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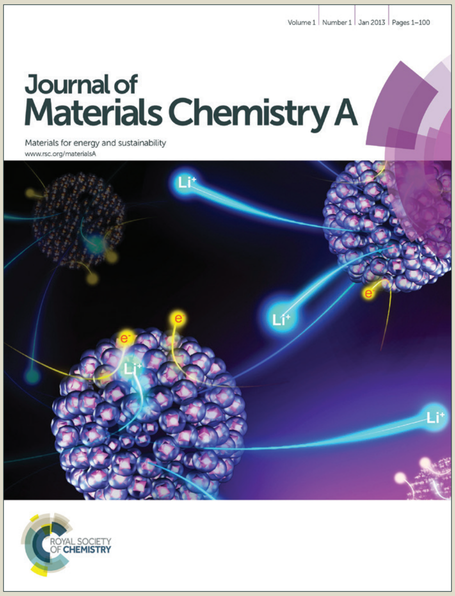

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Photocatalytically inactive microporous titanate nanofiber as an excellent and versatile additive to enhance TiO_2 photocatalytic activity

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The photocatalytic activity of TiO_2 under simulated solar light, evaluated by the oxidative decomposition of organic compounds in water, was substantially enhanced when a new and photocatalytically inactive TiO_2-based nanostructured material (microporous titanate nanofiber) was just mixed with the starting suspension, as a result of the unique electron capture ability to retard charge recombination.

Development of highly active solid photocatalysis systems is among the most attractive topics not only for environment purification but also for fuel production and fine chemical synthesis.[1-3] While acknowledging tremendous effort to design advanced photocatalysts like those including noble and rare metals, low-price photocatalysts are preferential for practical use. TiO_2 is one of the most promising photocatalysts because of its inexpensiveness, combined with long-term chemical stability and negligible toxicity. One weakness of TiO_2 is that it absorbs only ultraviolet light, occupying 3-5% of the incident solar light, and then shows negligible and low activity when used under visible light and solar light irradiation, respectively. One approach for highly active TiO_2 photocatalysis under such irradiation conditions in an economically benign fashion is to design new TiO_2 having noticeable structures or properties such as high surface area and high crystallinity,[4] anatase/rutile heterojunction[5] and predominantly exposed reactive facets.[6] Another is to develop operating environments (e.g. temperature,[7] light irradiation direction,[8] additives,[9] solvent compositions,[10] head-space atmospheres[[11]]) to enhance the activities of abundant TiO_2, though it is not easy to find such environments.

We have recently reported the synthesis of a new TiO_2-based nanostructured material, a microporous titanate nanofiber (MPTNF), and the unique properties such as well-restrained photocatalytic activity and extremely low refractive index.[12] Herein, we report an extraordinary and important finding that the photocatalytic activities of TiO_2 under solar light can be substantially enhanced by just using the photocatalytically inactive MPTNF as the additive of the reactions. We highlight a successful enhancement in the photocatalytic activity of a commercial TiO_2, P25 (mainly composed of anatase and rutile), which has frequently been used as a benchmark for photocatalysis because it is not easy to find and synthesize TiO_2 photocatalysts showing activities higher than that of P25.[6b] We anticipate MPTNF to be a key material for ultra-highly active and low-cost green photocatalysis.

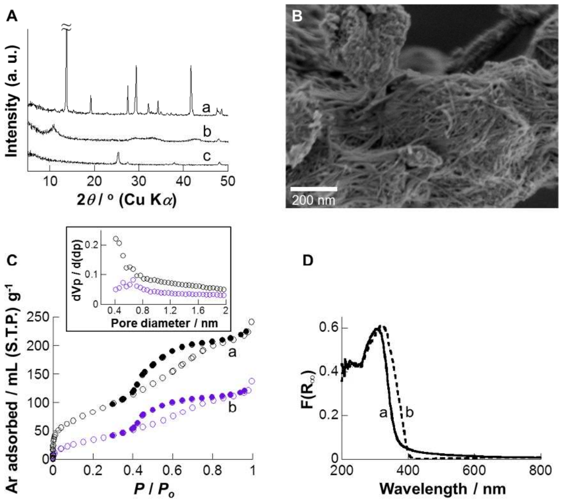

Fig. 1. (A) X-ray diffraction patterns of (a) $K_2Ti_2O_5$, (b) MPTNF and (c) P25 (mainly composed of anatase and rutile), (B) SEM image of MPTNF, (C) Ar adsorption (open circles)/desorption (filled circles) isotherms of MPTNF (a) before and (b) after crystal violet adsorption and (D) UV-vis spectra of (a) MPTNF and (b) P25. Inset shows the pore size distribution of MPTNF and crystal violet-adsorbed MPTNF by Horwarth-Kawazoe method applied to the adsorption isotherms.

