

Exploring the Structure-Function Relationship in Multifunctional Nanoparticles

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ABSTRACT

Nanoparticles of ZnO are increasingly being used as a pigment and UV absorber in personal care products (e.g. sunscreens), coatings and paints, predominantly because their absorbance efficiency increases with decreasing particle size. However, whilst protection against UV may be maintained at smaller particle sizes, the rate at which hydroxyl radicals are generated increases, due to the inherent photo-activity of these materials. This paper shows that photoactivity can be reduced (by over an order of magnitude) by doping the material with small amounts metallic cations (<1 atm%). To explore whether or not the dopants have been successfully incorporated within the lattice a new variation of atom location by channelling-enhanced microanalysis (ALCHEMI) has been used. It was found that some dopants were exclusively accommodated on the cation sublattice site, whereas others existed as a foreign phase or decorated the surface. The difference in dopant location may influence consequent photoactivity and other nanoparticle behaviour

KEYWORDS: doped nanoparticle, photoactivity, zinc oxide, ALCHEMI

INTRODUCTION

Nano-particles of ZnO and TiO₂ are increasingly being used as pigments and UV absorbers in personal care products (e.g. sunscreens), coatings and paints, predominantly because their absorbance efficiency increases with decreasing particle size. However, whilst protection against UV may be maintained at smaller particle sizes, the rate at which hydroxyl radicals are generated increases, due to the inherent photoactivity of these materials. Consequently, in the case of personal care products, there may be a negative effect on skin cells due to this increased photocatalytic

activity. There is little published data that correlates photoactivity of nanoparticles with biological effects. However, *in vitro* work has shown that supercoiled DNA is indeed damaged in the presence of nanoparticulate metal oxides and the rate of unwinding itself can be used as a measure of the photoactivity of the metal oxide [1].

Alteration of the band gap is of increasing interest and may be achieved by lowering the energy gap, relative to the original system, by the introduction of dopant atoms. The majority of published data on the use of dopants to control photoactivity has been with titania [2,3].

In this paper, observations are reported on a series of undoped and doped nanosized ZnO materials designed to quench photoactivity. These were tested for photoactivity, using chemical methods, when exposed to UV. Parameters such as crystallite size, dopant type and level have been considered. Nanoparticle structure, including the location of the dopant, using a new variant of a method related to atom location by channelling-enhanced microanalysis (ALCHEMI) was used [4] and this location explored in relation to particle properties.

EXPERIMENTAL

Characterisation of Materials

A series of undoped and doped zinc oxide was prepared by proprietary methods and characterised chemically and physically. Chemical analysis was performed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) methods. Crystallite phase was determined by using a Bruker ASX-D8 X-Ray Diffractometer using Cu K α radiation over a 2 θ range of 5° to 85° with a step size of 0.02°. Crystallite size was determined by performing a

Rietveld refinement of the diffraction data using Siroquant™ Version 2.5 software.

The method established and implemented for determining the photoactivity of metal oxide particles such as ZnO and TiO₂ was that initially proposed by Dransfield et al. [5]. It is a colorimetric test that follows the photobleaching of the stable radical 1,1-diphenyl-2-picrylhydrazyl (DPPH). Photoactivity is determined by the time it takes the DPPH radical, which is initially purple in colour, to convert to its reduced form, which is yellow. The reciprocal of the time taken for radical decomposition is defined as the Photoactivity Index (PI), with units of min⁻¹.

RESULTS

Results of chemical analyses, crystallite size and chemical photoactivity rating for the series of oxides examined are presented in Table 1.

Compound	Crystallite Size (nm)	Time taken for decay of DPPH radical (min)	PI (min ⁻¹)
ZnO	24	12	0.083
Dopant			
Fe (0.44wt%)	14	30 ⁺	<0.033
Ni (0.64wt%)	20	100	0.01
Co (0.7 wt%)	16	150 ⁺	<<.0066
Mn (1.1wt%)	21	150	0.0066
Dopant Level (wt%Mn)			
0.2		30	0.0333
0.3	23.3	38	0.0263
0.6	23	95	0.0105
0.8	18.3	220	0.0045

Table 1. Summary of Chemical analyses, Crystallite Size and Photoactivity Index (PI)

DISCUSSION

Photoactivity is expected to vary in direct proportion with surface area. A decrease in particle size from 80 nm to 40 nm may represent a two- to three-fold increase in surface area per unit weight. A consequent increase in photoactivity of the same order would be expected

It has been found that for undoped zinc oxide, there appear to be two distinct regions of photoactivity behaviour. For crystal sizes of less than 80 nm,

photoactivity is linearly dependant on size. However, for larger crystals, photoactivity is independent of size. The increase in photoactivity as particles reduce in size from 80 nm to 40 nm is about 30 %, compared with 2-3 fold increase expected from arguments based on relative surface area.[6].

