

Preparation and Application of Water-soluble TiO₂-ionic Liquids Hybrid Nanomaterials

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Abstract: With unique electronic effect, TiO₂ nanoparticles can be used as photocatalysts to reduce or eliminate the organic pollutants only under irradiation of sunlight. It is, therefore, highly desirable to improve its dispersion and solubility to broaden its application in different fields especially in environmental conservation. Here provides a case of two-step method to prepare yellow transparent water-soluble TiO₂-ionic liquids hybrid nanomaterial. In this hybrid system, organic sulfonate groups as canopy provide “self-solvent” for the dispersion of the TiO₂ nanoparticles. This dispersion experiment results indicated that the water-soluble organic canopy in the TiO₂-ionic liquids hybrid nanomaterial offered good solubility in water and the TiO₂-ionic liquids hybrid nanomaterials used in-home decoration could be easily wiped away on the surface of furniture. Data from photocatalytic degradation efficiency for decomposing formaldehyde demonstrated that the hybrid nanofluids possessed excellent photocatalytic performance. The water-soluble TiO₂-ionic liquids hybrid nanomaterials could be a promising candidate for environmental conservation in the future.

Key words: TiO₂-ionic liquids; hybrid nanomaterials; water-soluble; photocatalytic

In recent years, the environmental awareness is dramatically enhanced, especially in-home decoration. Indoor air pollution is becoming serious threat to human health in daily life due to complicated home decoration. Formaldehyde is one of the most typical pollutant^[1], in these indoor air pollution cases. It is pungent to the mucosa of the eyes, nose and respiratory tract and acts as a lachrymator to cause sneezing and coughing even at a very low concentration^[2-3]. Besides, formaldehyde is directly toxic causing protein misfolding, cell death and biological dysfunction^[4-6]. Therefore, it is of great significance to find a practical and effective method to reduce or even eliminate the pollution of the formaldehyde to protect our health.

In these studies, it is surprising that photocatalytic technology provides a straightforward and effective strategy to protect environment by eliminating formaldehyde^[7]. TiO₂ is made up of Ti-O₆ by titanium oxygen eight surface body octahedron including nature, rutile, and anatase types. In the industrial application, rutile typed TiO₂ materials are widely used in cosmetics industry and coatings industry. The anatase typed TiO₂ materials can be used as photocatalytic materials in degrading

various organic pollutants by using Ultra Violet (UV)^[8-10]. Fujishima group^[11] first found the features of TiO₂ photocatalysis, and then TiO₂ materials became popular in photocatalytic field^[12], especially TiO₂ nanoparticles because of their higher photocatalytic activity^[13]. TiO₂ nanoparticles show strong oxidation properties due to their unique electronic effect and can be used as photocatalyst to reduce or eliminate the organic pollutants, such as formaldehyde decomposing into carbon dioxide, water or other inorganic substances only under irradiation of sunlight^[14].

However, there is a serious problem that the TiO₂ nanoparticles are easy to emerge the second-level agglomeration during the preparation, storage and using, which is because of their powder shape. The methods of dispersion of the titanium dioxide in organic solvent or water after surface treatment of traditional nanofluids or emulsion, are introduced in order to overcoming the problem as mentioned before. The advantage of dispersion of titanium dioxide through those traditional methods is efficient, persistent, safe and economical. But traditional methods suffer from the following problems. For one thing, the content of nanoparticles is generally less

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than 5%. For another, easily reunion could be induced when it is preserved for a long time. And last, it is easy to cause spots when the white emulsion of TiO_2 nanocomposites are used in the glass or furniture with higher transparency.

