Reduction of the photocatalytic activity of ZnO nanoparticles for UV protection applications

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Abstract: The detrimental effects of UV radiation are having a significant impact on our life and environment. The development of effective UV shielding agents is therefore of great importance to our society. ZnO nanoparticles are considered to be one of the most effective UV blocking agents. However, the development of ZnO-based UV shielding products is currently hindered due to the adverse effects of the inherent photocatalytic activity exhibited by ZnO. This paper reports our recent study on the possibility of reducing the photoactivity of ZnO nanoparticles via surface modification and impurity doping. It was found that the photoactivity was drastically reduced by SiO₂-coatings that were applied to ZnO quantum dots using the Stöber method and a microemulsion technique. The effect of transition metal doping on the photoactivity was also studied using mechanochemical processing and a co-precipitation method. Cobalt doping reduced the photoactivity, while manganese doping led to mixed results, possibly due to the difference in the location of dopant ions derived from the difference in the synthesis methods.

Keywords: UV protection; ZnO; nanoparticles; photocatalytic activity; doping; surface modification.

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1 Introduction

Ultraviolet (UV) light in the wavelength range from 40 nm to 400 nm has sufficiently high energy to cause various damages to organic substances. UV light can excite covalent electrons into higher energy states and induce chain scission and cross linking in organic molecules [1]. At the same time, the sectioned molecules can become free radicals, which further induce chain scission and cross linking as well as generate oxy- and

peroxy-radicals by reacting with oxygen [2]. This chain reaction of photo-generated free radicals leads to the photodegradation of organic materials.

The UV rays from the sun is mostly filtered by the stratospheric ozone layer, so that only the UV rays with relatively low energy, i.e., UVB (290–320 nm) and UVA (320–400 nm) radiation, reach the Earth's surface. However, low-energy UV rays still cause adverse effects onto our body and other organic materials. For example, they are responsible for the development of various pathologies, including skin cancer, suppression of the immune system, cataracts, premature aging of the skin and inflammatory disorders [3,4]. UVA and UVB rays can also cause severe damage in plastics, paints, textiles, timber, artwork and other industrial/domestic products, in the forms of reduced mechanical properties, degraded appearance and decomposition, which in turn leads to safety risks, materials waste and economical damage. This situation has been aggravated over the years due to the recent ozone depletion caused by the increased generation of man-made catalyst gas molecules, such as nitric oxide, nitrous oxide and organo-halogen compounds [5]. Hence the development of effective UV shielding materials is of great importance to protect our health, society and environment [6].

The UV screening/absorbing agents are required to possess several key attributes, including lack of colour (i.e., high transparency), high photo-stability, low cost and high UV absorption coefficients. There are inorganic and organic UV absorbers commercially available that fulfil most of these requirements [7].

Organic UV absorbers are relatively cheap and generally transparent so that they are used in many consumer products such as sunscreens, food-packaging and textiles [8,9]. The majority of the organic UV absorbers are ultimately destroyed by the UV radiation that they absorb [7,10], which decreases UV absorption efficiency over time [11–14]. Most of the organic UV absorbers have a narrow UV absorption band and combinations of more than one organic UV absorbers are normally employed to achieve a broad spectrum UV protection. The interaction between different organic UV absorbers may cause unfavourable health effects and hence the United States Food and Drug Administration have limited the choice of the combination in sunscreen products [7]. There are other concerns associated with organic UV absorbers. Since they are small-sized molecules, they may leach out from plastics, paints and textiles, which may cause health problems once they contaminate food and drinks [15]. They can also penetrate the epidermal barrier [16]. Past research showed that the amount of organic UV absorbers penetrated the epidermis is too low to cause significant toxicity to human keratinocytes (the major constituent of epidermis) [17]. Nevertheless, the ability of organic UV absorbers to leach into the blood stream has raised concerns, since some of them are known to cause adverse effects to reproductive organs and the central nervous system [18,19]. It is known that organic UV absorbers can also generate free-radicals upon UV exposure [1,2,20].

In contrast to organic UV absorbers, inorganic UV absorbers such as ZnO and TiO₂ have excellent photo-stability [21] and are expected to provide a UV protective effect over a much longer period than organic UV absorbers. The mechanism of UV absorption in these semiconductor inorganic materials involves the use of photon energy to excite electrons from the valence band to the conduction band. For example, ZnO has a bandgap energy of ~3.3 eV that corresponds to the wavelengths of ~375 nm. UV rays with a shorter wavelength than 375 nm have the sufficient energy to excite the valence electrons, and hence are absorbed by ZnO. On the other hand, light

having a wavelength longer than 375 nm will not be absorbed, thus ZnO is colourless to visible light.

