Evaluating Photoreactivity of TiO\textsubscript{2} Using EPR Spectroscopy

I-Hsiang Tseng\textsuperscript{*} and Stephanie S. Watson
National Institute of Standards and Technology, Gaithersburg, MD 20899 (USA)
ihihsiang@nist.gov

Introduction
Titanium dioxide (TiO\textsubscript{2}) have been widely applied in a variety of industries including photocatalysis, coatings, and cosmetics. Based on the application, TiO\textsubscript{2} particles are tailored to meet the requirement of photoactivity and suspended/blended in various solvents/matrices. In this study, the photoreactivity of TiO\textsubscript{2} 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 TiO\textsubscript{2} particles or TiO\textsubscript{2}/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 radicals and forms spin adducts with characteristic EPR lines. In this study, the effects of solvent type and TiO\textsubscript{2} crystal phase and preparation on photoreactivity were investigated. Preliminary results show that the EPR methods can evaluate the photoreactivity of TiO\textsubscript{2}. Furthermore, only aqueous suspensions led to the formation of hydroxyl radicals from irradiated TiO\textsubscript{2}. Superoxide anion radicals were only observed in the presence of dimethyl sulfoxide (DMSO) in the TiO\textsubscript{2} 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-factor = hv/µB0, and h is Planck's constant, ν is frequency, µB is the magnetic moment of the electron, B\textsubscript{0} is the external magnetic field. A 500 W xenon arc lamp was used to directly illuminate the TiO\textsubscript{2} samples though the EPR cavity window for in-situ irradiation. A variety of commercial TiO\textsubscript{2} 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 TiO\textsubscript{2} suspensions. For spin trap measurements, the EPR sample was prepared by mixing spin trap solutions with TiO\textsubscript{2} suspensions and then the resultant EPR spectra were recorded over irradiation time at room temperature. Direct assessment of the generation of paramagnetic species on TiO\textsubscript{2} 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 TiO\textsubscript{2} powders before and after UV irradiation are shown in Figure 1. Different EPR signals before irradiation were linked to the various TiO\textsubscript{2} crystal phases and treatments and interpreted in terms of impurities or residuals from TiO\textsubscript{2} production processes. Spin trap studies of TiO\textsubscript{2} suspensions without UV irradiation revealed no decay in the spin trap EPR signal with time, indicating that the non-irradiated TiO\textsubscript{2} did not have the potential to react with any spin trap radicals. Under irradiation, a new group of cryostat EPR signals (g-factor = 2.020, 2.008 and 2.004 in Figure 1) were produced for all TiO\textsubscript{2} samples, which was related to hole-trapping sites on TiO\textsubscript{2}. A great diversity of electron-trapping centers (g-factor less than 2) was observed, which varied with the characteristics of TiO\textsubscript{2} particles. The position of the cryostat EPR signals revealed the potential structures of hole/electron centers on irradiated TiO\textsubscript{2} 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 TiO\textsubscript{2} 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 TiO\textsubscript{2} particles in different solvents. Hydroxyl radicals were the primary radicals generated from aqueous TiO\textsubscript{2} suspensions. Some methyl radicals were trapped by DMPO in methanol/water system. However, no measurable signals were observed for systems containing TiO\textsubscript{2}, 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 TiO\textsubscript{2} samples.

Significance
EPR analysis provides a quick, direct manner of evaluating the photoactivity of TiO\textsubscript{2} as well as the direct observation of generated paramagnetic species. TiO\textsubscript{2} 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 TiO\textsubscript{2} systems.

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* 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.

References