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Communication

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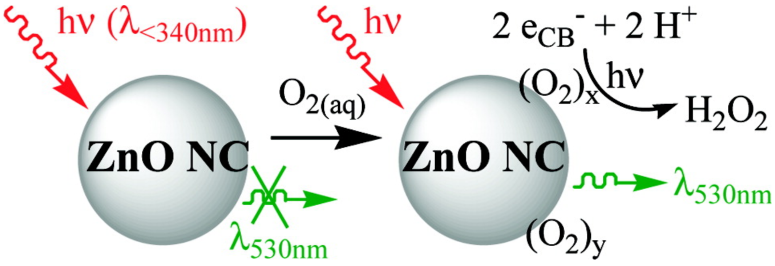

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COMMUNICATIONS

The Relationship of Oxygen Binding and Peroxide Sites and the Fluorescent Properties of Zinc Oxide Semiconductor Nanocrystals

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Although nanostructured zinc oxide is a promising photonics material[1] almost all preparations of zinc oxide nanocrystals (ZnO NCs) including various nanostructures and bulk crystals have a broad visible emission which is usually attributed to surface defect sites.[2−6] In addition, more than one peak has been observed in the visible range and these are attributed to dopants, structural features, or surface defects.[3,7] Even though the defect emission can be suppressed by coating the particles with surfactants,[8] or by post fabrication annealing with a hydrogen/argon mixture or with a hydrogen plasma,[9,10] the structure and origin of these surface defects remains an important unresolved problem.[5] In one of the earliest studies in this field Hoffman *et al.* demonstrated[11] that purging freshly prepared NCs with nitrogen results in ca. 80% reversible loss of defect emission. Although oxygen is implicated as being at least associated with the defect sites, most nanoparticle preparations take little precaution to regulate oxygen uptake or binding either during the synthesis or post fabrication processing. In this paper we demonstrate that ZnO NCs prepared in the absence of oxygen have nominal defect emission and that the quasi reversible titration of dioxygen free zinc oxide nanoparticles with dioxygen requires a model where at least two different surface sites are involved in the oxygen defect generation. These results are important for the development of both new photonic material and new photooxidation catalysts.

Oxygen adsorption on the surface of ZnO nanoparticulate or microcrystalline zinc oxide increases the visible luminescence by as yet an unresolved mechanism.[3,12] Although oxygen surface adsorption on ZnO nanoparticles is quasi-reversible, the stoichiometry, structure, and origin of the nonreversible component all remain speculative. The luminescent properties observed for ZnO nanoparticles under aerobic condition consist of a dominant visible emission and quenched UV emission. Deaeration of the solution results in a significant decrease of the visible emission and an observable increase of the UV emission as previously observed, however complete extinction of the visible luminescence from an aerobic system is unsuccessful (Figure 1).[11,13] Preparation of monodisperse crystalline nanoparticles (Supporting Information, pages S1−4) under anaerobic conditions affords comparable results, where the introduction of oxygen to the colloidal suspension resulted in the almost complete restoration of the visible emission and quenching of the UV emission. Clearly oxygen mediates the restoration of visible emission and consequent quenching of the UV emission of ZnO nanoparticles.

Attempts to quantify the oxygen required to restore fluorescence led to the observation of unique emission characteristics during the titration of oxygen into a closed anaerobic system (Figure 2). It is clear from our observations that oxygen interacts superficially with the ZnO NCs to facilitate visible emission. In addition we observe (1) partial restoration of visible luminescence, (2) incomplete decay of this luminescence upon repeated UV excitation, and (3) sequential exposure leads to reduced rates of fluorescent decay (Figures 2a−d and S3−S6). At approximately 25 mol % oxygen with respect to surface ZnO (Figure 2e) no further rapid luminescent decay was observed, and a saturated state is observed. These observations indicate a more complex system than formerly proposed, the explanation of which requires the application of more than one surface site contributing to the changes in ZnO luminescence.

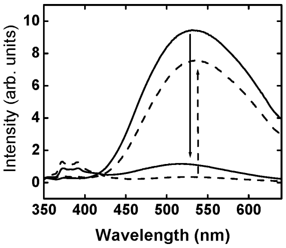

Figure 1. Photoluminescent spectrum of colloidal ZNO NP, λ_{ex}= 345 nm: prepared in aerobic conditions then deoxygenated (solid line) and under inert atmosphere, then exposed to oxygen (dashed line).

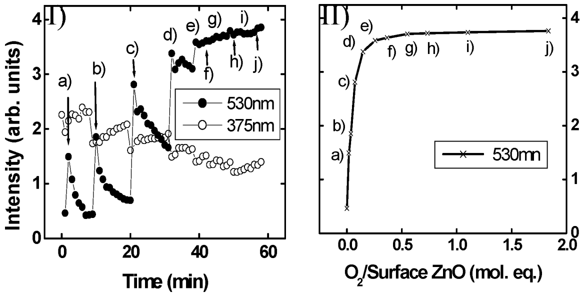

Figure 2. Titration of oxygen into anaerobic colloidal ZNO NP, λ_{ex} = 345 nm solutions. Examination of the UV, 375 nm, and visible, 530 nm, emission over time (I) and oxygen concentration (II) relative to surface ZnO present on the nanoparticles, *r* = 2.6 nm. Events a−j correspond to unique additions of $O_{2(g)}$ to the anaerobic solution via gastight syringe.