By using nano-scale UV-blocking particles, it is possible to achieve high transparency while retaining good UV absorption properties. Since the efficiency for the nanoparticles to scatter visible light decreases proportional to the 6th power of particle diameter, well-dispersed nanoparticle suspensions can possess significantly high transparency to the naked eye [22,23]. The nano-scale diameters can also realise uniform distribution of the particles in host matrices, resulting in high UV blocking efficacy [21,23,24].

ZnO has many advantages over other metal oxides. For example, ZnO has a long history of safe topical use and is known as an anti-irritant, astringent and skin-healing agent [25]. ZnO has the most broad-spectrum absorption range among many inorganic UV absorbers [21,24]. Since the refractive index of ZnO (2.0) is smaller than that of TiO₂ (2.4–2.7), ZnO nanoparticle suspensions give higher transparency than TiO₂ nanoparticles, providing the size and concentration of the particles are the same [24].

However, the photocatalytic activity of inorganic UV absorbers has raised much concern in many UV protection applications [26]. On absorption of UV light by TiO₂ or ZnO, the electrons in the occupied valence band are excited by the UV light into the unoccupied conducting band. The conduction band electrons and valence band holes thus created can migrate out to the particle surface to react with electron donors or acceptors that are adsorbed on the particle surface. In TiO₂ and ZnO, the photo-excited electrons and holes have suitable redox-potentials for inducing a wide range of catalytic reactions [27]. For example, when the photo-generated electrons and holes react with water or oxygen, they produce reactive superoxide ($\bullet\text{O}_2^-$) and hydroxyl ($\bullet\text{OH}$) free radicals. These free radicals are thought to be the primary cause for the degradation of organic materials [28]. Hence, the photocatalytic activity that is induced by absorbed UV light, may degrade the organic materials that TiO₂ and ZnO are supposed to protect from UV light. The situation is exacerbated by a reduction in particle size, due to the increased specific surface area providing more reaction sites on the particle surface [28].

While the modification of photocatalysis in TiO₂ and ZnO has been widely investigated, most research so far has been directed towards the *enhancement* of photoactivity, mainly for renewable energy production and environmental remediation applications [28]. Despite the importance of TiO₂ and ZnO in UV-screening applications, the research that aimed at the *reduction* of the photocatalysis of TiO₂ and ZnO have scarcely been reported [29,30]. This paper reviews the recent progress in our research group in the reduction of photocatalytic activity of ZnO nanoparticles [31–34].

2 Reduction of photocatalytic activity

2.1 Surface modification of ZnO nanoparticles

One approach to reduce the photocatalytic activity of ZnO nanoparticles is to coat the particles with non-conductive materials such as SiO₂ or Al₂O₃. This is based on the assumption that, if the coating layer is sufficiently thick for photo-excited electrons and holes to cross through, photo-generated excitons would be trapped within the coating layer so that free radical generation would be inhibited.

In our laboratory, SiO₂-coated ZnO nanoparticles were synthesised using the Stöber method [33]. ZnO quantum dots of 2.4–3.9 nm in diameter were prepared using a wet chemical precipitation method in ethanol from zinc acetate and sodium hydroxide. To form SiO₂ layers on ZnO nanoparticles, tetraethylorthosilicate and ammonium hydroxide were added into the particle suspension in ethanol. The effect of the surface modification on the photocatalytic activity of ZnO was studied by monitoring the degradation of Rhodamine B (RhB) dye caused by photo-generated free radicals [33]. Aqueous suspensions of ZnO nanoparticles in RhB solution were irradiated with simulated sunlight and the absorption peak of RhB was monitored as a function of irradiation time.

The reduction of the absorption peak corresponds to the degradation of RhB by photo-generated free radicals on the surface of ZnO nanoparticles. It was found that the SiO₂ coating markedly depressed the photocatalytic activity of ZnO (Figure 1(a)). As shown in Figure 1(b), the absorbance in the visible light region remained extremely low after the silica-coating, while the absorbance in the UV region was high, which satisfies key requirements as an effective UV screening agent. However, due to the quantum size effect, the absorption edge shifted to ~350 nm from the bulk value (~375 nm).

