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CONTROLLING THE FLOW OF NASCENT OXYGEN USING HYDROGEN PEROXIDE RESULTS IN CONTROLLING THE SYNTHESIS OF ZnO/ZnO_2

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A study has been carried for the oxidation of zinc hydroxide by controlled flow of nascent oxygen using sodium perborate ($NaBO_3$ $4H_2O_2$), which leads to the formation of nano-sized zinc oxide (ZnO), while the uncontrolled flow of nascent oxygen leads to the formation of zinc peroxide (ZnO_2). X-ray diffraction studies of the synthesized materials indicated pure phases and nanocrystalline nature of zinc oxide and zinc peroxide. The average crystallite sizes of the zinc oxide and zinc peroxide powders using Scherrer formula were estimated to be 20-30 nm and 5-6 nm, respectively. The oxidation process of zinc hydroxide were carried out at 50 ^{0}C ± 5 ^{0}C. Various steps for the synthesis of zinc oxide/zinc peroxide and synthesis mechanism has been discussed in this paper. The process is eco-friendly and does not add any toxic pollutants in the air. The scanning electron micrographs of the synthesized zinc oxide and zinc peroxide show the spherical nature of the particles.

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1. Introduction

The metal oxides have potential applications in fields like catalyst, magnetic materials, optoelectronic, semiconducting and sensor materials [1-7]. Out of these oxides zinc oxide is a transparent electro conductive and piezoelectric material having several applications in the electronic, photonic photo cells and laser diodes devices. Zinc oxide has a band gap of 3.37 eV and exciton binding energy of 60 meV and shows efficient UV stimulated emission at room temperature [8]. A substantial effort is therefore placed on utilizing such properties within a new generation of short wavelength photonic devices. The shape and the size of the nano zinc oxide govern its properties [9-11]. In wet chemical route most of the zinc oxide nanoparticles of various morphologies have been synthesized by the decomposition of zinc compounds through decomposition / oxidation at different temperatures.

Zinc peroxide is an odorless white or yellowish temperature stable solid. It decomposes at 150 ^{0}C and releases oxygen and converts in to zinc oxide. It is used for making a foamed product of high melting synthetic resin and as an accelerator in the vulcanization of polysulphide rubber. It is also used in explosives as an oxidant and oxygen donor.

Chemical route for synthesizing nanomaterials at low temperature provides excellent control over metastable phases, uniform homogeneity, particle sizes and morphologies of the synthesized nanomaterils. The wet chemical route has various advantages over the conventional high temperature solid-state reactions [12-16] as it requires some low cost instruments. Several researchers have reported preparation of metal oxides through wet chemical methods [17-20]. M. Sun et al [21] have synthesized zinc peroxide and zinc oxide under sunlight irradiation. In the

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*Corresponding authors: naharsingh@mail.nplindia.org present paper an attempt has been made to synthesize nano particles of zinc oxide and zinc peroxide through a simple wet chemical route at 50 ^{0}C ± 5 ^{0}C temperatures by oxidation of zinc hydroxide using control nascent oxygen generated from sodium perborate and uncontrolled oxygen generated by hydrogen peroxide respectively. The zinc peroxide can be synthesized at ambient temperature but here we have synthesized at 50 ^{0}C ± 5 ^{0}C to get more yield in less time and to check the effect of thetemperature. the formation of particles of zinc oxide has been explained using aqueous co-ordination chemistry of Zn^{2+} ion [22, 23].

2. Experimental

2.1 Synthesis of zinc oxide and zinc peroxide

For the synthesis of zinc oxide 6.58 gm of zinc acetate (make Loba Chemie India) was dissolved in minimum quantity of de-ionized water (18.2-mega ohm resistivity water prepared by Millipore Milli-Q element). Ammonia solution (make Merck India) was added to this solution drop by drop; initially zinc precipitated as zinc hydroxide and finally gets dissolved on adding 4-5 mL of ammonia solution. Further 2-3 mL of ammonia solution was added to the zinc oxide solution for complete dissolution of zinc hydroxide and to stop further precipitation. 100 ml methyl alcohol was added to clear the turbidity of the solution. Further, 4.62 g of sodium perborate was dissolved in 100 mL of de-ionized water and methanol mixture (20:80). This solution was added to the dissolved solution of zinc hydroxide at pH 10-10.5 slowly drop by drop with constant stirring using a magnetic stirrer at 50 ^{0}C ± 5 ^{0}C. The solution was further stirred for 2 hours and was kept for over night. The particles get precipitated as floating in the solution. While for the synthesis of zinc peroxide an equimolar solution of hydrogen peroxide solution was added drop by drop in the solution of zinc hydroxide at the same temperature range as in case of zinc oxide with constant stirring. The precipitates of both the reactions were boiled with 5% ammonium hydroxide and filtrated through Whatman filter paper number 42. The precipitates were washed several times with hot dilute 2% ammonical water and methanol to dissolve remaining impurities of zinc hydroxide, un-reacted sodium perborate etc. Finally both the precipitate were dried in oven at 105 ^{0}C.

