

Short communication

Hazard reduction for the application of titania nanoparticles in environmental technology

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Abstract

Photocatalytically active titania (TiO₂) nanoparticles are applied, and considered for application, in the degradation of hazardous substances. However, these nanoparticles are also hazardous by themselves. High efficiency immobilization of TiO₂ nanoparticles on large inorganic supports that are not vulnerable to photocatalytic degradation is conducive to hazard reduction. Immobilization should also aim at minimizing the release of TiO₂ nanoparticles from such supports due to attrition. In doing so there may be a trade off between hazard and photocatalytic activity.
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1. Introduction

Titania (TiO₂) nanoparticles, with a diameter <100 nm, are applied, and considered for application, in environmental technology [1–52]. The focus of this application is often the degradation of hazardous substances. The application of TiO₂ nanoparticles has been studied in the treatment of water (e.g., waste water and groundwater) with, often poorly degradable, organic substances (e.g., [1–10,21–23,26–29]), the removal of benzothiophene from diesel fuel [11], the breakdown of crude oil [12] and the degradation of air pollutants, especially nitrogenoxide(s), sulphuroxides and volatile organics (e.g., [13–16,21,24,25,30,32,40]). The reduction of metal ions in water has also been studied [36]. A number of studies have focussed on the performance of TiO₂ suspensions, as these allow for relatively high surface areas of catalysts per unit of reactor volume and maximum exploitation of the specific surface area of nanoparticles (e.g., [2,8,15,17–23,28,30,32]).

Degradation of hazardous substances by TiO₂ is linked to redox reactions. Absorption of photons by TiO₂ leads to photo-excitation: the formation of electron–positive hole pairs. Reaction with the positive hole is linked to oxidation and reaction with the electron to reduction [1,3,21,25]. The frequency of

such reactions per unit of mass of TiO₂ can be much enhanced by exploiting nanoparticles that have a relatively large surface area (e.g., [1–3,21,22,37–39]). Enhancement of photocatalytic activity is possible by manipulating the physico-chemical character of the nanoparticle surface, to increase adsorbability of hazardous substances that are to be degraded and to decrease the probability of recombination of electrons and positive holes [38,40].

A drawback of TiO₂ is that the photo-excitation requires photons in the near ultraviolet part of the spectrum, which corresponds with 3–5% of solar irradiation. This has led to efforts to shift photo-excitation to the visible part of the solar spectrum. Also, inactivation of TiO₂ may occur due to the deposition of organics on the particle surface. Maximizing the photocatalytic effect of TiO₂ nanoparticles, shifting photo-excitation to longer wavelengths and minimizing deactivation has become an active area of research, partly involving the combination of TiO₂ nanoparticles with other substances (e.g., as dopants or nanoparticles), including a variety of metals used as dopants (e.g., [1–4,6,16,22,23,25,28,33,34,38–52]).

Interestingly, the possibility that the TiO₂ nanoparticles themselves may be hazardous, has not figured prominently in considering applications of such particles in environmental technology. To the extent that hazard is referred to by authors involved in the development of TiO₂ nanoparticle applications, it has been stressed that photocatalytic TiO₂ nanoparticles are non-toxic [8,24,32,39,52–60], safe [13,33], or harmless [20,61].

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2. The hazard of TiO₂ nanoparticles

Substantial research has been done regarding the hazard of TiO₂ nanoparticles. This research has considered the inhalation of such nanoparticles by mammals, mammalian ingestion of TiO₂ nanoparticles, the effects of dermal contact, the effect on microbes and some aspects of aquatic ecotoxicity. It has turned out that whereas large TiO₂ particles are characterized by a very low hazard, the hazard of TiO₂ nanoparticles may be different.

On discharge into air, TiO₂ nanoparticles may be inhaled and deposited in the lungs. In this context, Warheit et al. [62] have studied the effect of intratracheally instilled TiO₂ particles in rats. They found evidence for pulmonary inflammation, cytotoxicity and adverse lung effects. The hazard of TiO₂ nanoparticles was less than that of quartz nanoparticles. In other studies, it has been found that the negative impact increases when the surface area of TiO particles increases and when the number of TiO₂ particles increases [63–67]. These phenomena may be mediated by oxidative stress and impaired phagocytosis by macrophages [64,66,67]. Dependent on other exposures to particulate matter, inhalation of TiO₂ nanoparticles may increase lung morbidity [64,68]. The hazard of a specified mass of TiO₂ nanoparticles to lung tissue increases when number and surface area increase, and may be further increased by the presence of metals such as V, Fe, Cr or Ni that may be used as dopants or are deposited on the TiO₂ nanoparticles during environmental applications [21,22,31,36,41,64,69–72]. Also, Kapp et al. [73] and Geiser et al. [74] have shown that 5 nm sized TiO₂ nanoparticles rapidly translocate from the rat lung to the vascular system. This may be linked with hazard of TiO₂ nanoparticles to the cardiovascular system [75] and to other organs [64,68]. The former may lead to increased cardiovascular morbidity [51,64,75].