Figure 1 (a) Photo-degradation of Rhodamine B dye molecules under simulated sunlight in the presence of uncoated and SiO₂-coated ZnO nanoparticles and (b) UV-Vis absorption spectra of SiO₂-coated ZnO nanoparticles (0.4 g/100 ml) prepared using the Stöber method and dispersed in ethanol (optical path length = 10 mm)

The yellowing of wool fabrics has been a challenging issue in the textile industry and is reported to be due to the damage of protein molecules by either UV light or free radicals [34]. It was demonstrated that wool yellowing was drastically suppressed by applying SiO₂-coated ZnO nanoparticles on wool fabrics (Figure 2), indicative of efficient UV-blocking property with suppressed photo-activity.

Monodispersed ZnO-core/SiO₂-shell composite nanoparticles were also produced using a microemulsion technique (Figure 3). Although the reverse micro-emulsion technique had been used to apply SiO₂ coatings on various nanoparticles in the past, to the best of our knowledge, this is the first time the technique has been successfully applied to ZnO [35]. It was demonstrated that the ZnO primary particles in the core remained as quantum dots after being enclosed in the SiO₂ shells. The shell thickness was varied from 11 nm to 25 nm by controlling the reaction conditions. The photoactivity

measurements using the RhB degradation technique showed significant reduction in the photocatalytic activity of ZnO nanoparticles (Figure 1(a)) [35].

Figure 2 Yellowing of wool fabrics after UV exposure for 10 hrs that are untreated (control) and treated with SiO₂-coated ZnO nanoparticles (ZnO@SiO₂) made using the Stöber method (see online version for colours)

Figure 3 Typical TEM image of SiO₂-coated multi-core ZnO nanoparticles synthesised by using a microemulsion technique [34]

2.2 Impurity doping of ZnO nanoparticles by mechanochemical processing

Another approach to reduce the photocatalytic activity of ZnO nanoparticles is to dope impurity ions. It is generally considered that dopant ions create chemical or physical defects in the crystal lattice that act as the trapping sites of photo-generated electrons and holes, promoting the recombination of those charged particles, resulting in reduced photocatalytic activity. Recently, the author's group and his collaborators have investigated the photoactivity of manganese and cobalt doped ZnO nanoparticles that are synthesised using mechanochemical processing and a sol-gel co-precipitation technique. Manganese and cobalt doping create deep bandgap impurity levels that are expected to act as efficient recombination sites for photo-generated electrons and holes [36,37].

The mechanochemical processing for the synthesis of doped ZnO nanoparticles was carried out via the following reaction paths [32]:

where M = Co or Mn. The synthesis involved the three stages, namely, mechanical milling to form doped zinc carbonate (equation (1)), heat treatment at 350°C to decompose carbonate into oxide (equation (2)) and washing process to remove the by-product NaCl. Up to 5 mol% of cobalt and manganese were doped into ZnO. It was found that increased amounts of doping led to higher specific surface areas and stronger colouration.

X-ray diffraction (XRD) study of the mechanochemically prepared doped ZnO revealed that manganese doping increased the crystal lattice constant in the c-axis direction, while cobalt doping decreased the lattice constant (Figure 4(a)) [32]. Shannon's ionic radii of zinc, manganese and cobalt for the coordination number of 4 are 0.60, 0.66 and 0.58 Å, respectively [38]. Hence, it is expected that the replacing zinc ions in the crystal lattice with cobalt will reduce the lattice constant, while manganese will expand the crystal lattice. Therefore, the XRD results indicate that manganese and cobalt were successfully crystal-doped using this synthesis technique.

Figure 4 (a) C-axis lattice constant of doped ZnO powders made by mechanochemical processing, determined by XRD (the solid lines are drawn as a guide to the eye) [32] and (b) photocatalytic activity of doped ZnO powders measured as the concentration of photo-generated hydroxyl radicals, as a function of dopant level

The photocatalytic activity of the mechanochemically prepared ZnO nanoparticles was evaluated using a spin-trapping technique with electron paramagnetic resonance (EPR) spectroscopy. ZnO powder suspensions in aqueous 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) solutions were irradiated with UV light of 300 nm in wavelength. The concentration of photo-generated hydroxyl radicals was measured as a function of irradiation time, by recording the intensity of the first central line of the first derivative EPR spectrum that corresponds to the DMPO-OH spin adduct. It was found that cobalt doping significantly reduced the photoactivity, while manganese doping enhanced the activity to a certain degree (Figure 4(b)).

