

Evaluating Photoreactivity of TiO₂ Using EPR Spectroscopy

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Introduction

Titanium dioxide (TiO₂) have been widely applied in a variety of industries including photocatalysis, coatings, and cosmetics. Based on the application, TiO₂ particles are tailored to meet the requirement of photoactivity and suspended/blended in various solvents/matrices. In this study, the photoreactivity of TiO₂ in various solvents was studied by using electron paramagnetic resonance (EPR) to monitor the free radical intermediates generated under ultraviolet (UV) irradiation. Due to the short lifetime of many radicals, EPR methods employing a lower temperature (77 K) and/or the addition of appropriate spin traps were used to prolong the lifetime of active free radical intermediates.

Nitroxide spin traps, such as 3-amino-proxyl (AP) and 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) have been commonly used in EPR spin trap techniques [1-3]. The AP photostable free radicals react with radical species generated from the UV-irradiated TiO₂ particles or TiO₂/solvent suspensions. A decrease in AP concentration with irradiation time indicates the consumption of radicals, but is not selective to a particular radical species. A more selective spin trap agent, DMPO, traps specific radicals and forms spin adducts with characteristic EPR lines. In this study, the effects of solvent type and TiO₂ crystal phase and preparation on photoreactivity were investigated. Preliminary results show that the EPR methods can evaluate the photoreactivity of TiO₂. Furthermore, only aqueous suspensions led to the formation of hydroxyl radicals from irradiated TiO₂. Superoxide anion radicals were only observed in the presence of dimethyl sulfoxide (DMSO) in the TiO₂ suspensions.

Materials and Methods*

EPR experiments were performed with a Bruker BioSpin ElexSys500 spectrometer. EPR signals were characterized using the g-factor position, where $g\text{-factor} = h\nu/\mu_B B_0$, and h is Planck's constant, ν is frequency, μ_B is the magnetic moment of the electron, B_0 is the external magnetic field. A 500 W xenon arc lamp was used to directly illuminate the TiO₂ samples through the EPR cavity window for in-situ irradiation. A variety of commercial TiO₂ particles with anatase and rutile phases and various surface treatments were studied in as-received powder form or suspended in spin trap solutions. Spin traps, such as nitroxide and DMPO, were dissolved in distilled water, methanol or DMSO depending on TiO₂ suspensions. For spin trap measurements, the EPR sample was prepared by mixing spin trap solutions with TiO₂ suspensions and then the resultant EPR spectra were recorded over irradiation time at room temperature. Direct assessment of the generation of paramagnetic species on TiO₂ particles was conducted using a liquid-He cryostat. The intensity of each EPR signal was compared and obtained by double-integration of indicated line in a spectrum.

Results and Discussion

Changes in the cryostat EPR spectra of TiO₂ powders before and after UV irradiation are shown in Figure 1. Different EPR signals before irradiation were linked to the various TiO₂ crystal phases and treatments and interpreted in terms of impurities or residuals from TiO₂

production processes. Spin trap studies of TiO₂ suspensions without UV irradiation revealed no decay in the spin trap EPR signal with time, indicating that the non-irradiated TiO₂ did not have the potential to react with any spin trap radicals. Under irradiation, a new group of cryostat EPR signals ($g\text{-factor} = 2.020, 2.008$ and 2.004 in Figure 1) were produced for all TiO₂ samples, which was related to hole-trapping sites on TiO₂. A great diversity of electron-trapping centers ($g\text{-factor}$ less than 2) was observed, which varied with the characteristics of TiO₂ particles. The position of the cryostat EPR signals revealed the potential structures of hole/electron centers on irradiated TiO₂ surfaces. Slow recombination of hole/electron centers was observed by removing UV illumination and the initial EPR spectra were always completely restored. The repeatability of the cryostat EPR spectra was excellent despite a number of UV irradiation cycles.

Suspending TiO₂ particles in various solvents influenced the species of radicals generated as well as the interaction with spin traps. Figure 2 shows the EPR spectra of DMPO spin adducts produced from anatase-rutile TiO₂ particles in different solvents. Hydroxyl radicals were the primary radicals generated from aqueous TiO₂ suspensions. Some methyl radicals were trapped by DMPO in methanol/water system. However, no measurable signals were observed for systems containing TiO₂, DMPO, and pure methanol. The addition of DMSO enabled the stabilization of the superoxide anion radicals [3] in the corresponding EPR spectra of the DMPO spin adduct and were directly observed on some cryostat anatase TiO₂ samples.

Significance

EPR analysis provides a quick, direct manner of evaluating the photoactivity of TiO₂ as well as the direct observation of generated paramagnetic species. TiO₂ particles with potential photoactivity usually produce abundant hydroxyl radicals, which can be trapped in spin trap solutions. The superoxide radicals are present on highly photoactive TiO₂ systems.

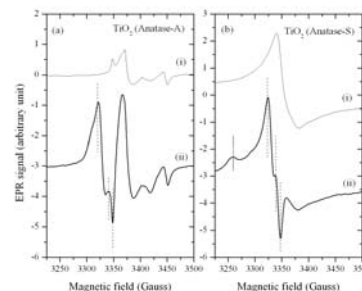


Figure 1. Cryostat EPR spectra of TiO₂ powders (a) Anatase-A and (b) Anatase-S in the dark (i) or under irradiation (ii). The standard uncertainty is $\pm 1\%$.

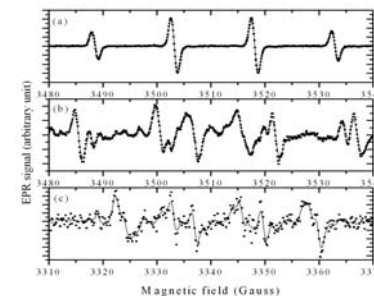


Figure 2. EPR spectra for irradiated anatase-rutile TiO₂ in a) DI-water, b) DI-water/methanol c) DMSO, with the presence of DMPO spin trap. The standard uncertainty is $\pm 1\%$.

References

1. E. M. Ceresa, L. Burlamacchi, M. Visca, *J Mater Sci*, 18, 289 (1983).
2. P. F. Schwarz, N. J. Turro, S. H. Bossmann, A. M. Braun, A. A. A. Wahab, H. Durr, *J. Phys. Chem. B* 101, 7127 (1997).
3. V. Brezova, S. Gabcova, D. Dvoranova, A. Stasko, *J. Photochem Photobio B: Biology* 79, 121 (2005).

* Certain instruments or materials are identified in this paper in order to adequately specify experimental details. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experimental procedure.