Giannelis, *et al* reported a series of solvent-free nanomaterials from gel to liquid at room temperature *via* a soft organic corona grafting covalently onto the various nanoparticles surface like TiO_2 , SiO_2 , CaCO_3 , carbon nanotubes^[15-20]. In the system, the nanoparticles were monodisperse and their diameters were generally about 10 nm. The solvent-free nanomaterials system is stable, no vapor pressure and no solvent pollution to the environment and can flow under the condition of room temperature or low temperature, which has a broad application prospect, *e.g.* transportation, microelectromechanical systems (MEMS), liquid electrolytes and magnetic fluid.

In this work, the water-soluble TiO_2 -ionic liquids hybrid nanomaterials were prepared *via* TiO_2 nanoparticles electrovalently bonding with potassium sulfonate nonyl-phenol ethoxylate (PSNE). Octadecyldimethyl(3-trimethoxysilylpropyl) ammonium chloride (OCA) were grafted onto TiO_2 nanoparticles by dehydration and condensation, and then the TiO_2 -ionic liquids hybrid nanomaterials were obtained by introducing PSNE on the surface of TiO_2 (Fig. 1). The catalytic activities for formaldehyde of the TiO_2 -ionic liquids hybrid nanomaterials were investigated by chemical titration method. The TiO_2 -ionic liquids hybrid nanomaterials exhibit excellent photocatalytic degradation efficiency for decomposing formaldehyde. The photocatalytic degradation rate increased up to 87.3%.

1 Material and methods

The synthetic process of TiO_2 -ionic liquids hybrid nanomaterials is showed in Fig. 1. The synthetic process of the water-soluble TiO_2 -ionic liquids hybrid nanomaterials is as follows: (1) 0.5 g TiO_2 powder was dispersed into deionized water (10wt%) then ammonia was added into the solution until pH reached 10; (2) 2.5 mL of OCA methanol solution (60%) was added into the solution in (1) while stirring, and then precipitated for 24 h at room temperature; (3) After centrifugation, the precipitation in (2) was washed with methanol and water mixed solution for three times, and then dried in the vacuum oven under 65°C ; (4) 1 g dried products in (3) was dispersed into distilled water, and then 15 mL 16.5% (wt/vol) PSNE were added into the solution with magnetic stirring at 70°C for 24 h. After drying, the yellow transparent nanometer fluid was obtained as called TiO_2 -ionic liquids

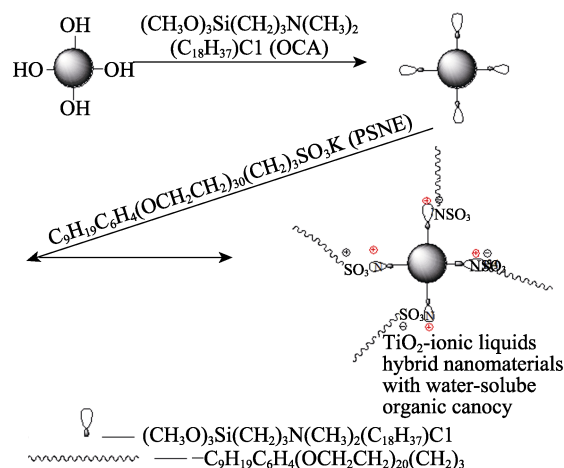
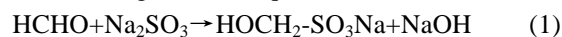


Fig. 1 Synthetic process for the TiO_2 -ionic liquids hybrid nanomaterials

hybrid nanomaterials. The titration method was introduced to determine the photocatalytic of the nanometer fluid.