Warheit et al. [62] performed acute dermal irritation studies on intact skin and found that TiO₂ nanoparticles are not a skin irritant or a dermal sensitizer. However, there is some evidence that when photocatalytically active TiO₂ nanoparticles are present on a skin with a damaged stratum corneum (upper layer), there may be a hazard [68]. In this case, when there is solar irradiation of the skin, there may be photochemical damage to living skin cells [68].

Acute oral toxicity studies have demonstrated very low acute toxicity of TiO₂ nanoparticles [62]. However, there is also evidence suggesting that TiO₂ nanoparticles may cause immune reactions of the intestines after oral intake, which may be linked to chronic toxicity, and there is a possibility that part of the ingested nanoparticles may be translocated from the intestines and deposited in organs [76–78]. At high levels of exposure this, in turn, may lead to inflammation [78].

Photocatalytically active TiO₂ nanoparticles may have antimicrobial effects in the presence of solar irradiation [64,79]. As to aquatic ecotoxicity, Warheit et al. [62] found that TiO nanoparticles exhibited medium concern in a 72 h acute test using the green algae *Pseudokirchinella subcapitata*. Exposure of rainbow trout to TiO₂ nanoparticles has shown to be associated with respiratory distress, intestinal erosion and disturbances in the metabolism of Cu and Zn [80].

All in all, there is evidence that TiO₂ nanoparticles present a hazard, though the determination of the precise character and size of that hazard awaits further investigation.

3. Hazard reduction strategies

Against this background, it would seem worthwhile to consider ways to limit hazards of TiO₂ nanoparticles applied in environmental technology.

Efforts limiting the hazard of TiO₂ particles attention have partly focused on the application of coatings and dopant ions that reduce the photocatalytic activity of these particles [81–83]. This strategy evidently makes no sense for applications in environmental technology as these rely on photocatalytic activity and actually tend to aim at maximizing such activity.

A second hazard reduction strategy regards the crystal structure of TiO₂ [76]. TiO₂ may occur as brookite, rutile or anatase. Research into photocatalytic applications of TiO₂ nanoparticles has mainly focussed on anatase and rutile.

Anatase and rutile differ in their interactions with cells. It has been pointed out that anatase is more cytotoxic than rutile [84]. However, TiO₂ preparations consisting mainly or fully of anatase also appear to be preferred in environmental technology. Often such preparations do better in the photocatalytic degradation of hazardous substances than rutile though occasionally anatase/brookite mixtures or anatase/rutile mixtures with occasionally high percentages of rutile did better than pure anatase (e.g., [2,22,39,43,44,85–87]). Thus, replacing anatase by rutile would seem a hazard reduction strategy with very limited potential.

A third hazard reduction strategy is to immobilize TiO₂ nanoparticles on supports or substrates. Such immobilization also circumvents a problem that has emerged in using TiO₂ nanoparticles in suspension: the troublesome separation of nanoparticles after treatment [13,21]. Many examples of technologies that may be considered for the immobilization of TiO₂ nanoparticles on supports have been described. The technologies that may be used for this purpose in part employ precursors, such as organic Ti compounds, for in situ growth of nanoparticles. Other technologies use pre-existing TiO₂ nanoparticles.

One approach to immobilization aims at composite nanoparticles. Here the focus has been on TiO₂ coated multiwalled carbon nanotubes [88–91]. Many authors (e.g., [1–3,8,9,15,16,24–27,29,35–38,40–43,53–55,92–98]) have studied the immobilization of TiO₂ nanoparticles on much larger supports, often in the form of coatings or thin films, by processes such as metal oxide chemical vapour deposition (CVD) and infiltration, liquid phase deposition, barrier-torch discharge-, ion beam enhanced-, arc- and pulsed laser deposition, sol–gel methods, including dip coating, a variety of technologies involving spraying and sputtering and electrophoretic deposition.

After immobilization part of the surface area of TiO₂ nanoparticles will be unavailable for photocatalysis. This leads, ceteris paribus, to lowered photocatalytic activity, and this phenomenon becomes relatively more important when particles become smaller [27,99]. Also the photocatalytically active

area per unit of reactor volume may be lower than in case of suspensions. On the other hand, especially when porous substrates such as zeolites or activated carbon are used, adsorption of pollutants may be enhanced, and this may favour photocatalytic conversion, though it should be noted that very high surface areas of such substrates might reduce photocatalytic activity [9,27,100]. Also immobilization may lead to reduced positive hole–electron recombination favouring the degradation of hazardous substances [9]. All in all, it has been found in a number of instances that immobilized TiO₂ may be an effective photocatalyst (e.g., [1–3,8,9,15,16,25–27,29,35,38]).