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MPTNF was synthesized via the simple hydrothermal treatment of a layered titanate, $K_2Ti_2O_5$.[12] The chemical formula of MPTNF was $H_{0.65}K_{0.75}Ti_{2.15}O_5$ (K and partial H are exchangeable cations),[12] which was different from that of the starting layered titanate. MPTNF showed the X-ray diffraction pattern different from that of the starting layered titanate and those of conventional TiO_2 and titanates such as anatase, rutile, layered titanates and titanate nanotube (Fig. 1A). MPTNF had a nanofibrous morphology with a diameter up to 10 nm and a length up to several hundreds of nm (Fig. 1B). From various analyses, it was suggested that MPTNF had several microchannels (tunnels) with a width of ca. 0.5 nm along a nanofiber axial direction in a nanofiber.[12] An example analysis is presented in Fig. 1C. The Ar adsorption/desorption isotherms of MPTNF exhibited the abrupt uptake of Ar at lower partial pressure, indicating the presence of micropores or microchannels (hysteresis resulted from inter-nanofiber mesopores, which were observed in Fig. 1B). An inorganic cation (Ca^{2+}) effectively adsorbed inside the particle, while a larger organic cation, crystal violet (CV, molecular size of $1.4\times1.4\times0.4$ nm^3), adsorbed much less effectively because CV was difficult to penetrate along a nanofiber axial direction due to diffusion limitation.[12] After CV adsorption (mainly in the vicinity of the particle outer surface), Ar uptake at lower partial pressure dramatically decreased (Fig. 1C a *vs* b). Such significant decrease must not be observed if MPTNF has randomly oriented micropores or microchannels perpendicular to or across a nanofiber axial direction, and similar phenomenon has been observed for a clay mineral sepiolite having ordered microchannels (so called “tunnels” with a cross-section dimension of about 1.1×0.4 nm^2) in a microfibrous particle.[13] The photocatalytic activity of MPTNF was evaluated by the oxidation of cyclohexane in acetonitrile and 2-propanol in water under simulated solar light irradiation ($\lambda >$ 320nm) to be negligible, which presumably resulted from the unique structure (e.g. low crystallinity as shown in Fig. 1A).[12]

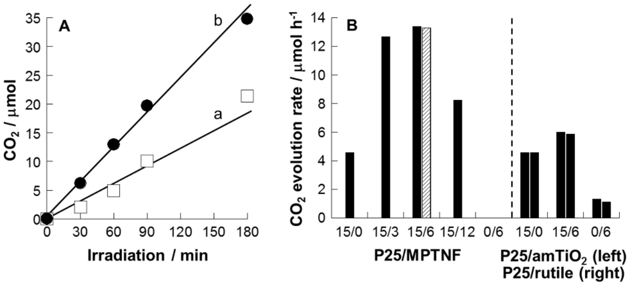

Fig. 2. (A) Time courses of CO_2 evolution from aerated aqueous solutions (5 mL) of formic acid containing (a) P25 (15 mg) and (b) P25/MPTNF mixture (15 mg/3 mg) under simulated solar light ($\lambda > 320$ nm). (B) CO_2 evolution rates at different P25/MPTNF, P25/amorphous TiO_2 and P25/rutile mixing ratios (mg/mg). Mesh bar indicates CO_2 evolution rate for reused P25/MPTNF mixture after washing with water.

