Estimation of the fundamental properties of Zinc Oxide molecule: A nanoparticle based study in a photodynamic system

Vinamra Chaturvedi, Mukesh Kumar Roy

Abstract— Zinc Oxide (ZnO) makes and excellent starting material for several applications in the cosmetics,paints,semiconductors and the other 'green' industries.Diverse processing technologies enable control of properties like shape and size of the dust sized powdered particles. Robust checking of the particles at the nano-size level is important to retain purity of the content .This is possible by monitoring the chemical processes involved during the manufacturing as well as the application stage .This approach eliminates unwanted risks associated with re-engineering (for example,expensive highly processed semiconductor grade products finding way into cosmetic industry).Since powder grade ZnO has found way into skin protection creams, benefits of such a rigourous testing are many including large scale production from chemically repeatable processes as well as reuse of exotic and expensive materials in drug industry.The present communication,attempts to establish a procedure to engineer such material systems at a molecular level.Fourier Transform Infra Red (FTIR) based spectroscopic data is used to roughly estimate the bond length of the molecule.Another important parameter called the Moment of Inertia is calculated with a rigid rotor assumption.As the paper suggests ,both of the parameters play an important role in determining the strength of the material system in a complex photo-dynamic environment such as the one that exists on a sun-tan cream covered human skin.

Index Terms—Zinc Oxide (ZnO),Nano-particles, Fourier Transform Infra Red Sepctroscopy,Thin Films,X-Ray Diffraction (XRD), Scherrer Approximation,Bond Length.

1 INTRODUCTION

The bulk physical properties, of Zinc Oxide (ZnO) material system, make it an interesting candidate for applications as diverse as semiconductor technology, optoelectronics, cosmetics, paints and medicine [1]. There are several research groups engaged in studying the properties, that test the diversity of its application .While most of the research efforts are directed towards studying specific application, important fundamental properties need particular attention. This is important, to mitigate, the deleterious effects of indiscriminate use in the wide technology spectrum.

One such example is the usage of Metal Oxides based nanoparticles in "skin-protection" creams. While the major intent of adding ZnO in cosmetic creams is the protection, against the harmful UV radiations, an unwanted side effect of this application is the "breakage" of ZnO bond into harmful radicals ,commonly known as reactive oxygen species[2] (ROS). Since the reaction is triggered by the exposure of UV rich sun-light, the phenomena needs to be investigated further.Recent reports have pointed out towards the presence of such radicals enhancing the risks of cancer rather than providing protection against it..

We have limited our study to the theoretical physio-chemical aspect of ZnO based nanoparticles, with an aim to study the fundamental properties that are linked to the breakage of bond between Zinc and oxygen in a photodynamic environment such as the one present over the sun tan cream protected human skin.

SOME BACKGROUND INTO THE SCALE OF OUR PROBLEM

Of the several approaches towards the limiting this breakdown into benign species (rather than ROS), changing the composition to non-Zinc based material system has been debated extensively. Efforts to standardize chemical contents of such sunscreen protection face several difficulties including : a) variable UV-exposure on the Earth surface, b) multi-branding of skin treatment creams c)possibly loose and somethimes contradictory regulatory frameworks realted to the Global Food and Drug quality administration, particularly in case of dermatology d) preferred delivery method (creams, lotions, masks etc.,)

ZnO is an interesting candidate for such a study, not only because it is readily used in skin based cosmetics, but, also because it can be processed using multiple chemical processing techniques. Additionally, ZnO based nanoparticles, are considered as cheap and biocomaptiable when compared to other metal based oxides [3].

2 EXPERIMENT

2.1 Chemical Processing

ZnO Samples were processed using a conventional wet chemistry route. A molar solution of Acetic Acid (CH_3COOH) and Sodium Hydroxide (NaOH) was prepared. The solution was thermally activated at a temperature of 80^0C and subsequently transferred to a partially anaerobic furnace (preheated at 150^0C).The reaction was allowed to proceed, while the changes in physical state of the reactants (so far in liquid phase) were closely monitored at short (minute sized) intervals.

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It was noticed that the liquid transforms itself into an agglomerated state of "fluffy mass " with dark brownish appearance. While it is very difficult to monitor the chain of events on a real time basis due to the enclosed nature of the furnace, it can be stated with some degree of confidence that the process of the formation of fluffy mass is akin to the physical state of milk beyond its boiling point but way before tarring sets in. The "fluffy" system of the remaining mass is, then brought out of the furnace to facilitate rapid heat dissipation.

Upon cooling, the fluffy system is crushed using laboratory grade butter paper (using hand pressure in simple roller action).This results in a powdery mass of dark brownish substance.