TiO_2 powder was dispersed in OCA methanol solution first. Because of the higher surface free energy, nanoparticles were easy to flocculate and agglomerate. OCA composites were introduced onto the TiO_2 surface to decrease the surface free energy. Those added groups on the TiO_2 surface could reduce the short-range attraction among adjacent TiO_2 nanoparticles *via* steric hinerance. After that, the sulfonic acid groups ($-\text{SO}_3^-$) in PSNE composites were introduced into the system replacing Cl^- on the TiO_2 surface by ion exchange. In this hybrid system, organic sulfonate (PSNE) groups as canopy can provide “self-solvent” for the dispersion of the TiO_2 nanoparticles. The organic shell acts like a lubricant between the core nanoparticles leading to a liquid-like behavior. The TiO_2 -ionic liquids hybrid nanomaterial was added into 100 g 1wt% formaldehyde aqueous solution. And then this mixed solution was put to the sun. The titration method was introduced to determine the photocatalytic of the nanometer fluid in different time according to the following reaction equation:



With thymolphthalein as indicator, the consuming volumes of sulfuric acid standard solution were used to calculate the residual rates of formaldehyde in different time.

2 Results and discussion

The structure of PSNE and the TiO_2 -ionic liquids hybrid nanomaterials were studied by FT-IR in Fig. 2. The peaks at 1620 cm^{-1} , 833 cm^{-1} represent $\text{C}=\text{C}$ and $\text{H}-$ at 1,

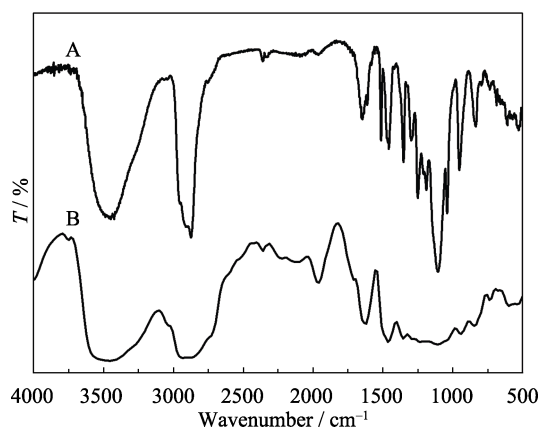


Fig. 2 FT-IR spectra for (A) PSNE and (B) the TiO₂-ionic liquids hybrid nanomaterial

4 sites on the benzene of PSNE, respectively. The absorption peak at 725 cm^{-1} , represents bond of Ti–O, –Si–O–Ti and –CH₂–N⁺ occur at 941 cm^{-1} , and 1465 cm^{-1} , respectively. The peak at 1357 cm^{-1} represents methyl symmetry in the nanometer fluid. The peaks at 2885 cm^{-1} and 1110 cm^{-1} are associated with the stretching vibration of –CH₂ and C–O, respectively. The peaks appear both in the Fig. 2(A) and (B) curves meaning that PSNE was successfully grafted onto the surface of TiO₂ nanoparticles as the organic corona to obtain TiO₂-ionic liquids hybrid.

The microstructure of the nanometer fluid was clearly observed from the TEM images in Fig. 3(a) and (b). As shown in Fig. 3(b), the diameter of TiO₂ in the nanometer fluid is about 5 nm. The TEM image (Fig. 3(a)) and the photo of the yellow nanometer fluid (inserted in Fig. 3(a)) indicate that the TiO₂ nanoparticles in the nanometer fluid monodisperse, and the introduction of PSNE onto the surface of TiO₂ could avoid the further precipitating

