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Importance of doping, dopant distribution, and defects on electronic band structure alteration of metal oxide nanoparticles: Implications for reactive oxygen species

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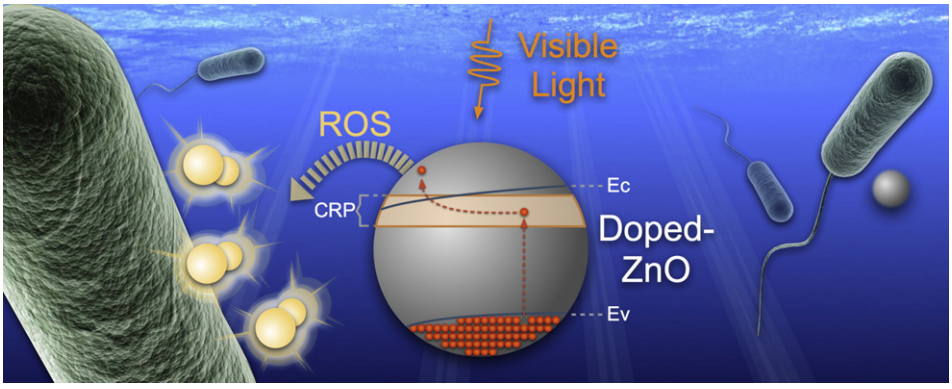
HIGHLIGHTS

- Metal oxide nanoparticles (MONPs) produce reactive oxygen species (ROS)
- Band structure of pristine MONPs is different than those with dopants/defects
- Dopants/defects modulate band structures of MONPs and can alter ROS generation
- Some MONPs with dopants/defects may generate ROS, and be nanotoxicologically relevant
- Correlating MONP band structure with ROS is essential for their safer applications

GRAPHICAL ABSTRACT



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ABSTRACT

Metal oxide nanoparticles (MONPs) are considered to have the potency to generate reactive oxygen species (ROS), one of the key mechanisms underlying nanotoxicity. However, the nanotoxicology literature demonstrates a lack of consensus on the dominant toxicity mechanism(s) for a particular MONP. Moreover, recent literature has studied the correlation between band structure of pristine MONPs to their ability to introduce ROS and thus has downplayed the ROS-mediated toxicological relevance of a number of such materials. On the other hand, material science can control the band structure of these materials to engineer their electronic and optical properties and thereby is constantly modulating the pristine electronic structure. Since band structure is the fundamental material property that controls ROS-producing ability, band tuning via introduction of dopants and defects needs careful consideration in toxicity assessments. This commentary critically evaluates the existing material science and nanotoxicity literature and identifies the gap in our understanding of the role of important crystal structure features (i.e., dopants and defects) on MONPs' electronic structure alteration as well as their ROS-generation capability. Furthermore, this commentary provides suggestions on characterization techniques to evaluate dopants and defects on the crystal structure and identifies research needs for advanced theoretical predictions of their electronic band structures and ROS-generation abilities. Correlation of electronic band structure and ROS will not only aid in better mechanistic assessment of nanotoxicity but will be impactful in designing and developing ROS-based applications ranging from water disinfection to next-generation antibiotics and even cancer therapeutics.

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1. Introduction

Metal oxide nanoparticles (MONPs) are one of the most prepared and used engineered nanomaterials with applications in electronics, optical devices, medical processes and devices, catalysis, alternative energy production, and environmental remediation and as antimicrobial sprays and coatings (Murphy et al., 2005). Manufacturing processes, and end-of-life disposal events for these applications might serve as exposure pathways to humans and the natural environment and thus raise concerns for eco- and nano-toxicity (Klaine et al., 2008; Nel et al., 2006; Saleh et al., 2015). The key mechanisms for toxicity from MONPs include dissolved ions, alteration of redox potential and subsequent catalytic reaction, and reactive oxygen species (ROS) and their interaction with biological entities (Aich et al., 2014; Ju-Nam and Lead, 2008; Saleh et al., 2015; Sarkar et al., 2014; von Moos and Slaveykova, 2014).

ROS, e.g., singlet oxygen, hydrogen peroxides, and superoxides, are known to cause toxicological stress to cells via alteration of redox-mediated cellular processes and damage to cell-membranes and other cellular components (Nel et al., 2006; Saleh et al., 2014; von Moos and Slaveykova, 2014). Some of the key interactions include lipid peroxidation leading to disruption of the cell-membrane (Nel et al., 2006), protein oxidation resulting in imbalance of enzymatic activities (Kumar et al., 2011), nucleic acid oxidation followed by genetic mutation and developmental toxicity (Nel et al., 2006). The free radicals can participate in membrane protein remodeling, both in prokaryotic and eukaryotic cells, to alter permeability through the membranes (Pacurari et al., 2011; Zhang et al., 2010). The radicals also can reduce the production of natural antioxidants such as glutathione, superoxide dismutase, and catalase (von Moos and Slaveykova, 2014).