On the basis of our previous successes to control the photocatalytic activities of semiconductor photocatalysts using photocatalytically indifferent materials, such as layered silicates and mesoporous silicas, as additives,[9c-g] we conceived to use MPTNF as the additive of TiO_2 photocatalysis. First, we tried to enhance the photocatalytic activity of P25, because P25 is one of the best TiO_2 photocatalysts for various reactions.[14] Here we evaluated the photocatalytic activity of P25 and P25/MPTNF mixture by the decomposition of formic acid to evolve CO_2 from an aerated (molecular O_2-saturated) aqueous solution, a representative reaction to test the performance of photocatalysts for organic pollutant removal.[6b,15] Fig. 2A shows the time course of CO_2 evolution from an aerated aqueous solution of formic acid containing P25 or P25/MPTNF mixture under simulated solar light irradiation ($\lambda > 320$ nm). With P25, the amount of CO_2 for formic acid decomposition linearly increased with irradiation time as reported previously.[6b,15] To our surprise, P25/MPTNF mixture showed considerably higher photocatalytic activity than did P25. MPTNF was inactive for the reaction (Fig. 2B), which was consistent with our previous results.[12] Therefore, a probable synergetic effect of the co-presence of P25 and MPTNF was revealed (MPTNF acted neither to concentrate organic molecules near P25 surface nor to scatter light to lead to better light adsorption of P25, enhancing the photocatalytic activity as described below). The enhancement of the photocatalytic activity of P25 was up to three times by changing amounts of the added MPTNF (Fig. 2B). On the other hand, other photocatalytically inactive or low-active TiO_2, such as amorphous TiO_2[16] and rutile (JRC-TIO-6)[11e,14], did not synergetically enhance the activity of P25 (the activity of P25/amorphous TiO_2 (or P25/rutile) mixture was similar to the sum of the activities of each TiO_2, Figure 2B). Furthermore, P25/MPTNF was successfully reused without losing the original activity (Fig. 2B, mesh bar), as a result of the chemical stability of MPTNF.[12] All results described above indicates an importance of our MPTNF as the additive of TiO_2 photocatalytic reactions.

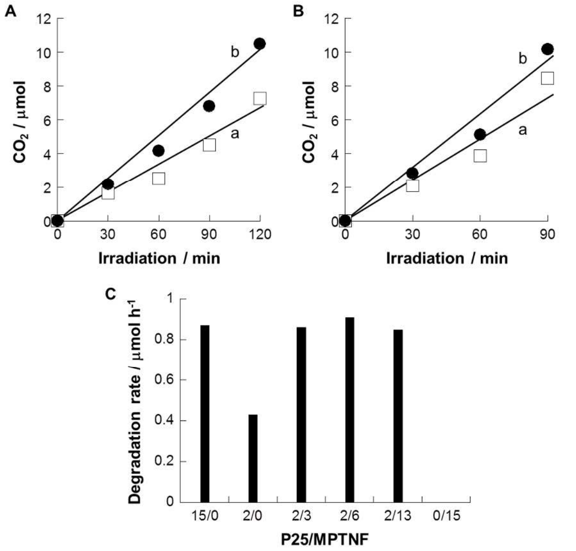

Fig. 3. Time courses of CO_2 evolution under simulated solar light irradiation ($\lambda > 320$ nm) from an aerated aqueous solutions (5 mL) of (A) methanol containing (a) P25 (15 mg) and (b) P25/MPTNF mixture (15 mg/3 mg) and (B) formic acid containing (a) anatase (15 mg) and (b) anatase/MPTNF mixture (15 mg/3 mg). (C) Rates for photocatalytic degradation of phenol in aerated aqueous solutions (40 mL) containing P25/MPTNF mixtures (mg/mg) at different mixing ratios under a full arc of Xe lamp ($\lambda > 320$ nm).

MPTNF was further used to enhance activities of other TiO_2 photocatalytic reactions. Fig. 3A compares time courses of photocatalytic decomposition of methanol in aerated aqueous solutions containing P25 and P25/MPTNF mixture under simulated solar light irradiation ($\lambda > 320$ nm). MPTNF could enhance the photocatalytic activity of P25 also for this reaction. Moreover, as shown in Fig. 3B, the photocatalytic activity for the oxidative decomposition of formic acid on anatase, not but P25, was also significantly enhanced when MPTNF was added into the starting suspension. These results confirm the versatility of MPTNF as additives to enhance photocatalytic reactions.