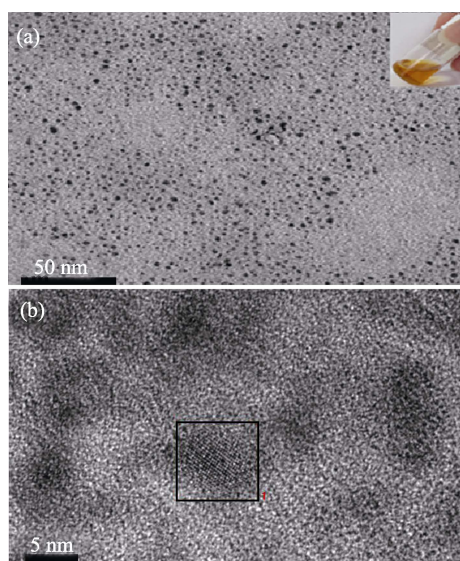


Fig. 3 TEM images of the TiO₂-ionic liquids hybrid nanomaterial

and reaggregating of TiO₂ nanoparticles. The PSNE self-assemble grafted onto the surface of TiO₂ to form an inorganic-organic core/shell hybrid materials *via* ion exchange. The obtained yellow transparent nanometer fluid as shown in the photo of Fig. 3(a), can isolate the inorganic nanoparticles effectively, and improve the stable dispersion of the nanoparticles. The small diameter, monodisperse and low content (calculated from Fig. 3(a) and (b)) of TiO₂ are decisive factors for forming the transparent material in this case. And the peripheral organic shell of TiO₂ provide a lubricant, which endow fluid behavior for the hybrid materials. Finally, the TiO₂-ionic liquids hybrid nanomaterials show the yellow transparent fluid behavior (insert in Fig. 3(a)).

As shown in Fig. 4, the values of shear-loss modulus G'' throughout the measured shear rate range are much higher than the storage modulus G' of the TiO₂-ionic liquids hybrid nanomaterial, which suggest that there was a fluid behavior. The G' and G'' curve of the obtained TiO₂-ionic liquids hybrid nanomaterial are both decreased to low modulus with shear rate increasing. Namely, the hybrid nanomaterials system shows shear thinning behavior, which suggests that TiO₂-ionic liquids hybrid nanomaterials exhibit the pseudoplastic fluid.

The dispersion of TiO₂-ionic liquids hybrid nanomaterials in water was observed through ultraviolet spectrophotometer (UV-Vis). Water is as reference solution, and the samples with different concentration were scanned, and then draw the linear calibration curve. The upper liquid after deposited was scanned, and then calculated their concentration to evaluate the dispersion of TiO₂-ionic liquids hybrid nanomaterials. In order to evaluate the solubility and dispersion stability in water, the 0.15 mg/g of the TiO₂-ionic liquids hybrid nanomaterial in deionized water were prepared with different standing time (25 h–200 h) *via* determining their dispersion by UV-Vis. The solution concentration decreases 3% from 0.15 to 0.145 mg/g (in Fig. 5) after the solution

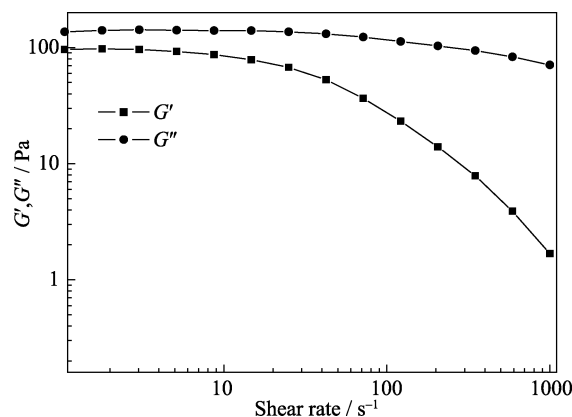


Fig. 4 Rheological response of the TiO₂-ionic liquids hybrid nanomaterial

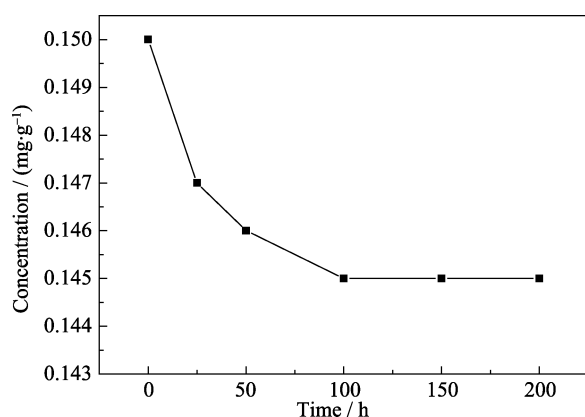


Fig. 5 The curve of concentration versus time for hybrid nanomaterial in water

precipitating for 100 h, and then it trended to stability till 200 h. The stable dispersion of the hybrid nanomaterial in the water owned to the steric hinerance of the water-soluble organic canopy bonding on the surface of TiO_2 nanoparticles, which could prevent the nanoparticles from agglomeration. The water-soluble organic canopy in the TiO_2 -ionic liquids hybrid nanomaterial offer good solubility in water and could be easily wiped away on the surface of furniture in home decoration.