2.2 Formation of zinc peroxide and zinc oxide

Hydrogen peroxide acts as a strong oxidizing agent in acidic as well as alkaline medium and readily forms nascent oxygen when dissolved in water. The 50% solution of hydrogen peroxide contains minimum 23.5% active oxygen. The strength of O-O bond is of fundamental importance in a variety of chemical process and a value of 34 kcal/mol has been ascribed to a generic O-O bond energy. The bond dissociation energy in hydrogen peroxide is 47 kcal/mol. When 50% aqueous solution of hydrogen peroxide gets mixed with water it decompose into water and nascent oxygen. When hydrogen peroxides decompose one volume of hydrogen peroxide releases ten volumes of oxygen and the nascent oxygen oxidized zinc hydroxide in alkaline medium in zinc peroxide. The reaction takes place as follows:

$$H_2O_2 \longrightarrow H_2O + 1/2\ O_2 \qquad \Delta G^0 = -122.6\ \text{k J}$$

$$Zn(OH)_2 + [O] \longrightarrow ZnO_2 + H_2O$$

On the other hand sodium perborate trihydrate contains maximum 10.4% active oxygen which is less than half of the evolved by the direct hydrogen peroxide and dissociation energy of sodium perborate trihydrate is higher than the hydrogen peroxide. So it takes larger times to release nascent oxygen to oxidize zinc hydroxide. Under hydrolysis with water, sodium perborate forms hydrogen peroxide very slowly in comparison to direct hydrogen peroxide because the dissolution rate of sodium perborate trihydrate in water is approximate 6 to 8 minutes(2 g/L) at 15 ^{0}C), which releases oxygen step by step in a control way and forms zinc oxide. The possible mechanism of formation of zinc oxide could be explained in two-step process i.e. (i) Nucleation of zinc oxide crystal, (ii) Growth of zinc oxide crystal. Nucleation of zinc oxide crystal depends upon the concentration of the precursors, pH and temperature. In this method the possible reaction is as follow:

$$Zn(CH_3COO)_2 + 2NH_4OH \longrightarrow Zn(OH)_2 + 2CH_3COO\,NH_4$$

$Zn(OH)_2$ formed is amphoteric and it dissolves in excess of NH_4OH and forms $[Zn(OH)_4]^{-2}$.

$$Zn(OH)_2 + 2NH_4OH \longrightarrow [Zn(OH)_4]^{-2}$$

The Raman spectra of Zn^{2+} ions (of $ZnCl_2$ in aqueous solution), had shown the presence of $[Zn(H_2O)_6]^{2+}$, $ZnCl^+$, $ZnCl_2$ and $[ZnCl_4(H_2O)_2]^{2-}$ ions. Analogous to this, it is proposed that in the intermediate solution $[Zn(OH)_4(H_2O)_2]^{-2}$ is formed instead of $[Zn(OH)_4]^{-2}$ and $Zn(OH)_2$ forms tetra amine zinc(II) ions as given below.

$$Zn(OH)_2 + 4NH_4OH \longrightarrow [Zn(OH)_4(H_2O)_2]^{-2} + [Zn(NH_3)_4]^{+2} + 2OH^- + 4H_2O$$