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Fig. 3C shows the rates for the photocatalytic degradation of phenol in an aerated aqueous solutions containing P25 and P25/MPTNF mixtures at different mixing ratios under a full arc of Xe-lamp irradiation ($\lambda > 320$ nm). MPTNF could enhance the activity of P25 also for this reaction, suggesting again the versatility of this material. It should be noted here that when the reaction was conducted with MPTNF, only two-fifteenth (ca. 13%) amounts of the photocatalyst were required to obtain the comparable reaction rate without MPTNF. This motivates us to use considerably reduced amounts of highly active state-of-the-art photocatalysts, like those including novel and rare metals, with MPTNF for much lower-cost photocatalysis.

We investigated the possible mechanism for the enhanced photocatlytic activities of TiO_2 in the presence of MPTNF. It has been reported that when photocataysts particles are mixed with adsorbents ones like clay minerals, adsorbents can concentrate substrates near photocatalysts to promote the photocatalysis. This did not apply to the present case, because MPTNF hardly adsorbed formic acid, methanol and phenol in water (probably due to the narrow channels and the surface hydrophilicity[12]). Also, we considered the possibility that MPTNF efficiently scattered light to lead to better light absorption of P25. Fig. 4 shows the photographs of aqueous suspensions containing P25, MPTNF and P25/MPTNF mixture. MPTNF was considerably more transparent than P25 when suspended in water, which was as a result of much lower refractive index (ca. 1.7).[12] Therefore, the positive light scattering effect of MPTNF on P25 photocatalysis was not predominant.

While, the photocatlytic decomposition of orgnic compounds into CO_2 often proceeds effciently only under aerated conditions and the plausible mechanism involves capture of photoexcited electrons with molecular O_2 to produce relatively stable superoxide radical anion and retard electrons-holes recombination[17] (although another involves production of peroxy radicals, as a caririer for radical chain reaction, through reaction with radical species evolved by the reaction of holes with organic substrates[18]). Here, we investigated electron transfer from P25 to MPTNF by monitoring Ti^{3+} formed in P25 rutile, by trapping the photoexcited electrons,[19] with electron spin resonance (ESR) analysis. As shown in Fig. 5A, when irradiated by UV light ($\lambda > 330$ nm) in the presence of molecular O_2, P25 created a broad signal due to Ti^{3+} ($g = 1.980$), in addition to signals due to superoxide-type oxygen anion (O_2^-; $g_{xx} = 2.003$, $g_{yy} = 2.010$, $g_{zz} = 2.022$) which was formed by the reduction of O_2 with the photoexcited electrons.[20] On the other hand, when P25/MPTNF mixtures were irradiated under the identical condition, Ti^{3+} yeild (based on P25 contents) decreased depending on amounts of the added MPTNF (Fig. 5A and B), suggesting efficient electron transfer from photoexcited P25 to MPTNF to retard electrons-holes recombination on P25 and enhance the photocatalytic activity. Such electron transfer may occur, because the conduction band potential of MPTNF is similar to that of P25 on the basis of speclation from their band gaps (Fig. 1D). As shown in Fig. 5C, P25/MPTNF showed much higher photocatalytic activity than P25 also under the irradiation of monochromatic light, 390 nm, under which only P25 was excited (Fig. 5C). This confirms the above hypothesis. The photocatalytic activities of P25/MPTNF mixtures did not depend on amounts of the added MPTNF (Fig. 2B), which probably resulted from that redudant MPTNF, which did not interact with P25, just absorbed UV light to reduce UV light absorption by P25.

Fig. 4. Photographs of aqueous suspensions containing (left) MPTNF, (middle) P25 and (right) P25/MPTNF mixtures. 6, 15 and 15/6 mg of powders, respectively, were suspended in 5 mL of water.

