Effects of nano-ZnO/nano-TiO₂ coexistence on nano-ZnO dissolution and toxicity

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Introduction
The early 21st century is witnessing the transition of nanotechnology from discovery to commercialization. Engineered nanomaterials (ENMs) are incorporated into numerous commercial products ranging from pharmaceuticals and cosmetics to alternative energy and electronic devices, leading to a global market projected to reach $3 trillion in 2020. As a result, diverse ENMs (such as nano-TiO₂, nano-ZnO, nano-Ag, carbon nanotubes and fullerenes) will be inevitably released into the environment, generating growing concerns about their potential toxicity to natural organisms. Considerable effort has been exerted to understand the environmental behavior and risks of ENMs. Information about the ecotoxicological effects of ENMs has been gathered for almost all the major ENMs and a broad range of taxa (e.g., bacteria, algae, plants, invertebrate, and vertebrate). However, these previous studies are mostly limited in scope to evaluate the fate or toxicity of only one nanomaterial at a time, and thus their results overlook the potential interactions between different ENMs. Consequently, little is known about the effects of co-contaminant interactions on ENM fate, transport, and the corresponding toxicity potentials.

The primary study, sponsored by the National Science Foundation (NSF), addresses the fate and toxicity of nano-TiO₂ and this complementary project supported by the Institute for Sustainability and Energy at Northwestern (ISEN), explores the chemical interactions between nano-TiO₂ and nano-ZnO (Figure 1). In particular it investigates how nano-TiO₂ affect nano-ZnO dissolution and toxicity. We chose these two semiconductor metal oxides because they are among the most extensively used ENMs in industry. According to studies by Muller et al. and Gottschalk et al., the annual production volume and predicted environmental concentrations of nano-TiO₂ and nano-ZnO are much higher than those of other frequently studied ENMs (including nano-Ag, carbon nanotubes and fullerenes). Therefore, coupled with their wide applications in personal-care products and industry, nano-TiO₂ and nano-ZnO are the most likely to coexist and interact with each other in nature. The major findings obtained in this study are listed below.

Figure 1. TEM micrographs of nano-TiO₂ P25 (left) and nano-ZnO (right).
Major findings

1. **Nano-TiO2 surfaces control the concentration of dissolved Zn during nano-ZnO dissolution.**

   We show that the adsorption of Zn\(^{2+}\) onto nano-TiO2 (Evonik P25 was used as the representative of nano-TiO\(_2\)) controls the concentrations of dissolved zinc ions in solution (e.g., when ZnCl\(_2\) is dissolved in water) and also the concentrations of dissolved Zn released as a result of nano-ZnO dissolution (Figure 2A and 2B). However, in the case of the dissolution of nano-ZnO, \([\text{Zn}]_{\text{dis}}\) reaches time-dependent plateaux when the nano-ZnO is only partially dissolved, depending on the concentrations of nano-TiO\(_2\) present in suspension (Figure 2C).

![Figure 2](image)

**Figure 2.** \([\text{Zn}]_{\text{dis}}\) from (A) 0.5 mg/L Zn in the form of ZnCl\(_2\), (B) 0.5 mg/L nano-ZnO, and (C) 1 mg/L nano-ZnO in the presence of P25 with different concentrations. 0.5 mg/L and 1 mg/L of nano-ZnO represent fully- and partially-dissolved nano-ZnO in LMW after a 2d-incubation respectively, according to the stoichiometry.

2. **The nano-ZnO/nano-TiO2 interaction is synergistically mediated by Zn (II) adsorption on nano-TiO2 and further dissolution of remaining nano-ZnO as a Zn\(^{2+}\) reservoir.**

   When nano-ZnO and nano-TiO\(_2\) coexist as particles in suspension, dissolved zinc is released from nano-ZnO and then partially adsorbed at the surface of nano-TiO\(_2\), as described by the following two reactions:

   \[
   \text{ZnO}(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2O(l) \quad (1)
   \]

   \[
   Zn^{2+}(aq) + \equiv TiOH(s) \rightleftharpoons \equiv TiOZn^+(s)^* + H^+(aq) \quad (2)
   \]

   The occurrence of Reaction 2 decreases the concentration of Zn\(^{2+}\) and drives Reaction 1 to the right. Then the remaining nano-ZnO behaves as a reservoir of Zn\(^{2+}\), which further dissolves and compensates the loss of \([\text{Zn}]_{\text{dis}}\) due to the adsorption by nano-TiO\(_2\). This explains the plateaux present in the \([\text{Zn}]_{\text{dis}}\) variations as a function of the concentration of nano-TiO\(_2\) P25 (Figure 2C). When the P25 concentration surpasses a certain threshold (e.g., \(\geq 20\)mg/L in Figure 2C), however, the dissolution of remaining nano-ZnO is not sufficient to maintain the level of \([\text{Zn}]_{\text{dis}}\) and a decrease of \([\text{Zn}]_{\text{dis}}\) becomes visible. As shown in Figure 3, synchrotron-based X-ray adsorption spectroscopy confirms the coexistence of zinc as nano-ZnO and adsorbed on nano-TiO\(_2\), and linear combination fittings of the XANES and EXAFS spectra consistently quantify their percentages. These results provide quantitative evidence to support our explanation from the molecular perspective.
3. A simple kinetic model is developed to predict the experimental data.

