon' \tan \delta$$

where $\tan \delta = \epsilon'' / \epsilon'$.

B. Cell Culture and Treatment

The SH-SY5Y and HEK-293 cancerous and healthy human cell lines, respectively, were purchased from American Type Culture Collection (Manassas, VA). Both type of cells were maintained in Dulbecco's Modified Eagle's Medium (DMEM) (Sigma-Aldrich) supplemented with 10 pct fetal bovine serum (FBS) and grown at 310 K (37 °C) in a humidified environment with 5 pct CO_2 plus 95 pct air separately. Both type of cells were seeded in 96-well plates and allowed to attach for 48 hours. The suspension of $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures was applied to both types of cells. The cells without nanostructures were used as a control in these experiments. CCK-8 analysis was done for cell viability assay, and pictures were taken from a phase contrast microscope. Reactive oxygen species (ROS) detection was carried out by flow cytometry.^[32,33]

III. RESULTS AND DISCUSSIONS

XRD patterns of the prepared samples in the 2θ range of (20–80) are depicted in Figure 1. For the synthesized $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ samples, all peaks in XRD patterns are well indexed to the cubic fluorite structure of CeO_2 . No peaks related to Mg, MgO, or any other impurities were found, which demonstrates that Mg ions are successfully doped into the cubic fluorite structure of CeO_2 . The lattice parameters of ceria have been calculated by using the relation:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

where d is the interplanar distance between the parallel planes and a is the lattice constant of a simple cube. The values for the lattice constant a have been observed to decrease, varying from 5.44 to 5.33 Å with Mg doping. This decrease in lattice constant values may be assigned to the smaller ionic radii of Mg ions as compared to Ce ions.^[34] The Scherer formula as given below has been used to obtain average crystallite sizes from the (111) peak for all the samples:

$$D = \frac{0.9\lambda}{B \cos \theta}$$

where θ is Bragg's angle in radians, B is the full width at half maximum (FWHM), and λ depicts the wavelength ($\lambda = 0.154$ nm) of the $\text{Cu K}\alpha$ radiation used to obtain the XRD patterns. The calculated values of the crystallite size have been observed to decrease from 9 to 5 nm, which may also be attributed to the difference in the ionic radii of dopant and host ions.

The SEM micrographs of CeO_2 with varying Mg doping levels are shown in Figure 2. Figure 2(a) shows the morphology of the undoped CeO_2 sample, which depicts the presence of large grains having flake-like

Fig. 1—XRD patterns of undoped and $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$.

shapes with an average thickness of 200 nm. These large grains may be formed due to the self-aggregation of small nanocrystals into large flakes during the annealing process. Furthermore, a morphological transformation from flakes to rods has been observed with Mg doping.

This morphological transformation may be explained on the basis of Pauling electronegativity. As is well known, if ions with higher Pauling electronegativity are replaced by ions having lower Pauling electronegativities, then the growth rate and orientation may be changed, which leads to morphological transformation.^[35]

An FTIR technique is used to determine the surface chemistry and modes of vibrations of chemical bond present in the samples. FTIR spectra of the prepared nanostructures are given in Figure 3, which have been recorded at the room temperature in a spectral range of 400–4000 cm^{-1} . The peak located at 1729 cm^{-1} is related to the H-O-H functional group. The absorption band observed at 1450–1200 cm^{-1} is a characteristic peak for the hydroxyl group, whereas the band located at 881.9 cm^{-1} shows the C=O₂ functional group. The absorption band at 489–462 cm^{-1} is related to the Ce-O stretching vibrations.^[36]

UV-visible absorption spectroscopy has been used to investigate the optical characteristics of $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures. Figure 4 shows the absorption spectra of $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures, respectively, in the range of 200–800 nm. The typical absorption peak that appears at 315 nm (3.93 eV) for bulk CeO₂ is due to the charge transfer from 2p (O) orbital to 4f (Ce) orbital.^[37] The

Fig. 2—SEM images of (a) undoped (b) 1 pct Mg (c) 2 pct Mg (d) 3 pct Mg (e) 4 pct Mg and (f) 5 pct Mg doped CeO₂.