The contents are poured into regular high temperature crucibles .The crucibles are further heat treated in hourly cycle's of elevated temperature (ranging from 350^{o}C to 950 ^{o}C).Each temperature cycle lasts for an hour (including the loading and unloading time, which is negligible in our case).Further mechanical crushing of the samples, results in powdery substance that assumes striking color contrast as seen in Figure 1.

Fig. 1. Samples A, B, C & D were processed at 350^{o}C, 500^{o}C, 650^{o}C & 900^{o}C in a furnace for an hour.

Mechanical crushing, into powder form, using standardized procedure was done to further the granularization.

2.2 Material Analysis of Sample

Analytical tests were conducted on the samples in order to confirm the formation of ZnO particles in the aforementioned powder.

X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) studies[4] conducted on these samples resulted in rocking curves with 2θ peaks appearing at between 30 & 40 (see Figure. 2).These results confirm the presence of a crystallite state of the Zinc Oxide material system in the powdered samples. A full wave half maximum analysis (FWHM) approach of using, Scherrer's approximation [5] to XRD peaks, results in particle size ranging from 15 nm to 50 nm. It may be noted that this estimate is based upon spherical geometries approximation

While X-Ray diffraction is a standard procedure in powder grade samples as well as thin films, it is sometimes considered insufficient as it focused on the end product more than the process [6].

Further investigation s were thus conducted in order to adapot a in-situ approach to the quality check procedure.here we have adapted the Fourier Transform based Infra red (FTIR) based test procedure to monitor the quality of the reaction products.

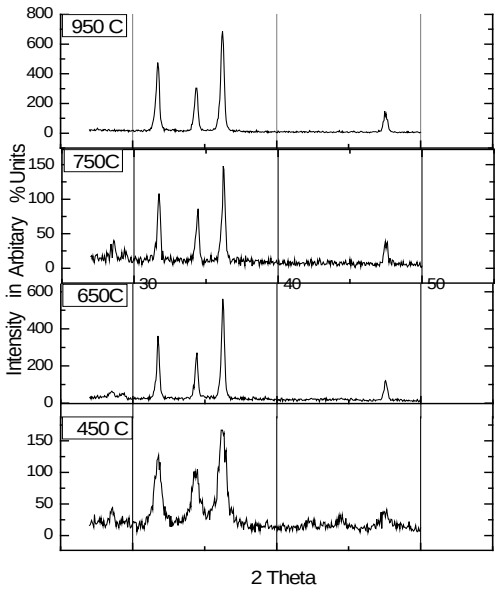

Fig. 2. XRD Plots of two different samples processed at different temperature with "stable" peaks, confirming presence of Zinc Oxide in crystalline s.

Fourier Transform Infra-Red Spectroscopy (FTIR)

The basic FTIR graph [7] (as shown in Fig3) is an attempt to confirm the existence of ZnO as an inorganic functional group in the overall reaction. Additionally and perhaps more importantly, it serves as a starting point for the Mathematical treatment. From the FTIR micrographs of ZnO "dust-like particles" (see FIG 3.) we approximate the physical parameters (like Bond Length & Moment of Inertia) of a simple diatomic hetero-structure. In doing this we have approximated the breakdown of Born-Oppenheimer approximation that deals with the "real" versus "ideal" part of the rotational and vibrational spectrums .Additionally it restricts itself to the rigid rotor model that forms the basis of many molecular spectroscopy based studies.

Recent reports [8], point towards the existence of ZnO molecule around the 400 to 500 wavenumber range in a FTIR micrograph .In our case a distinct peak around 432 wavenumber points towards the presence of ZnO group.

It should be noted that most of the spectroscopic testing in case of a wide bandgap semiconductor like ZnO should be conducted on a wide range equipment as the exciting wavelength of the radiations involved in such studies falls under the borderline values of the equipments.Careful calibrations using standardized powder was done before the start of an experimental run.[9]

Samples are carefully diluted in order to make sure that physio-chemical reactions don't happen during the act of spectroscopic investigation.This is absolutely necessary to make sure that the original state of the sample is retained even after the light based investigations are completed.

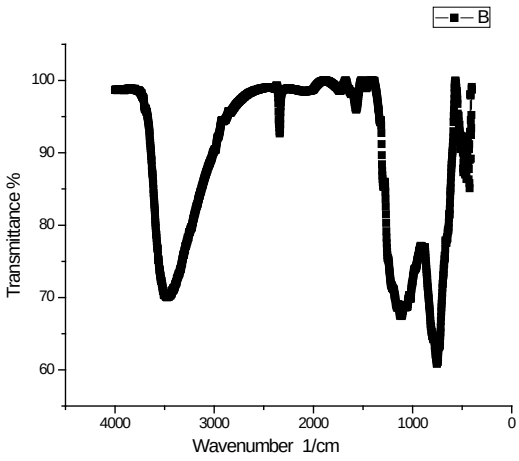

Fig. 3. Fourier Transform Infra-Red (FTIR) spectrograph of powdered bulk sample conducted on a Shimadzu test tool.