Thus, it is proposed that in the intermediate solution $[Zn(OH)_4(H_2O)_2]^{-2}$ and $[Zn(NH_3)_4]^{+2}$ ions are present. The aqueous solution of sodium perborate dissociates itself to give nascent oxygen. The released nascent oxygen approaches $[Zn(OH)_4(H_2O)_2]^{-2}$ ion in between the ligands as shown schematically in the fig-1. In the process to approach Zn^{++} central metal ion it takes charge from the OH^- ligand ions and forms O^{-2} ions and further forms zinc oxide. The bond formation energy of zinc oxide at room temperature and 60 ^{0}C - 70 ^{0}C is accomplished by breaking of four OH^- and two H_2O co-ordinate bonds with the central metal ion Zn^{2+}, while O^{-2} ion is approaching Zn^{2+} ion of the intermediate complex, $[Zn(NH_3)_4]^{+2}$ ion present in the solution tries to approach O^{-2} ion and form zinc oxide bond. The breaking of the four co-ordinates NH_3 bonds with the Zn^{2+} ion supports the energy of bond formation. This process repeats and the crystal growth takes place. The reaction takes place as follows:

$$Zn(OH)_2 + Na\,BO_2H_2O.3H_2O \longrightarrow ZnO + NaOH + 4H_2O + HBO_3$$

3. Results and discussion

Synthesized zinc oxide and zinc peroxide powders were characterized for it various phases by X-ray diffraction (XRD) using Bruker AXS D8 Advance Diffractometer. Data collection and analysis were carried out using Diffrac^{plus} software. Diffractograms were recorded using CuKα radiation. The diffraction patterns were recorded in the 2θ range from 20^0 to 70^0 for ZnO and 20^0 to 80^0 for ZnO_2 as given in the Fig. 2(a) and 2(b). XRD pattern of the zinc oxide powder is shown in Fig.2 (a) while XRD pattern of the zinc peroxide is given in the fig. 2(b). All observed diffractions peaks in fig. 2(a) correspond to hexagonal zinc oxide (PDF# 36-1451) and those in fig.2(b) correspond to zinc peroxide (PDF # 13-0311) confirming formation of a single-phase material in each case. Crystallite sizes were estimated by using Scherrer's equation [24]. The FWHMs of the peaks were estimated by fitting analytical profiles to the experimental profiles. Contributions of instrumental broadening to the FWHMs were estimated by using XRD standard reference material such as silicon powder from NIST USA. The crystallite size of zinc oxide particles is estimated to be about 20-30 nm whereas crystallite size of zinc peroxide particles is about 5-6 nm.

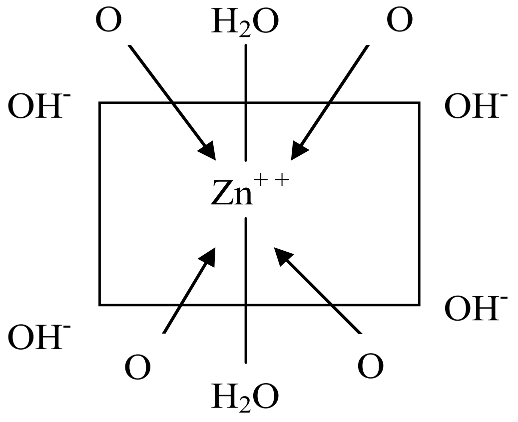

Fig. 1. Schematic diagram for the proposed mechanism for the synthesis of zinc oxide