At last, the photocatalytic degradation efficiency for decomposing formaldehyde of pure TiO_2 powder (in Fig. 6(a)) and the TiO_2 -ionic liquids hybrid nanomaterial (in Fig. 6(b)) were studied. For both kinds of the nanomaterials, the residual rates of formaldehyde in the solution decreased with the illumination time prolonging. Compared with the TiO_2 -ionic liquids hybrid nanomaterial, pure TiO_2 powder exhibits higher photocatalytic degradation efficiency. After 80 min, the residual content of formaldehyde is about 10% (Fig. 6(a)) due to the larger contact area of TiO_2 and formaldehyde. The grafted organic canopy on TiO_2 -ionic liquids hybrid nanomaterial result in the decreased photocatalytic degradation efficiency. In Fig. 6(b), the residual content of formaldehyde by the TiO_2 -ionic liquids hybrid nanomaterial is about 12.7% after 240 min, which indicates that the TiO_2 -ionic liquids hybrid nanomaterials still have excellent photocatalytic performance. Furthermore, the TiO_2 -ionic liquids hybrid nanomaterials show good solubility and stability in water and could be easily wiped away on the surface of furniture in home decoration compared to pure TiO_2 powder. These outstanding properties can make it easy to eliminate the formaldehyde pollution in home decoration, such as coating field.

3 Conclusions

In summary, the water-soluble TiO_2 -ionic liquids hybrid nanomaterial was successfully prepared by a two-step

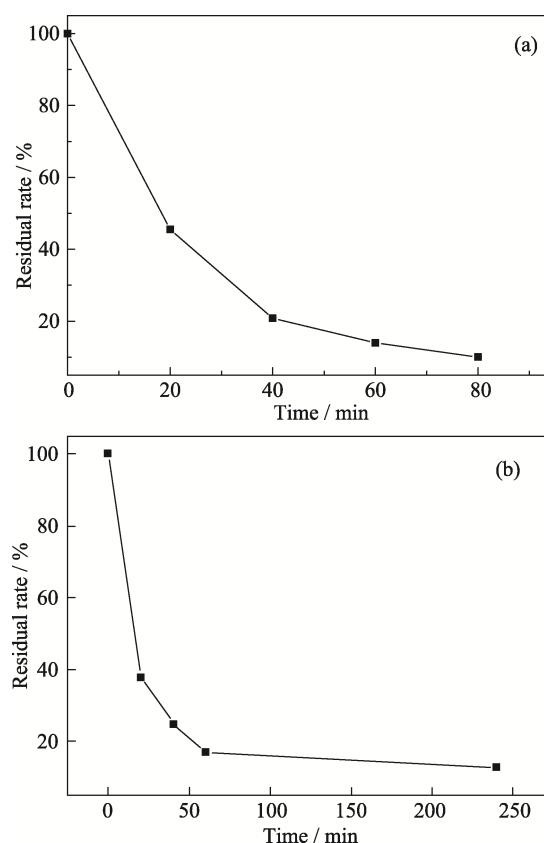


Fig. 6 The photocatalytic degradation efficiency of the pure TiO_2 powder (a) and the water-soluble TiO_2 -ionic liquids hybrid nanomaterial (b) for decomposing formaldehyde