Whilst experiment shows a monotonic increase in photoactivity with surface area for particles less than 100 nm in size, the increase in photoactivity is less than expected were surface area the dominant controlling factor. Possible reasons for this are (i) other intrinsic or extrinsic material factors, either physical and/or chemical, besides surface area diminish or influence photoactivity (ii) the conditions under which tests were performed affect either the photoactivity or the measurement of photoactivity.

Characterisation suggests that it is unlikely that intrinsic material factors vary significantly between samples of undoped ZnO, and this may be discounted as a significant influence on photoactivity. Extrinsic factors may thus provide a strong influence on photoactivity of which efficient dispersion is likely to be the most significant.

Figure 1 shows that photoactivity of ZnO may be quenched by the incorporation of a dopant material. All dopants used in this study are effective in reducing photoactivity by a significant amount, as shown in Figure 1. The most effective dopants are Mn, Co and Ni, with Fe being less effective. Depending on dopant concentration, photoactivity could be reduced by a factor of 5 or 10 compared with that exhibited by ZnO at a similar crystallite size. Other dopants (not reported here) were tested and displayed less significant changes in photoactivity than Mn, Ni, Co and Fe.

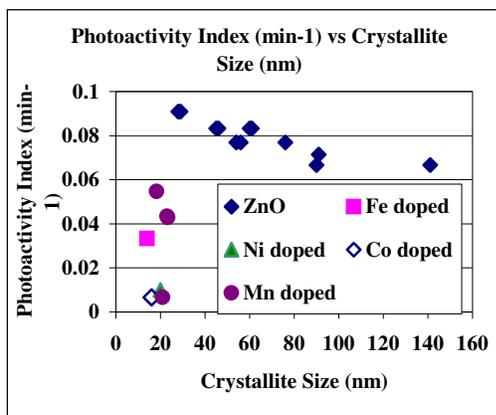


Figure 1 Summary of Photoactivity Index versus Crystallite Size

ALCHEMI of nanoparticles

The question arises as to whether the dopant is in the lattice or merely decorating it and whether differences in photoactivity are correlated with dopant location. In order to ascertain whether or not the dopants are incorporated within the lattice of the nanoparticles, a method related to atom location by channelling-enhanced microanalysis (ALCHEMI) was used [4]. Here a relatively broad but collimated 200 keV electron beam is focused onto a small particle. This particle is then tilted into a low index crystallographic zone axis orientation, and minor adjustments are made to mechanical or electronic tilt such that the beam propagates precisely down the zone axis.

Whilst it should be, in principle, quite straightforward to determine by ALCHEMI whether or not dopant atoms are within the lattice, the analysis of nanoscale particles provides a challenge. The ability to use automated beam rocking is excluded by the necessity to use a small beam in nanoprobe mode. In any event, low count rates and lateral shift incurred whilst electronically rocking the beam excludes, at this stage, automated acquisition of X-ray channelling patterns from nanoscale crystals for analysis [7].

When the nanoparticle is tilted well away from the zone axis orientation, the periodic squeezing of the wavefront onto or between atomic columns within the unit cell is relaxed, and quasi-kinematic diffraction conditions approximate the propagation of the electron wavefront to that of a plane wave. Analogous to Rutherford backscattering (RBS) analysis of charged particles on crystal surfaces, the zone axis orientation is regarded as a 'channelling' orientation, whilst the tilted orientation is regarded as the 'random' orientation.

Thus, in order to reduce the ALCHEMI experiment to a simple determination, we assume that, if incorporated in the lattice, dopant atoms randomly occupy the Zn cation sublattice site. Then, by acquisition of two EDX spectra, one at a 'channelling' orientation and the other at a 'random' orientation, a clear distinction is possible, analogous to RBS analysis, as to whether the introduced cations are incorporated on the Zn sublattice site or not. This provides a useful tool for nanoparticle analysis and crystallographic information not readily accessible by X-ray Rietveld refinement, since the response from each atomic species is individually isolated.

The situation is illustrated schematically in Figure 2. If, on the one hand, Co is incorporated on Zn sublattice sites, the rate of X-ray emission from both Zn and Co will increase in a similar way as the nanoparticle is brought to the zone axis orientation. On the other hand, if Co dopants are in a different phase or form part of a coating on the particle, the emission rate from Co will be invariant with crystal orientation.