2.3 Impurity doping of ZnO nanoparticles by co-precipitation

Doped ZnO nanocrystalline powders were also synthesised using a sol-gel co-precipitation method via the following reactions [31]:

where appropriate amounts of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were replaced with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, depending on the target doping levels. The ZnCO_3 precipitates were heat treated at 350°C to decompose it into ZnO.

Similar to mechanochemically processed samples, increased amounts of doping led to higher specific surface areas and stronger colouration. However, the c-axis lattice parameter did not change for manganese doped samples but was decreased for cobalt-doped samples (Figure 5(a)). The results indicate that the co-precipitation method was not able to crystal-dope manganese in ZnO. Figure 5(b) shows the results of Extended X-ray Absorption Fine Structure (EXAFS) measurements, which represent the local atomic arrangement around the atoms of interest, i.e., zinc for undoped ZnO and manganese for manganese-doped ZnO. The peak positions in the spectra represent the distance between the central atom and surrounding atoms, while the peak height is associated with the number of surrounding atoms. It is evident that the spectrum of manganese-doped ZnO was markedly different from that of undoped ZnO. This result indicates that the local atomic arrangement around manganese atoms was different from that around zinc in ZnO and hence manganese did not substitute zinc in the ZnO crystal lattice. Further study on the determination of dopant location is in progress.

The photoactivity measurements using the RhB degradation technique showed that both manganese and cobalt doping decreased the photocatalytic activity of ZnO nanopowders (Figure 6). It is interesting to note that crystal-doped manganese increased the photocatalytic activity (Figure 4(b)), whilst surface-doped manganese decreased the activity. Figure 7 shows UV-Vis absorption spectra of doped ZnO nanoparticles dispersed in water, calculated from specular transmittance values. Although manganese and cobalt doped ZnO are strongly coloured in a dry state, they look relatively transparent once dispersed in a transparent medium. It is also evident in Figure 7 that, under well-dispersed states, doping did not alter the UV-absorption onset wavelength under the doping level lower than 2 mol%.

Figure 5 (a) C-axis lattice constant of doped ZnO powders made via a co-precipitation method, determined by XRD (the solid lines are drawn as a guide to the eye); (b) Fourier transform of the zinc K-edge (undoped ZnO) and manganese K-edge (manganese-doped ZnO) EXAFS oscillation $k^3\chi(k)$, where k is the wave number of X-rays

Figure 6 Photo-degradation of Rhodamine-B dye molecules under simulated sunlight in the presence of (a) cobalt doped and (b) manganese doped ZnO nanoparticles (see online version for colours)

Figure 7 UV-Vis absorption spectra of doped and undoped ZnO nanoparticles dispersed in water, calculated from specular transmittance

3 Summary

Our initial study demonstrated that the reduction of the photocatalytic activity of ZnO nanoparticles is in fact possible through surface modification and impurity doping. SiO₂-coated ZnO nanoparticles showed drastically reduced photoactivity compared to uncoated ZnO nanoparticles. Cobalt doping also reduced the photoactivity. On the other hand, manganese doping led to mixed results, possibly due to the difference in the location of dopant ions derived from the difference in the synthesis methods. Further investigation is on-going to elucidate the role of dopant ions and types of surface modification for the effective reduction of photoactivity in ZnO nanomaterials.

Currently, the safety of nanoparticles in consumer goods and personal care products is extensively debated [39–42]. To date, 18 scholarly reports on the skin penetration of sunscreen-grade ZnO and TiO₂ nanoparticles showed no evidence of skin absorption by human skin or pig skin that is most suitable substitute to human skin for the research [43–60]. Based on the analysis of ~400 peer-reviewed scholarly papers, Environmental

Working Group, a US based non-governmental organisation, has released a statement recommending sunscreens that contain inorganic nanoparticles [61]. Their study shows that consumers who use sunscreens without ZnO and TiO₂ are likely exposed to more UV radiation and greater numbers of hazardous ingredients (average 4 times more) than consumers relying on ZnO and TiO₂ products for sun protection. By the reduction of photocatalysis, ZnO is expected to be used as a safe UV-screening agent in many applications.

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