Fig. 3—FTIR spectra of $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures.

typical band gap absorption peak of the synthesized undoped CeO_2 nanostructures appears at 311 nm (3.98 eV), which is blue shifted as compared to the bulk CeO_2 , as shown in Figure 4. This shift is also previously reported and is suggested to be due to the quantum confinement effects.^[38] The main absorption edge peak has been observed to undergo further blue shift with Mg doping as compared to that of undoped CeO_2 , as shown in Figure 4. This indicates the widening of the CeO_2 band gap with Mg doping. This enhancement in the band gap energy of CeO_2 nanostructures with Mg doping may be due to the large band gap of MgO (7.8 eV). Furthermore, Mg doping can lead to a higher abundance of Ce^{4+} ions as compared to Ce^{3+} ions in the CeO_2 matrix, which can also result in widening of its band gap.^[39]

To study the Mg doping induced effects on the electrical characteristics of CeO_2 nanostructures, the AC conductivities of all the prepared samples have been determined and shown in Figure 5. Figure 5 shows the variation of AC conductivity of all the prepared nanostructures as a function of AC frequency at room temperature. In all samples, the AC conductivity is nearly constant at low frequencies and then increases above a certain characteristic point with the increase in frequency according to the power law, which states that the AC conductivity is directly proportional to the AC frequency. It is observed from Figure 5 that at any frequency, the AC conductivity of CeO_2 nanostructures increases with the increase in Mg doping concentration levels. As with Mg doping, the Mg^{2+} ions replaces Ce^{4+} ions. Hence, it is reasonable to argue that with Mg doping there will be more electrons in the system, which results in the increase of AC conductivity of CeO_2 nanostructures. Furthermore, to attain charge neutrality, defects will be created in the system that in turn will lead to enhanced electrical conductivity.

To evaluate the cytotoxicity of $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures for cancerous SH-SY5Y cell lines and healthy HEK-293 cell lines, both cell lines were grown separately in DMEM with 10 pct FBS for 24 hours and their effects

Fig. 4—UV-visible absorption spectra of the synthesized nanostructures.

Fig. 5—AC conductivity vs AC frequency plot for nanostructures.

on SH-SY5Y cells and HEK-293 cells were tested. To investigate the cell viability, optical microscopy of both types of cells was performed. As a result, the total cell number was quantified both with and without doped and undoped nanostructures.

The cell viability assay, as depicted in Figure 6, indicates that $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures show selective cytotoxicity. These prepared samples were found to be cytotoxic for SH-SY5Y cell line as the graphs indicate that the number of cancer cells after treatment with the synthesized $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures was decreased significantly. However, it can also be concluded from cell viability assay that undoped CeO_2 nanostructures as well Mg doped ceria nanostructures are noncytotoxic for HEK-293 cells as there is no change observed in the cell viability assay of HEK-293 cells, thus, making all synthesized samples biocompatible. Now, the question of why the synthesized nanostructures have this differential cytotoxicity arises. Uncontrolled and excess production of ROS in cells always has damaging effects on the cells. Therefore, exposing the cells to external chemicals induces oxygen-containing radicals in the

Fig. 6—Effect of the prepared $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures on neuroblastoma and HEK-293 cells viability.

cells, thus, creating imbalance in the amount of ROS within the cells. The excess ROS generated causes oxidative stress in the cells, thus, leading to the destruction of cells *via* cell membrane rupture, apoptosis, and even necrosis. ROS generation is strongly dependent on the type and environment of the cells. Healthy cells provide a basic atmosphere that supports the redox cycle between +3 and +4 oxidation states of cerium, thus, resulting in no increase in ROS in the cell. However, cancer cells have a slightly acidic atmosphere that does not support this redox cycle between oxidation states but increases the generation of free radicals by oxidation of lipids, proteins, and various enzymes present in the cancer cells. As a result, the ROS level in the cell increases and the oxidative stress causes cell death.^[40–44]

To evaluate whether the differential cytotoxicity of the $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures is due to ROS generation, the ROS generation analysis for both types of cell lines was conducted. It can be observed from Figure 7 that ROS generation in cancer cells has increased considerably after treatment with undoped CeO_2 and increases only slightly after incubation of Mg doped CeO_2 . The increased ROS has drastic effects on cancer cells, thus, confirming that the prepared samples can be employed for neuroblastoma treatment. Figure 7 also depicts that a negligibly small increase can be observed in ROS production for the HEK-293 cells, thus, making $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures biocompatible and safe for healthy cells. Hence, the selective cytotoxicity of the synthesized nanostructures may be attributed to the ROS generation.