It is known that the exposure of ZnO nanoparticles, in a reduced oxygen environment, to UV radiation results in quenching of the visible emission, which is attributed to photoinduced desorption of chemisorbed O_2 via formation of H_2O_2 and the subsequent accumulation of photogenerated electrons on the ZnO surface.[14−16] Restoration of visible emission upon introduction of oxygen into the system of ZnO nanoparticles has been ascribed to the electron scavenging abilities of oxygen.[11,14,15] Collectively these theories and our observations are consistent with a multiple-site model.

Exposure of the oxygen-titrated sample to UV excitation results in a limited quenching of the visible emission. Subsequent additions of oxygen result in similar trends however, with decreasing rates of decay (Figure S2−S6). We propose that there is rapid binding of oxygen to the surface, and that this is followed by a relatively slow but incomplete quenching of the fluorescence. The addition of oxygen to the closed system results in an increase in visible emission interpreted as oxygen adsorption on the surface of the ZnO NCs. Upon UV excitation the observed decay in luminescence

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Scheme 1

$$ZnO + O_{2(g)} \underset{k_{desorp}}{\overset{k_{ads}}{\rightleftharpoons}} ZnO(O_2)_{x+y} \qquad 1.$$

$$ZnO(O_2)_{x+y} + 2\,e_{CB}^{-} + 2\,H^{+} \xrightarrow[k_{cat}]{h\nu} ZnO(O_2)_y + H_2O_2 \qquad 2.$$

$$2\,ZnO + H_2O_2 \longrightarrow 2\,ZnO(OH)_x \qquad 3.$$

is due to the photoreduction of oxygen on a more reactive site (*x*) to produce H_2O_2 (Scheme 1, eq 2). Oxidation of the nanoparticle surface, by H_2O_2 (Scheme 1, eq 3) results in a poisoning of the catalytic site *x*, observable as a decrease in the rate of decay of luminescence after each addition of oxygen. The irreversible changes on the surface, attributed to the modification of the highly catalytic site-*x*, account for the diminishing catalytic activity, where the less reactive sites (*y*) and the oxidized (*x*) site account for the residual luminescence intensity observed after repeated UV excitation. It is the irreversibly modified *x* site that is thought to account for the difficulty in complete extinction of the visible emission from ZnO NCs prepared in air.

These observations help us understand the origin of the visible luminescence. The source of the visible emission has been carefully scrutinized, and it is described as originating from a variety of recombination pathways. First identified as a recombination event occurring between chemisorbed $O_2^{\bullet -}$ (singly reduced by e_{CB}^{-}) on the surface and an intrinsic trapped state in the ZnO NC.[8] Later, it was recognized as the recombination of a shallowly trapped electron with a deeply trapped hole.[14,15] Where the deep trap level is identified as an oxygen vacancy, $V_o^{\bullet\bullet}$ (of zero charge in relation to a O^{-2} state), oxidized to $V_o^{\bullet}$ through the interaction of the h_{VB}^{+} with a surface system (O^{-2}/O^{-}). This surface system has been questioned, and a more recent study suggests that these sites are amine binding surface hydroxides (OH^{-}_{s}).[17]

We observe that there are highly active catalytic sites, *x*, on the surface of ZnO NCs which are present if the nanocrystals are prepared under anaerobic conditions. These sites contribute to fluorescence, either as a surface system[11,17] or as an electron accepting adsorbate,[14] but in either case the sites are also easily poisoned (Scheme 1, eq 3), resulting in a reduction in the overall catalytic activity. The generated surface hydroxides, and the less reactive oxygen-adsorption sites (*y*), contribute to the visible fluorescence, as observed from the residual fluorescence after each aliquot of oxygen; this is in support of the observations made by Gamelin[17] where he observed a direct correlation between surface hydroxides and the visible luminescence.

From these data it is evident that previous theories, individually, do not fully describe the surface related luminescent characteristics of ZnO NCs. Through the investigation of the surface features of ZnO NCs, we have concluded that the fluorescent character of the visible emission reflects more than one type of surface site, denoted *x* and *y*, each with a different reactivity. The structures and photoreactivity of *x* and *y* sites are currently under investigation. These novel features warrant further investigation utilizing the unique features of the different sites toward enhancing the photocatalytic activity of the nanocrystals as sensitizers in advanced oxidation processes and increasing control of the visible and UV emissions in photonic applications of ZnO NCs.

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Supporting Information Available: Experimental procedures, fluorescent decay plots and rates, and oxygen binding plot and fit. This material is available free of charge via the Internet at http://pubs.acs.org.

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