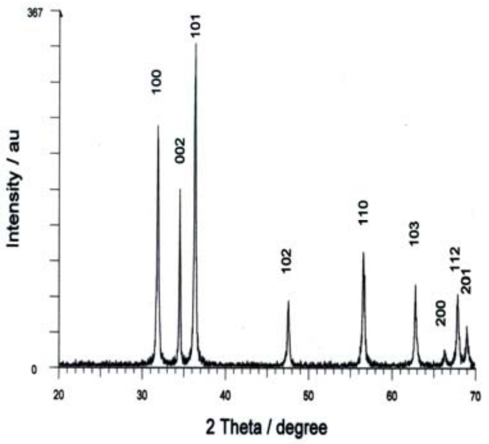

Fig. 2 (a) XRD Pattern of ZnO

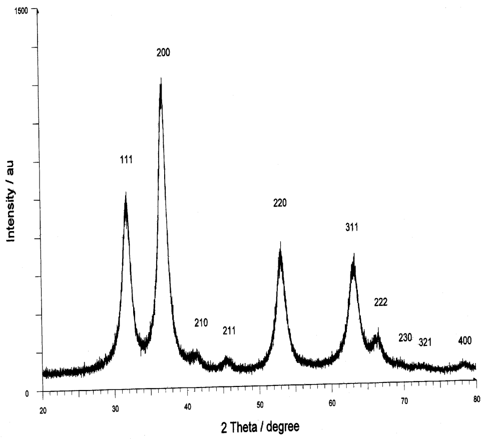

Fig. 2 (b) XRD pattern of ZnO_2

The surface morphology of both the samples was examined by using LEO 440 Scanning Electron Microscope (SEM). The SEM photographs are as shown in the fig.3 (a) &3(b) for zinc oxide at two different magnifications, while 4(a) & 4(b) represents the micrograph for zinc peroxide at different magnifications. The micrographs were recorded at 2.5 kX and 5 kX magnifications and are presented in fig. 3(a) and fig. 3(b) for zinc oxide and fig. 4(a) and fig. 4(b) for zinc peroxide. The surface morphology as given in fig. 3(a) at 2.5 kX magnification for zinc oxide shows flower like microstructures with needle-like projections and 5 kX magnification shows spherical shaped particles as presented in fig. 3(b). But in some of the flowers agglomerations tendency were also observed. SEM micrographs for zinc peroxide as given in fig. 4(a) and fig. 4(b) at 2.5 kX and 5 kX magnifications shows hexagonal morphologies of the synthesized material. The morphology for both materials has been recorded throughout the sample implying homogenous nature of the zinc oxide.

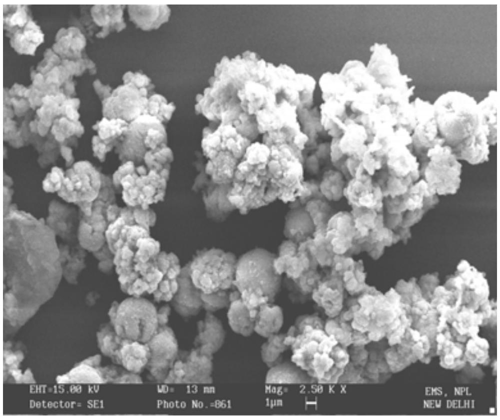

Fig. 3(a) SEM micrograph of ZnO powder at 2.5kX magnification

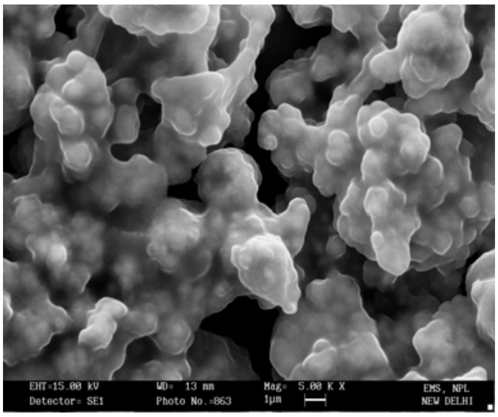

Fig. 3(b) SEM micrograph of ZnO powder at 5kX magnification

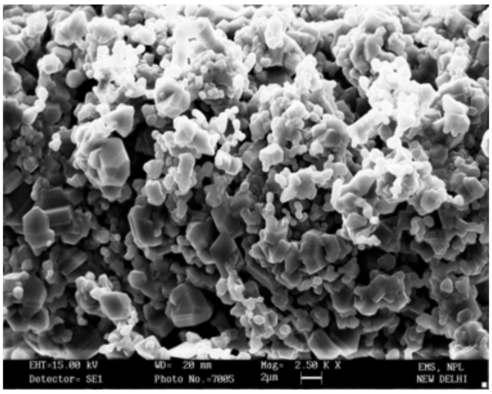

Fig. 4(a) SEM micrograph of ZnO_2 powder at 2.5 kX magnification *powder at 2.5kX magnification*

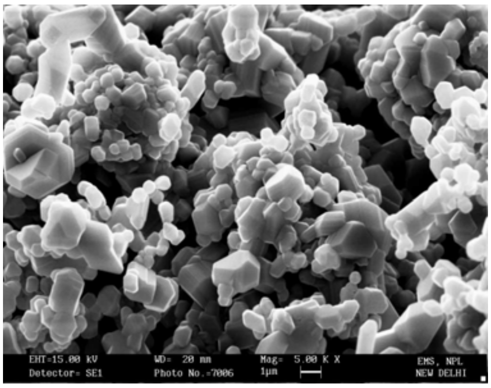

Fig. 4(b) SEM micrograph of ZnO_2 *powder at 5kX magnification*

4. Conclusions

We have described the synthesis mechanism of crystalline zinc oxide and zinc peroxide nanoparticles by the reaction of zinc acetate via zinc hydroxide with sodium perborate and hydrogen peroxide respectively in 30% methanol at temperature of 50 0C ± 5^{o}C. The process gives information on how zinc oxide and zinc peroxide are formed by the reaction of zinc hydroxide with sodium perborate containing hydrogen peroxide and hydrogen peroxide alone. The method also suggests the role of controlled oxygen in the formation of zinc oxide and zinc peroxide. The method is very simple, eco friendly to the environment and the method does not release any toxic gases in the environment.