IV. CONCLUSIONS

In conclusion, Mg ions are successfully doped into CeO_2 host lattice. It has been found that Mg doping has decreased the lattice constants and average crystallite sizes. FTIR spectra also supports the formation of a single-phase cubic fluorite structure for undoped and

Fig. 7—Reactive oxygen species (ROS) production in neuroblastoma and HEK-293 cells after incubation with $\text{Mg}_x\text{Ce}_{1-x}\text{O}_2$ nanostructures.

Mg doped nanostructures. It can be concluded that the optical band gap energy of CeO_2 nanostructures is significantly reduced upon Mg doping. Furthermore, electrical conductivity is observed to increase with Mg doping. The prepared nanostructures have inhibited the cancer cell viability without damaging the healthy cells. The differential cytotoxic nature of synthesized $\text{Mg}_x\text{CeO}_{2-x}$ nanostructures makes them a potential option for future anticancer therapeutic applications.

ACKNOWLEDGMENTS

This work is funded by the Higher Education Commission of Pakistan (HEC) IPFP (Grant No: PM-IPFP/HRD/HEC/2011/3386) to Dr. Javed Iqbal Saggi. Plagiarism of this article was carried via turnitin (ID: 586264114).

CONFLICT OF INTEREST

The authors report no conflict of interest in this work.

REFERENCES

1. A.I.Y. Tok, F.Y.C. Boey, Z. Dong, and X.L. Sun: *J. Mater. Process. Technol.*, 2007, vol. 190, pp. 217–22.
2. J. Kaspar, M. Graziani, P. Fornasiero, K.A. Gschneidner, Jr, and L. Eyring: *Handbook on the Physics and Chemistry of Rare Earths: The Role of Rare Earths in Catalysis*, Springer, Berlin, 2000, vol. 29, pp. 159–267.
3. C.W. Sun, H. Li, and Q.L. Chen: *Energy Environ. Sci.*, 2012, vol. 5, pp. 8475–505.
4. A. Corma, P. Atienzar, H. Garcia, and J.Y.C. Chin: *Nat. Mater.*, 2004, vol. 3, pp. 394–97.
5. L. Yang, S.Z. Wang, K. Blinn, M.F. Liu, Z. Liuand, and Z. Cheng: *Science*, 2009, vol. 326, pp. 126–29.
6. C. Xu and X. Qu: *NPG Asia Mater.*, 2014, vol. 6, p. e90.
7. A. Trovarelli: Catalytic Science Series, in *Catalysis by ceria and related materials*, G.J. Hutchings, ed., Imperial College Press, London, 2002.