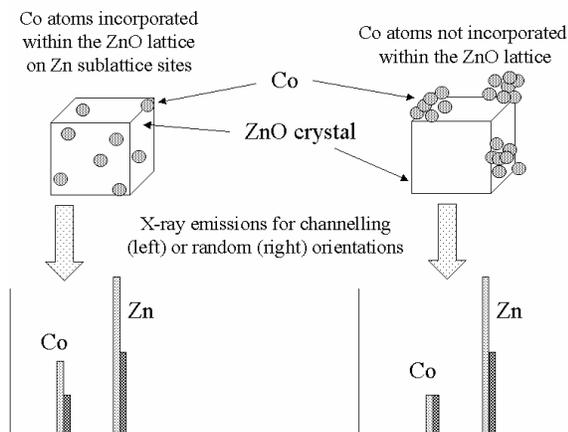


Figure 2 Schematic representation of X-ray yields for Zn and Co with Co in the lattice (left) and Co as a foreign phase (right). The light bar represents a channelling orientation and the dark bar a random orientation.

A comparison of the two EDX spectra is shown in Fig. 3(a) on a log-lin scale. Low energy emissions are from oxygen and Zn L-shell excitations, and a Cu peak is produced by scattered electrons which impinge on the copper grid bars. Fig. 3(b) shows a portion of the two EDX spectra on a linear scale, where the dynamical increase in the Co emissions is more evident.

Concentrations of Co and Mn derived from analyses of different particles under channelling and random diffraction conditions, showed that the apparent Co concentration remains steady within standard deviation for all analyses, indicating it is accommodated on the Zn sublattice site. However results from Mn showed significant variations for channelling and random orientations, as well as differences between different particles. This indicates that a significant portion of Mn atoms exist as a foreign phase or surface coating on the ZnO particles, and that it is not incorporated on the Zn sublattice site.

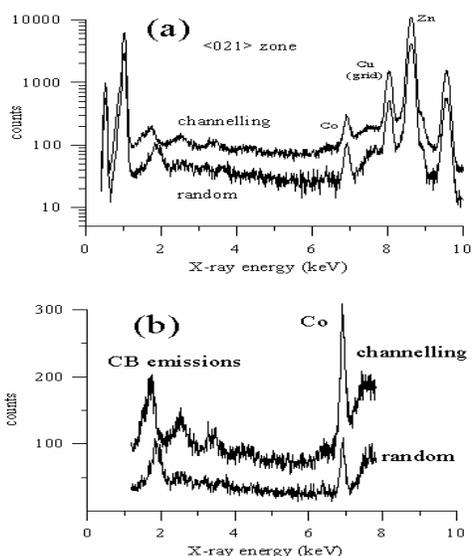


Figure 3 Lin-log plot of full EDX spectra (a), and a linear plot of CB radiation and Co peaks (b).

This data shows reasonable agreement between experiment and theory. Thus this variant form of ALCHEMI, reducing the analysis to two EDX spectra, one acquired under a zone axis channelling configuration and the other under a random orientation, demonstrates that Co is accommodated on Zn sublattice sites, whilst Mn is excluded from the lattice and exists as a foreign phase. This provides a useful tool for nanoparticle analysis and crystallographic information not readily accessible by X-ray Rietveld refinement.

In photoactive nanoparticles, material factors (besides surface area, crystallite size dispersion efficiency etc) will influence the relationship between structure and function. The consequent effect of adding a dopant will be determined by its location (in or on the lattice) as this will affect the mechanism by which photoactivity is quenched. If the dopant is in the lattice the width of the band gap will be determined intrinsically. On the other hand if the dopant decorates the lattice the width of the band gap will not be altered but will effect the fate of radicals generated. The relative contribution that either location makes is unknown for these systems. There is some indication from the preliminary data presented here that the dopant located within the lattice is more effective than that decorating the lattice. For example, the Co dopant appears to be more effective at reducing photoactivity than does the Mn, Ni or Fe and that to achieve a similar level of

photoactivity using dopants that do not appear to be in the lattice, increased coverage seems to be required.

CONCLUSION

In general, the photoactivity of nanophase zinc oxide has been found to increase with decreasing particle size but may be controlled by the incorporation of selected dopants. The location of these dopants has been determined by the technique of electron channelling and gives some insight into the method by which the photoactivity of the nanoparticle is controlled together with how preparation conditions may affect the design of additional functionality into the material of interest.

The combination of empirical testing with structural analysis provides a powerful combination to allow the design of nanoparticles with enhanced and/or additional functionality.

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