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Studies on polymer-coated zinc oxide nanoparticles: UV-blocking efficacy and *in vivo* toxicity

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ABSTRACT

Zinc oxide (ZnO) is explicitly used in sunscreens and cosmetic products; however, its effect *in vivo* is toxic in some cases. The UV blocking efficacy of ZnO nanoparticles is lost due to photocatalysis. To isolate a lower toxic species of sunblockers, ZnO nanoparticles were synthesized and coated with chitosan – a natural polymer (ZnO–CTS) and polyethylene glycol (PEG) – a synthetic polymer (ZnO–PEG). Coating with CTS and PEG circumvented the photocatalytic activity, increased the stability and improved the UV absorption efficacy. The effect of ZnO, ZnO–CTS and ZnO–PEG nanoparticles *in vivo* on zebrafish embryo revealed lower deposition of ZnO–CTS and ZnO–PEG nanoparticles atop the eggs compared to ZnO. The survival of zebrafish embryos was always found to be higher in case of ZnO–CTS with respect to ZnO-treated ones. PEG coating exhibited better UV attenuation, but, *in vivo* it induced delayed hatching. Thus, one of the reasons for better survival could be attributed to lower aggregation of ZnO–CTS nanoparticles atop eggs thereby facilitating the breathing of embryos.

1. Introduction

Zinc oxide (ZnO) is one of the widely used semiconductor metal oxides which exhibit several applications including UV blocking products (in various topical skin care products, such as sunscreens), photocatalytic and antibacterial materials [1–3]. TiO_2 is another very important semiconductor materials used in photocatalysis. Studies with bare TiO_2 nanoparticles or decorated with graphene nanosheets, coated over Ag nanoparticles, or embedded in hybrid nanostructures have been reported [4–7]. Studies on the biological effects of TiO_2 and ZnO are exploited by many researchers. Skin penetration of ZnO nanoparticles through the outer layer to the viable cells within the deeper skin layers has been investigated in a large set of *in vitro* and *in vivo* studies. The outcomes of these studies indicated an apparent inability of ZnO nanoparticles to reach the viable cells in the dermis [8]. Some studies, however, showed increased concentrations of zinc in the internal organs of mice receiving short term topical application of ZnO nanoparticles [9]. To be an active UV protector, the photocatalysis of ZnO was undesirable, because it may lead to oxidative stress in the skin. The profound use of nanoparticles offered threat to the vertebrates in the aquatic system. Studies evidenced that ZnO nanoparticles were toxic to zebrafish embryos at different extents [10,11]. To retard the oxidation and photocatalytic activity of the ZnO nanoparticles, it was coated with different agents like zinc aluminate [12], aluminium hydroxide ($Al[OH]_3$), polymers and inert oxides of silica, anti-oxidant compounds like vitamins (A, E, C) [13]. However, the biological acceptability of such coated nanoparticles has not been studied. To isolate a lower toxic species of ZnO, with a higher efficacy to attenuate UV light is thus warranted.

In the present study, we have synthesized ZnO nanoparticles using simple beaker chemistry [14], and coated them with two types of polymer – a natural polymer – chitosan, (CTS) and a synthetic polymer – polyethyleneglycol, (PEG). Literatures evidenced that CTS-coated ZnO absorbed UV light more efficiently when used in cotton fabrics [15]; however, their effect *in vivo* was not explored. Optical properties of ZnO nanoparticles, coated with PEG showed increased fluorescence, compared to bare ZnO [16]; although the data evidencing the effect on any viable system are lacking. Studies on aliphatic polyether-coating of ZnO nanoparticles showed slower dissolution and uptake in different cell lines [17]. To investigate the effects of polymer coating on UV scavenging efficiency of ZnO as well as explore the effect of the synthesized nanoparticles in the aquatic environment, we have executed this present study. We have studied the effect of ZnO, ZnO–CTS and ZnO–PEG nanoparticles on the viability of zebrafish embryo, to detect a

Abbreviations: ZnO, zinc oxide; PEG, polyethyleneglycol; ZnO–PEG, zinc oxide nanoparticles coated with PEG; ZnO–CTS, zinc oxide nanoparticles coated with chitosan.

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probable substitute for ZnO nanoparticles used in the sunscreens and cosmetic products.

2. Materials and methods

2.1. Materials

Zinc acetate dihydrate, sodium hydroxide, poly ethylene glycol, sodium chloride, magnesium sulphate, sodium bi carbonate and ascorbic acid were obtained from SRL, India; chitosan, disodium hydrogen phosphate, potassium di hydrogen phosphate and methanol were obtained from HIMEDIA Laboratories; methylene blue (MB) and potassium chloride were obtained from Merck, India; 1,1 diphenyl-2-picryl-hydrazyl (DPPH) was obtained from Sigma Chemicals, USA; ethanol was obtained from Yang Chemical Corporation, China; calcium chloride was obtained from Rankem, India and other laboratory chemicals were purchased locally.