For the purpose of hazard reduction the use of TiO₂ coated multiwalled carbon nanotubes may be considered doubtful. The precise hazards of such nanotubes have been studied incompletely, but research done so far has not been favourable. There is evidence that carbon nanotubes may elicit a toxic response when they are inhaled and deposited in the lungs that is much stronger than in case of amorphous carbon nanoparticles [101]. Moreover carbon nanotubes have characteristics that suggest a possible accumulation along the food chain and high persistence [101]. It also seems likely that the nanotubes may be subject to photocatalytic degradation [29,42,94], leading to deterioration of the catalytic performance [102] and possibly to the release of TiO₂ nanoparticles.

The use of larger supports would seem a more promising approach to hazard reduction. The hazards linked to the preparation thereof should be considered. In this context, the precursors used (often organotitanium compounds), additives used in processing such as organic solvents [103], and the nanoparticles that do not become immobilized merit consideration. To limit the hazard from the latter high efficiency *in situ* growth of TiO₂ particles, minimizing the amount of nanoparticles not immobilized on the support, would seem an interesting option.

To facilitate bonding of TiO₂ in case of fixation on synthetic organic supports coupling agents have been used [96] and in case of polycarbonate pre-treatment to increase the presence of phenolic OH groups [97].

When TiO₂ nanoparticles are immobilized by linking them to large supports, there is the possibility that they may be released. When TiO₂ particles are immobilized on an organic support such as carbon [29,42,102], synthetic organic polymers [37,96,102] or fibrous material [54,104], it is possible that the support is photocatalytically degraded during its application and this may lead to the release of nanoparticles.

In the case of a stainless steel support, there is evidence that photocatalytic activity may lead to the release of Fe and Cr cations [98], and this in turn may lead to the loss of TiO₂ nanoparticles. Moreover it would seem that when photocatalytic activity affects the substrate the conversion of air and water pollutants can be negatively affected [98,102].

Glass, silicate, zeolite and ceramic supports do not seem to be influenced by nanoparticulate photocatalytic activity. However, when ceramic inorganic supports are used to degrade volatile organics in the gas phase, loss of photocatalytic activity due to erosion has been noted [92]. In case of commercially available glass beads covered with TiO₂ nanoparticles significant attrition of the TiO₂ film was found on application in water

treatment [105]. It is not clear in these cases what the size was of the particles that were released on erosion or attrition. Loss of photocatalytically active nanoparticles from substrates with immobilized TiO₂ may also be linked to processes such as maintenance (e.g., cleaning and regeneration) and wear due to processes in the disposal or recycling stage [82].

Loss of nanoparticles from supports that are not photocatalytically degraded would seem to depend partly on the strength of bonding between nanoparticles and the substrate used. In this context it may be noted that on application of some varieties of sol–gel technologies and chemical vapour deposition technology, bonding strength between TiO₂ nanoparticles and substrates has been found to be low [44].

There is evidence that bonding on inorganic supports can be improved when TiO₂ is subjected to melting [42]. However this strongly favours the formation of rutile [28,46,106–109], which, though more wear resistant [110] is, as pointed out above, in many cases less conducive to photocatalytic degradation of hazardous substances than anatase. It may also be noted that better bonding between substrate and nanoparticles and better resistance against nanoparticle loss can be correlated with decreased specific surface area available for photocatalysis [22]. This implies that there may be a trade off between photocatalytic activity and the actual release of nanoparticles.

Still from the point of view of hazard reduction, immobilization of TiO₂ nanoparticles should be designed in such a way that the release of nanoparticles during the life cycle of the catalyst ('from cradle to grave') is minimized, while the immobilization of TiO₂, usually preferentially anatase, nanoparticles is favoured. To the extent that immobilization is not irreversible, design should preferably be such that relatively large inorganic particles are released. The preference for relatively large inorganic particles is linked to the finding that hazard of such particles, *ceteris paribus*, tends to increase when the diameter becomes smaller [64,67]. As to the potential for this approach, a parallel may be drawn with the nanoparticulate Pt group catalysts that are applied in catalytic converters for motorcars. In this case, >>90% of the Pt that is released from converters has been found in inorganic particles > 100 nm [111–114].

4. Conclusion

High efficiency immobilization of TiO₂ nanoparticles on large inorganic supports that are not vulnerable to photocatalytic degradation is conducive to hazard reduction. Immobilization should also aim at minimizing the release of TiO₂ nanoparticles from such supports due to attrition. In doing so there may be a trade off between hazard and photocatalytic activity.

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