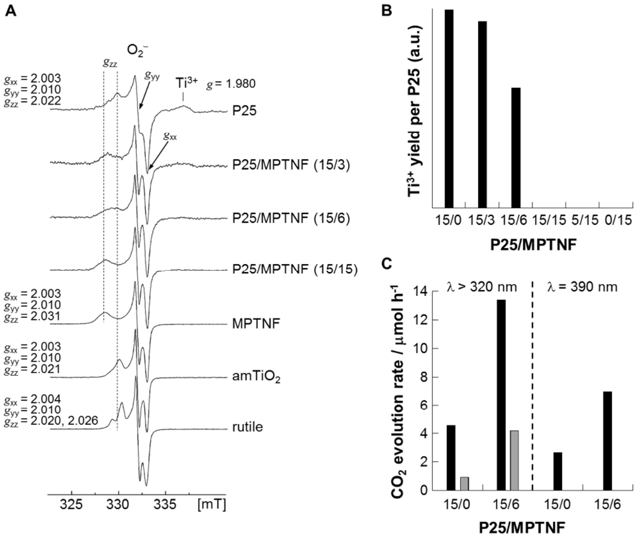

Fig. 5. (A) ESR spectra of P25, MPTNF, P25/MPTNF mixtures with different mixing ratios by weight, amorphous TiO_2 and rutile. The samples (10 mg) were treated with O_2 under UV light irradiation ($\lambda > 330$ nm) at room temperature and measured at 77 K after evacuation. (B) Variation of Ti^{3+} yields per P25 contents as a function of P25/MPTNF mixing ratios (mg/mg).

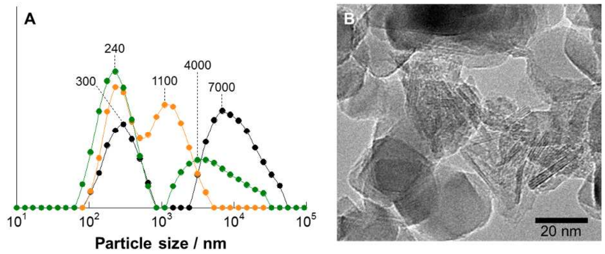

Fig. 6. (A) Particle size distribution determined by DLS of (black) P25 (15 mg), (orange) MPTNF (6 mg) and (green) P25/MPTNF mixture (15/6 mg) suspended in water (5 mL). (B) TEM image of P25/MPTNF mixture (1/0.2 mg) suspended in water (15 mL) after evaporation of water.

Fig. 5C (gray bars) shows the photocatalytic formic acid decompositon rates on P25 and P25/MPTNF mixture in deaerated aqueous solutions (in the absence of O_2). P25 hardly gave CO_2, while, P25/MPTNF mixture produced significant amounts of CO_2 even under such deaerated condition (CO_2 was thought to be evolved from formic acid mainly via radical chain reaction initiated by holes, where electrons is not included[18]). This results again support our hypothesis that MPTNF can capture electrons photoexcited on adjacent P25, like molecular O_2, to retard electrons-holes recombination on P25 (the degree (31%) in lowering of CO_2

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evolution rates without O_2 for P25/MPTNF mixture was slightly larger than that (20%) for P25, therefore, we could not rule out the possibility that MPTNF captured electrons from P25, namely, acts as a good additive for P25, only in the presence of O_2 for some reason).

To further discuss the feasibility of electrons transfer between P25 and MPTNF during photocatalytic reactions, we investigated the mixing state of P25 and MPTNF in the aqueous suspension. Fig. 6A shows the particle size distribution of P25, MPTNF and P25/MPTNF mixture suspended in water determined by dynamic light scattering (DLS). P25 showed bimodal distribution with particle sizes of ca. 300 and 7000 nm, which are assigned to small and large aggregates, respectively, of the primary particles (ca. 20-50 nm). MPTNF also showed bimodal size distribution at ca. 240 and 1100 nm, which corresponds to aggregated MPTNF particles observed in the SEM image (Fig. 1B). On the other hand, P25/MPTNF mixture showed a peak at ca. 4000 nm which P25 and MPTNF solely did not show, in addition to a peak at ca. 240 nm like P25 and MPTNF solely. From these results, it is thought that when just mixed in water, a part of P25 and MPTNF can form aggregates in which P25 particles can directly contact to MPTNF particles. We observed the TEM image of P25/MPTNF mixed suspension after the evaporation of water, finding that P25 and MPTNF particles contacted each other (Fig. 6B).