2.2. Synthesis and polymer coating of zinc oxide nanoparticles

ZnO nanoparticles were synthesized according to Ajay Kushwaha et al. [14], with slight modifications. 20 mM zinc acetate dihydrate was added to 50 mL of ethanol and stirred for 15 min. 0.5 g of sodium hydroxide was added to the above solution and stirred for 2 h to obtain a white precipitate of ZnO. Then, it was centrifuged at 5000 rpm for 10 min and washed twice with distilled water and calcinated at 300 °C for 1 h. The resulting white powder was crushed using a mortar pestle and preserved for further characterization. For studies using ZnO solution, ZnO nanoparticles were dissolved in distilled water and sonicated (100 W and 40 KHz), for 1 h (20 min × 3 times) to yield a homogeneous solution (100 mg/L). Coating of ZnO nanoparticles with CTS was done by following the method of AbdElhady [15] with slight modifications. 1% CTS stock was prepared in 1% aqueous acetic acid solution. 10 mg of ZnO was dissolved in 0.025% of CTS solution which was made up to a final volume of 100 mL with distilled

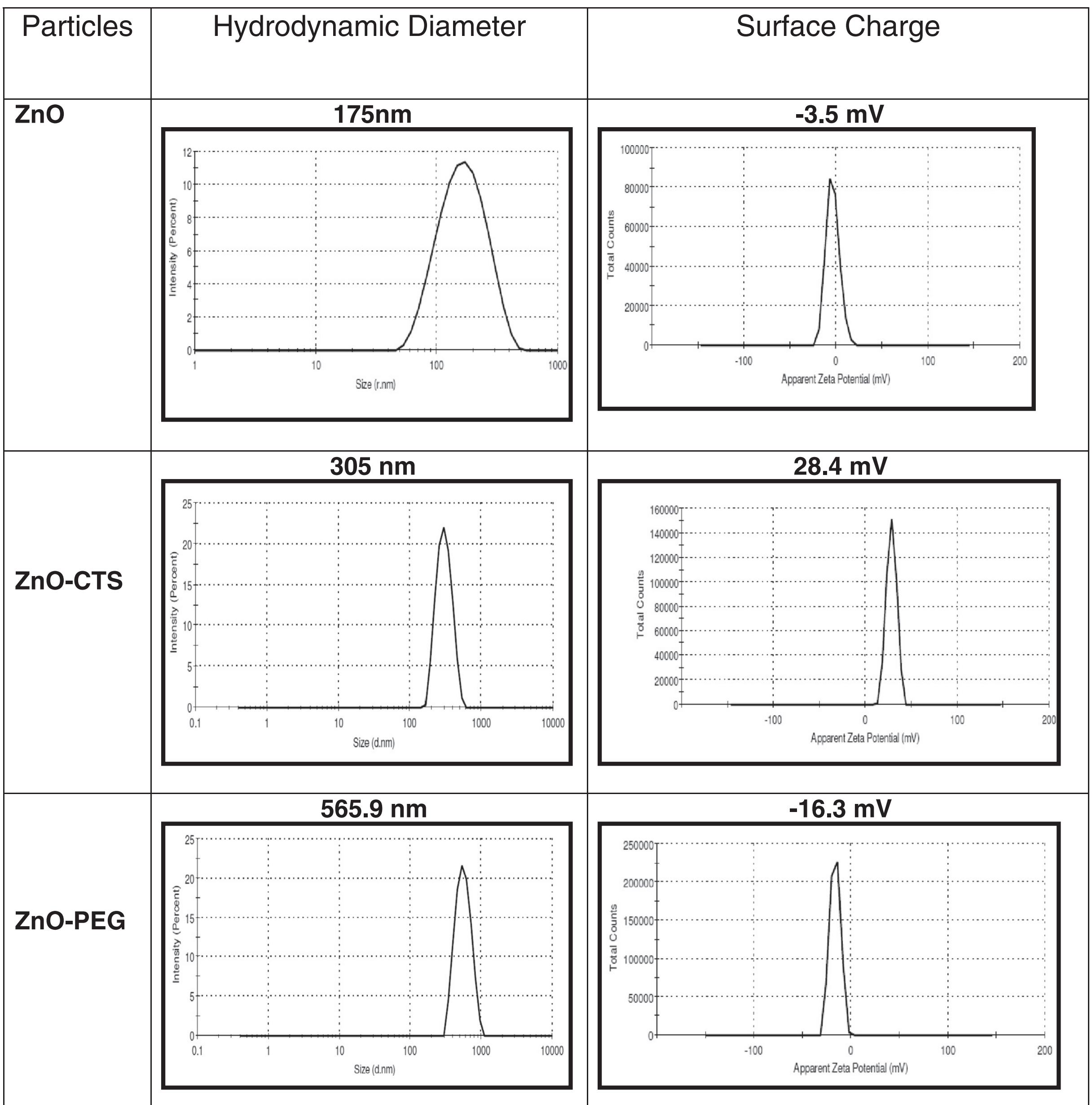

Fig. 1. Particle size and charge distribution of ZnO, ZnO–CTS and ZnO–PEG nanoparticles.