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References

[1] H. Zhang, D. Yang, X. Ma, Y. Ji, J. Xu and D. Que, Nanotechnology; **15**, 622 (2004).
[2] C. C. Hsu, N. L. Wu, J. Chin. Colloid & Interface Soc; **26**, 191(2004).
[3] V.A. Karpina, V. I. Luzorenko, C. V. Lashkarev, V.D. Dobrowolski, I. I. Kopylova, V. A. Baturin, S. A. Pustovoytov, A. Ju. Karpenko, S.A. Eremin, P. M. Lytvyn, V. P. Ovsyannikov and E. A. Mazurenko, Cryst. Res. Technol; 39, 980 (2004).
[4] Y. Yan, P. Liu, M. J. Romero and M.M. Al-Jassim, J of Applied Physics; **93**, 4807(2003).
[5] S. P. Singh, O. Perales-Perez, M.S.Tomar, A. Parra-Palomino, A.Ruiz-Mendoza, NSTI-Nanotech; **2**,1(2005).
[6] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, W. E. Russo R and Yang, Science; **292**, 1897(2001).
[7] Z. Fan, D. Wang, P.C. Chang, W. Y. Tseng and J.G. Lu, Appl. Phys. Lett; **86**, 5923(2004).
[8] Karpina V A et al. Cryst. Res. Technol; **39**, 980(2004).
[9] J. Zhang, Y. Yang, B. Xu, F. Jiang and J. Li, J of Crystal Growth; **280,** 509 (2005).
[10] C. X. Xu, A. Wei, X. W. Sun and Z. L. Dong, J. Phys. D. Appl. Phys; **39**, 1690 (2006).
[11] L. Vayssieres, Adv. Mater; 15, 464 (2003).

[12] Z. Gui, R. Fan, W. Mo, X. Chen, L. Yang, H. Yuan, Material Research Bulletin; **38**, 169(2003).

[13] H. Zhang, D. Yang, Y. Ji, X. Ma, J. Xu and D. Que, The J of Phy Chem B; **108**, 3955(2004).

[14] F. Zhnag L. Q. Jin and Siu –Wai Chan, J. Applied Phys; **95**, 4319(2004).

[15] H. Zhang, D. Yang, D.Li, X. Ma, S.Li and D. Que; J. of Crystal Growth and Design; **5**, 547 (2005).

[16] J. Zhang, Y. Yang, B. Xu, F. Jiang and J. Li, J. of Crystal Growth; **280**, 509 (2005).

[17] B.G. Wang, E.W.Shi, W.Z.Zhong, Cryst. Res. Rechnol; **33**, 937 (1998).

[18] J. Zhang, L. Sun, J. Yin, H. Su, C. Liao and C. Yan, Chem. Mater;**14**, 4172(2002).

[19] J. Liu, X. Huang, Y. Li, Q. Zhong and L. Ren, Materials Letters; **60**, 1354 (2006).

[20] F. Wen, W. Li, J.H. Moon, J.H.Kim, Solid State Communications; **135**, 34(2005).

[21] M. Sun, W. Hao, C. Wang and T. Wang; Chemical; Physics Letters, **443**, 342(2007).

[22] F. Albert. Cotton and Geoffrey Wilkinson, Advanced Inorganic Chemistry, Third edition, Publisher Wiley Eastern Limited New Delhi, 511-512 (1986).

[23] Nahar Singh, P. Johri, D. Soni, Rashmi, S. Singh, S.P. Singh, Prabhat K. Gupta, K. N. Sood, and H. Chander; Main Group Metal Chemistry; **30**, 213(2007).

[24] B.D. Cullity, Elements of X-ray Diffraction, second edition, Addition Werkey, USA, 978, P102.