Finally, we discussed the possible reason for the efficient electron capture and O_2 reduction abilities of MPTNF. As shown in Fig. 5A, MPTNF exhibited a larger g_{zz} value for O_2^- than conventional TiO_2 such as P25, amorphous TiO_2 and rutile. This indicates weaker intractions between MPTNF and O_2^-.[21] We then believe that MPTNF can effectively adsorb and reduce O_2 by promptly releasing the once-generated O_2^- from its surface and then effectively capture electrons newly photogenerated on neighboring TiO_2, as a result of the unique structure. Because a wide variety of TiO_2-based materials with different structures is available[22] and electron migration behaviors in TiO_2-based materials are known to be affected by the structures,[23] further systematic studies are worth conducting to clarify the mechanism of the unique electron capture and O_2 reduction abilities of MPNTF.

In summary, we have reported that the photocatalytic activities of TiO_2 for the decomposition of organic compounds in water can be substantially enhanced by just adding a new and photocatalytically inactive TiO_2-based nanostructured materials, microporous titanate nanofiber, into the starting suspensions. This resulted from the unique electron capture ability of the titanate from photoexcited TiO_2 to retard the charge recombination. We are currently investigating the effect of microporous titanate nanofiber and other nanostructured materials as additives on various photocatalytic reactions.

Experimental

Materials. MPTNF was synthesized by the hydrothermal treatment of $K_2Ti_2O_5$ in the presence of tetrapropylammonium hydroxide and ammonium fluoride.[12] P25 and rutile (JRC-TIO-6) were supplied by Nippon Aerosil and Catalysis Society of Japan, respectively. Anatase and amorphous TiO_2 (surface area of 180-300 m^2 g^{-1}) were purchased from Kanto Chemical and Wako Pure Chemical, respectively. The all TiO_2 samples were used as received.

Photocatalytic activity tests. Oxidative decomposition of formic acid and methanol was performed in a stainless-made container (75 mL) equipped with Pyrex window as follows: The sample (TiO_2 powder or both TiO_2 and additive powders) was added in an O_2-saturated aqueous solution (5 mL) containing 5 vol% formic acid and 50 vol% methanol, respectively, and the suspension was ultrasonicated for 3 min and then irradiated by a solar simulator (San-Ei Electric, $\lambda > 320$ nm, 1000 W m^{-2}) under stirring. The gas in the container was withdrawn with a gas-tight syringe and quantified using a BID gas chromatograph (Shimadzu BID-2010 plus) equipped with a Micropacked ST column. In some of the experiments, irradiation was performed after bubbling the starting mixture with Ar to remove dissolved O_2. Phenol degradation was also performed in the stainless-made container (75 mL) equipped with Pyrex window. In this case, the sample was suspended in an O_2-saturated aqueous solution (40 mL) containing 60 ppm of phenol, the suspension was irradiated by a full arc of Xe lamp (Bunko Keiki, 150 W, $\lambda > 320$ nm) with magnetic stirring, and the amount of the remained phenol in the supernatant was quantified by a HPLC (Shimadzu LC-20AD) with a Union UK-C18 column.

ESR analysis. The ESR spectra were recorded on a JEOL JES RE-1X spectrometer (X-band). The magnetic field was calibrated and radical yields were determined using Mn^{2+}/MgO as a standard marker. The samples were mixed in a mortar and a portion (10 mg) of the mixture was placed in a quartz ESR tube, which was evacuated at 423 K for 1 h and cooled to room temperature. O_2 (20 Torr) was introduced into the tube and kept for 10 min. The tube was photoirradiated at room temperature using the 500 W-Xe lamp at $\lambda >$ 330 nm for 5 min. The tube was then evacuated for 10 min to remove excess O_2 and analysed at 77 K.

DLS analysis. DSL was performed on a Micromeritics NanoPlus zeta potential and nano particle analyser. The measurement was carried out with water (5 mL) containing P25 (15 mg), MPTNF (6 mg) or P25/MPTNF (15 mg/6 mg) mixture, after ultrasonication for 3 min and the subsequent stirring for 20 min.

Notes and references

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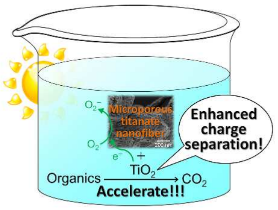

When just mixed with a new and photocatalytically inactive material (microporous titanate nanofiber), TiO_2 showed largely enhanced photocatalytic activities.