3 Equations & Calculations

Most of the spectroscopic studies are based on the principle of exciting the existing states to a higher level and observing the resulting radiation while the source of excitation is withdrawn.[10]

In order to raise a molecule from the state J to state J+1, the wave number peaks would shift from $\nu_{J \to J+1}$.

Mathematically this transition is depicted by

$$\nu_{J \to J+1} = 2B\,(J+1)\ cm^{-1},$$

where B is the Rotational Constant and is given by $B = (h)/8\pi^2 I_B c$ with I_B being the Moment of Inertia of the diatomic hetero-molecule under rotational and vibrational excitation, c the speed of light , h being the Planck's constant.

&

Where, 'J' is the Rotational Quantum number, depicting the allowed quantum states (arising out of the release of energy due to the Rotational Motion of the molecule)

From Figure (3) the ZnO peaks appear at $432/cm^3$.Now assuming a simple transition from ground state to state

$$\nu_{0 \to 1} = 432\ cm^{-1} = 2B\ cm^{-1}$$

Hence, $B = 216\ cm^{-1}$

$I_B = (h)/8\,(\pi)^2\, B\, c$

Where, $h = (6.626 \times 10^{-34}$ Joule sec)

&

$c = 2.99793 \times 10^{10}$

Therefore,

$I_B = 12.9517 \times 10^{-47}\ kg\ m^2$

Furthermore,

The Moment of Inertia (I_B) of a Diatomic Rigid Hetero Molecule (within the limits of Born -Oppenhiemer approximation [11]) can also be written as

$$= \mu r_0^2 \qquad \mu = (m_{Zn}\, m_O)/(m_{Zn} + m_O)$$

Where ,

μ Reduced Mass of the system

&

r_0 = Bond length of the diatomic molecule.

Given the relative atomic weight of

Zinc (Zn) = 65.38 & Oxygen (O) = 15.994,

Avogadro 's number = 6.022×10^{23}

Bond Length, $r_0^2 = (I_B)/\mu$

Thus,

Bond Length $= 7.779056 \times 10^{-11} = 0.779\ A^o$

4 Some Comments

MOTIVATION FOR OUR RESEARCH

While, it is important to confirm the presence of ZnO nanoparticles into the bulk powder samples, the contents of our sample should not be allowed, to be used for cosmetic sun screen protection at this point, because of the presence of molecular size impurities.

The mechanism of UV breakdown of ZnO bonds into "unmanageable" radicals (ie., the Reactive Oxygen Species, ROS) could be the result of additional impurities, (arising as remnants of chemical processing techniques) or more importantly the bio-chemical impurities present on the shallow skin).These provide the physical sites for the UV enhanced reaction to proceed. The result of such a reaction is the appearance of highly ROS.Thus a biologically active skin provides a *fertile* site for such a reaction to proceed. The variables guiding the rate of such a reaction can be several including biological factors like a)skin type, b) presence or absence of enzymes, c) cleanliness of the skin , before the treatment, etc.,

Since our approach is limited to the physiochemical reactions, we have adopted a simplistic model to study the breakdown phenomena. A diatomic hetero-structure of Zinc and Oxygen participates in UV enhanced bio-physical reaction as a rigid rotor .The resulting chemical population is rich in radicals, before the photodynamic system assumes stabilization. Thus, it becomes interesting to estimate the fundamentals physical parameters like bond length of the ZnO molecule, which may help in predicting the overall stability of the system. At this point we have limited our studies to the bond length estimates. Neither the population inversion associated with the formation of ROS during the chemical reaction nor the chemical energetics of the resulting species are considered in the above calculations.

CURRENT STATE OF RESEARCH

At this juncture of shape studies involving Scanning Electron Microscopy (SEM), appears to be the logical step to comment on the "stability" of nanostructures. The present communication, however is, restricted to the theoretical findings of the bond length parameter

.We believe that this should serve as an important first approximation indicator of the quality of nanoparticles, used, in UV protection.

Furthermore, as an "off-shoot" of this research is the purposeful controlled contamination of ZnO (also known as doping in semiconductor industry) towards the final aim of Energy and Optical band engineering.

5 Conclusion

Metal based oxides of Zinc were prepared using a simple chemical process.Several spectroscopic tests were conducted to confirm the true phase of the material.results of these tests were used to calculate basic parameters of the ZnO molecule .These basic parameters are important in judging the quality of the material and its fitment to industrial or cosmetic use.

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