Generation of these reactive species occurs by electron transfer from the MONP surfaces, initiated by the energetic positioning of the electronic bands (Fig. 1) as indicated by recent literature (Burello and Worth, 2011; Gajewicz et al., 2015; Kaweeteerawat et al., 2015; Zhang et al., 2012). Fundamental electronic structure and distribution of metals control the electronic band positioning. However, imperfections at the nano-scale (Janotti and Van de Walle, 2007; Laks et al., 1991) and introduction of secondary metals as dopants (Buonsanti and Milliron, 2013), further modulate the band structure (Fig. 2). Such modulation can either be incidental (during synthesis) or engineered (to extract desired electronic properties) and both can contribute to an altered ability to generate ROS. Furthermore, the confounding conclusions about the key mechanisms of MONP nanotoxicity (Djurišić et al., 2015; von Moos and Slaveykova, 2014) should consider crystal defects and dopants due to, their ability to generate a wide range of ROS. Identifying the thermodynamic favorability of dopant or defect mediated ROS-generation by MONPs will eventually enable screening of MONPs for ROS-generation kinetics. However, the effects of unintentional nano-scale imperfections or intentional defects and dopant distribution of MONPs on their ROS-generation ability have not been systemically evaluated in most nanotoxicity studies. This commentary focuses on band structure alteration of doped and defected MONPs and discusses the toxicological consequences and potential future strategies to better characterize lattice defects and dopants.

2. Mechanisms of metal oxide nanoparticle toxicity

Nanotoxicity of a large set of metal oxide (e.g., TiO_2, CuO, ZnO, cerium oxide (CeO_2), iron oxide (Fe_2O_3), manganese oxide (Mn_2O_3)) particles has been assessed, and quantitative structure activity relationship

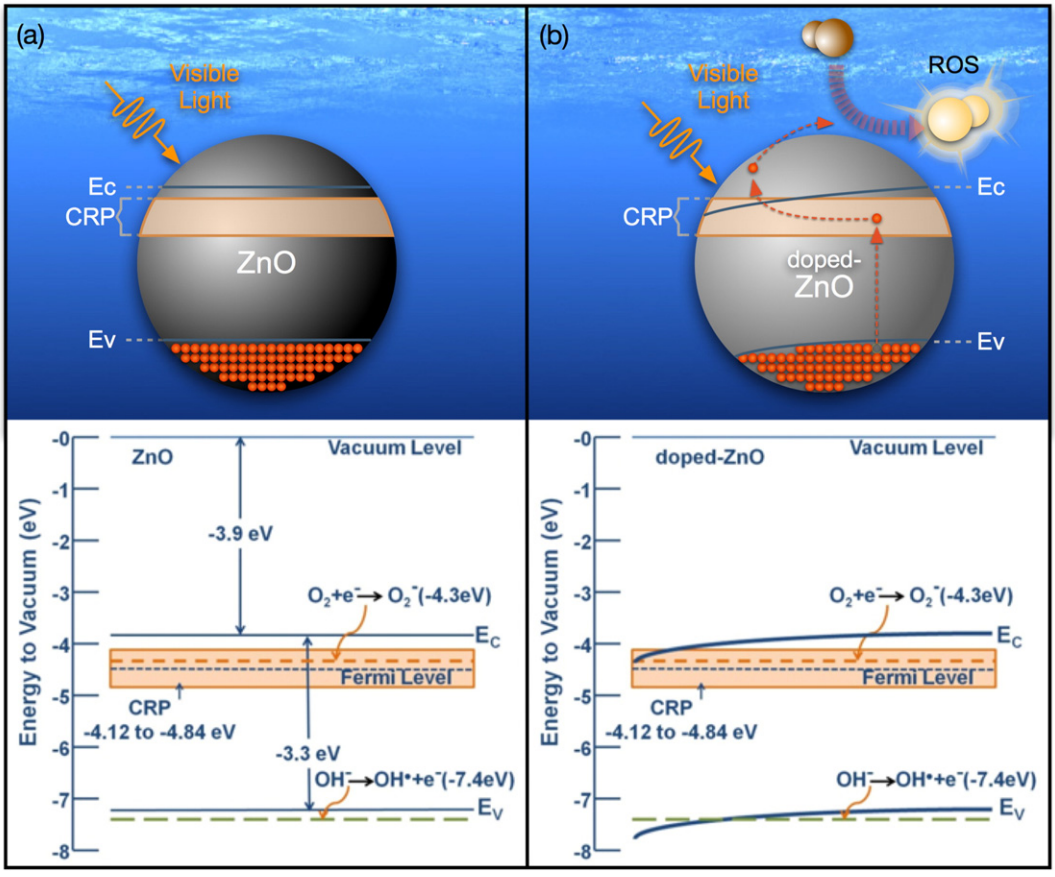

Fig. 1. (a) Un-doped ZnO nanoparticle and its band structure showing electrical conduction band (E_c) distant from cellular redox potential (CRP). (b) ROS active doped-ZnO nanoparticle and its E_c re-positioning within CRP via doping-induced band bending.

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