FORMATION OF SINGLET OXYGEN FROM COLLOIDAL TiO₂ NANOPARTICLE SURFACE

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Abstract: Photocatalytic detoxification of organic pollutants with the aid of TiO₂ nanoparticles or layers is a promising tool for purification and sterilization of environmental aqueous media. The photocatalytic reaction is initiated by electrons and positive holes photoinduced within the TiO₂ bulk or at the surface. Recently singlet oxygen (O₂) are reported to be generated in the primary TiO₂ photocatalytic stage. The direct observation of O₂ at the irradiated TiO₂ surface has been mentioned by Nosaka’s group, suggesting that ¹O₂ may contribute to the oxidation of some organic molecules. However, there have been remarkably few investigations concerning the production of O₂ under visible light irradiation at different pHs. We use time-resolved Nd:YAG laser equipped with Ge photodiode detector to quantitatively measure the production of O₂ generation using TSPP as reference (ΦΔ = 0.64 in D₂O). The formation of O₂ is observed by detecting its phosphorescence at 1270 nm in air-saturated colloidal TiO₂ (particle size 1-5 nm) D₂O solutions under 532 nm irradiation. The quantum yields of O₂ generation are found to be constant (0.5-0.6) within acceptable error range at pHs between 4 and 8 but slightly decreased (0.4) when pH goes up to 9. The decrease in quantum yield may result from the fast quenching rate of O₂ by TiO₂ nanoparticles at higher pH. Since the quantum yield is relatively high, a contribution of O₂ to the more conventional photocatalytic reactions may arise when the reactants are adsorbed on the TiO₂ surface. Moreover, as two-photon absorption in TiO₂ nanoparticles under visible light irradiation has been observed by Kobbe et al., it is possible that two-photon ¹O₂ photosensitization is involved in our system. We would like to point out here that experimental errors may be introduced when using one-photon absorption photosensitizer TSPP as a reference for two-photon photosensitization. A clarification of the photosensitization mechanism requires further investigation.