8. D.G. Shchukin, D.G. Shchukin, and R.A. Caruso: *Chem. Mater.*, 2004, vol. 16, pp. 2287–92.
9. L. Qian, J. Zhu, W. Du, and X. Qian: *Mater. Chem. Phys.*, 2009, vol. 115, pp. 835–49.
10. N. Izu, W. Shin, N. Murayama, and S. Kanzaki: *Sens. Actuat. B*, 2002, vol. 87, pp. 95–98.
11. CW Sun, Z Xie, CR Xia, H Li, and LQ Chen: *Electrochem. Commun.*, 2006, vol. 8, pp. 833–838.
12. Y. Huang, Y. Cai, D Qiao, and H Liu: *Particuology*, 2011, vol. 9, pp. 170–73.
13. Y. Fu, C Lin, and C.S. Hsu: *J. Alloy. Compd.*, 2005, vol. 391, pp. 110–14.
14. S. Mitra, A. Mandal, S. Banerjee, A. Dutta, S. Bhattacharya, A. Bose, and D. Chakravorty: *Indian J. Phys.*, 2011, vol. 85, pp. 649–55.
15. J. Bhadra and D. Sarkar: *Indian J. Phys.*, 2010, vol. 84, pp. 1321–25.
16. H. Li, G. Wang, F. Zhang, Y. Cai, Y. Wang, and I. Djerdj: *RSC Adv.*, 2012, vol. 2, pp. 12413–23.
17. A. Hadi and I. Yaacob: *Mater. Lett.*, 2007, vol. 61, pp. 93–96.
18. H. Schulz, W.J. Stark, M. Maciejewski, S.E. Pratsinis, and A. Baiker: *J. Mater. Chem.*, 2003, vol. 13, pp. 2979–84.
19. X. Dong, G. Hong, D. Yu, and D. Yu: *J. Mater. Sci. Technol.*, 1997, vol. 13, pp. 113–16.
20. H. Oh and S. Kim: *J. Aerosol Sci.*, 2007, vol. 38, pp. 1185–96.
21. H.S. Kang, Y.C. Kang, Y.C. Kang, H.Y. Koo, S.H. Ju, S.H. Ju, D.Y. Kim, and S.K. Hong: *Mater. Sci. Eng. B*, 2006, vol. 127, pp. 99–104.
22. S. Kim and J. Maier: *J. Electrochem. Soc.*, 2002, vol. 149, pp. 73–83.
23. M. Kamruddin, P.K. Ajikumar, R. Nithya, A.K. Tyagi, and B. Raj: *Scripta Mater.*, 2004, vol. 50, pp. 417–22.
24. J. Hu, Y. Li, X. Zhou, and M. Cai: *Mater. Lett.*, 2007, vol. 6, pp. 4989–92.
25. L. Li and Y. Chen: *Mater. Sci. Eng. A*, 2005, vol. 406, pp. 180–85.
26. F. Bondioli, A.B. Corradi, T. Manfredini, G. Leonelli, and R. Bertoncello: *Chem. Mater.*, 2000, vol. 12, pp. 324–30.
27. K.B. Zhou, X. Wang, X.M. Sun, Q. Peng, and Y.D. Li: *J. Catal.*, 2005, vol. 229, pp. 206–12.
28. M.M. Natile, G. Boccaletti, and A. Glisenti: *Chem. Mater.*, 2005, vol. 17, pp. 6272–86.
29. J.C. Yu, L. Zhang, and J. Lin: *J. Colloid Interface Sci.*, 2003, vol. 260, pp. 240–46.
30. E.N. Ndifor, T. Garcia, B. Solsona, and S.H. Taylor: *Appl. Catal. B*, 2007, vol. 76, pp. 248–56.
31. D. Channei, B. Inceesungvorn, N. Wetchakun, S. Phanichphant, A. Nakaruk, P. Koshy, and C.C. Sorrell: *Ceram. Int.*, 2013, vol. 39, pp. 3129–34.
32. F. Abbas, J. Iqbal, T. Jan, M.S.H. Naqvi, A. Gul, R. Abbasi, A. Mahmood, I. Ahmad, and M. Ismail: *J. Alloy. Compd.*, 2015, vol. 648, pp. 1060–66.
33. F. Abbas, T. Jan, J. Iqbal, I. Ahmad, M.S.H. Naqvi, and M. Malik: *Appl. Surf. Sci.*, 2015, vol. 357, pp. 931–36.
34. V. Thangadurai and P. Kopp: *J. Power Sources*, 2007, vol. 168, pp. 178–83.
35. J. Iqbal, T. Jan, M. Ismail, N. Ahmad, A. Arif, M. Khan, M. Adil, and A. Arshad: *Ceram. Int.*, 2014, vol. 40, pp. 7487–93.
36. T. Wang and D.C. Sun: *Mater. Res. Bull.*, 2008, vol. 43, pp. 1754–60.
37. F. Chevre, F. Munoz, C.F. Baker, F. Tessier, O. Larcher, S. Boujday, C. Colbeau-Justin, and R. Marchand: *J. Solid State Chem.*, 2006, vol. 179, pp. 3184–90.
38. S. Phoka, P. Laokul, E. Swatsitang, and V. Promarack: *Mater. Chem. Phys.*, 2009, vol. 115, pp. 423–28.
39. N. Shehata, K. Meehan, K. Meehan, M. Hudait, M. Hudait, and N. Jain: *J. Nanopart. Res.*, 2012, vol. 14, pp. 1173–82.
40. X. Zhou, L.L. Wong, A.S. Karakoti, S. Seal, and J.F. McGinnis: *PLoS ONE*, 2011, vol. 6, p. 16733.
41. F. Abbas, T. Jan, J. Iqbal, and M.S.H. Naqvi: *Curr. Appl. Phys.*, 2015, vol. 15, pp. 1428–34.
42. J. Chen, S. Patil, S. Patil, S. Seal, and J.F. McGinnis: *Nat. Nanotechnol.*, 2006, vol. 1, pp. 142–150.
43. T. Xia, M. Kovoichich, M. Liong, L. Madler, B. Gilbert, H. Shi, and A. Nel: *ACS Nano*, 2008, vol. 2, pp. 2121–34.
44. W. Lin, Y.W. Huang, X.D. Zhou, and Y. Ma: *Int. J. Toxicol.*, 2006, vol. 25, pp. 451–57.