In order to establish a predictive understanding of the nano-ZnO/nano-TiO₂ interactions shown in this study, we developed a simple kinetic model that considers both the processes of nano-ZnO dissolution and adsorption of the released zinc on nano-TiO₂. This model successfully predicts the trend and values of the $[\text{Zn}]_{\text{dis}}$ curves for both fully- and partially-dissolved nano-ZnO mixed with P25, in particular the $[\text{Zn}]_{\text{dis}}$ plateaux observed in Figure 2C (Figure 4).

4. Both nano-TiO₂ and nano-ZnO are photoactive, but their phototoxicity is not additive.

Nano-TiO₂ and nano-ZnO share similar band gaps and band edge energies. Both materials are used as photocatalysts and their phototoxicity has been reported in the literature. Therefore, we probed the co-toxicity of nano-TiO₂ and nano-ZnO under simulated solar irradiation. As shown in Figure 5, both nano-TiO₂ and nano-ZnO exhibited phototoxicity to bacteria E. coli, but their phototoxicity was not additive. For example, the presence of 1 mg/L nano-ZnO surprisingly eliminated the phototoxicity of 10 mg/L nano-TiO₂ P25, and the presence of 25 mg/L nano-ZnO, which reduced bacterial viability by 40%, did not increase the phototoxicity of P25. We monitored the production of hydroxyl radical (‘OH), which is believed
to cause nano-TiO$_2$ phototoxicity$^{23}$, by using a selective probe HPF$^{21}$. Results show that the 'OH production did not correlate well to the phototoxicity of nano-TiO$_2$/nano-ZnO, indicating that other mechanisms may be responsible to explain the phenomena observed in Figure 5.

**Environmental Implications**

According to a recent review article by Lowry et al.$^7$, nanomaterials are subjected to various physical, chemical, and biological transformations in natural environments, which determine their fate, transport and corresponding toxic potentials. As a variety of ENMs are commonly used in industry and consumer products and are then discharged into the environment, co-contamination of multiple ENMs is likely to occur, which creates complex interactions that can alter ENMs availability and exposure. In our study, the presence of nano-TiO$_2$ is found to mediate both the dissolution of nano-ZnO and the concentration of zinc in solution. Considering the toxicity of nano-ZnO is largely attributed to the release of dissolved ionic zinc$^{24-27}$, our results indicate the potential importance of other ENMs such as nano-TiO$_2$ or environmental surfaces in controlling the fate, mobility, and ultimately, the bioavailability of nano-ZnO. Accordingly, the incorporation of ENMs interactions into risk assessment models will lead to a more in-depth understanding of their environmental fate and ultimately, potential impacts on human and ecological health as a result of applications and discharges of diverse ENMs.

**Research outcomes and future work**

This study has led to one manuscript (which will be submitted to *Environ. Sci. & Technol.*) and one presentation at mainstream national conference (see appendix). Our ongoing and future work will be focused on:

1. The mechanisms of the co-phototoxicity of nano-TiO$_2$ and nano-ZnO (shown in Figure 5). Various selective probes targeting different ROS species (e.g., 'OH, $^1$O$_2$, and O$_2^-$) will be used to systematically measure ROS produced by nano-TiO$_2$ in the presence/absence of nano-ZnO. Also, the contact of bacterial cells with nano-ZnO/nano-TiO$_2$ nanoparticles will be visually studied by transmission electron microscopy with a liquid holder.

2. The interactions between nano-TiO$_2$ and nano-Ag. It was actually proposed in this ISEN study. But due to the time- and labor-constraints, we invested most of our time and efforts on the interactions between nano-TiO$_2$ and nano-ZnO, as shown above. Nano-Ag is widely applied as an antibacterial agent and Ag will undergo more complex physical and chemical transformations in the aquatic environments. Based on our experiences obtained from this ISEN grant, we will focus on the dissolution and photochemistry of nano-Ag in the presence of nano-TiO$_2$. 

![Figure 5. Phototoxicity and 'OH productions of nano-TiO$_2$ P25, nano-ZnO and nano-TiO$_2$/nano-ZnO mixtures.](image-url)
Appendix: publications


References