method. Siloxane organic salt (OCA) is jointed on the surface of TiO_2 nanoparticles by dehydration and condensation. The water-soluble TiO_2 -ionic liquids hybrid nanomaterial was obtained by ion exchange with a PEGs-substituted tertiary amine (PSNE). The surface functionalization on TiO_2 offers novel exciting properties to TiO_2 nanoparticles such as monodispersity, fluidity, well water-solubility, and good processability. The water-soluble TiO_2 -ionic liquids hybrid nanomaterial have superb photocatalytic degradation efficiency for decomposing formaldehyde, with 12.7% residual formaldehyde left in sunlight for 4 h. The water-soluble TiO_2 -ionic liquids hybrid nanomaterials should be a promising candidate for environmental conservation in the future.

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References:

- [1] FENG L, MUSTO C J, SUSLICK K S, *et al.* A simple and highly sensitive colorimetric detection method for gaseous formaldehyde. *J. Am. Chem. Soc.*, 2010, **132**: 4046–4047.

- [2] SQUINAZI F. Physical and chemical pollutants of indoor air: sources and health effects. *Environnement Risques & Santé*, 2008, **7(6)**: 425–430.
- [3] JONES A P. Indoor air quality and health atmos. *Environ.*, 1999, **33(28)**: 4535–4564.
- [4] LI F, LI F X, LU J, *et al*. Formaldehyde-mediated chronic damage may be related to sporadic neurodegeneration. *Prog. Biochem. Biophys.*, 2008, **35(14)**: 393–400.
- [5] MIAO J Y, LU J, ZHANG Z J, *et al*. The effect of formaldehyde on cell cycle is in a concentration-dependent manner. *Prog. Biochem. Biophys.*, 2013, **40(7)**: 641–651.
- [6] CHEN J B, CHE H N, HUANG K, *et al*. Fabrication of a ternary plasmonic photocatalyst CQDs/Ag/Ag₂O to harness charge flow for photocatalytic elimination of pollutants. *Appl. Catal. B*, 2016, **192**: 134–144.
- [7] LAKSHMI S, RENGANATHAN R, FUJITA S. Study on TiO₂-mediated photocatalytic degradation of methylene blue. *J. Photoch. Photobio. A*, 1995, **88**: 163–167.
- [8] GU Z R, CHEN A P, DAI Z M, *et al*. Active carbon and nano-titanium dioxide photocatalyst web for air purification. *J. East China Univ.*, 2000, **26(4)**: 367–371.
- [9] GU Z R, CHEN A P, DAI Z M, *et al*. Mechanism of mutual enhancing ability of purification between photo catalysis agent and active carbon on air purification sieve. *Chem. Ind. Forest Prod.*, 2000, **20(1)**: 6–10.
- [10] FUJISGIMA A, HONDA K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 1972, **238(5358)**: 37–38.
- [11] HOFFMAN M R, CHOI W, BAHNEMANN D W. Environmental applications of semiconductor photocatalysis. *Chem. Rev.*, 1995, **95**: 69–96.
- [12] MARTIN S T, HENMANN H, FUJISHIMA A. Light-induced amphiphilic surfaces. *Nature*, 1997, **388(6641)**: 431–432.
- [13] ZHANG J M, SUN X, GAO L, *et al*. Influencing factors of photocatalytic degradation of methyl orange by nanometer titanium dioxide in aqueous solutions. *Journal of the Chinese Ceramic Society*, 2007, **35(9)**: 1169–1173.
- [14] BOURLINOS A B, CHOWDHURY S R, JIANG D D, *et al*. Layered organosilicate nanoparticles with liquid like behaviour. *Small*, 2005, **1(1)**: 80–82.
- [15] BOURLINOS A B, GIANNELIS E P, ZHANG Q, *et al*. Surface-functionalized nanoparticles with liquid-like behavior: the role of the constituent components. *Eur. Phys. J. E.*, 2006, **20(1)**: 109–117.
- [16] LEI Y A, XIONG C X, GUO H, *et al*. Controlled viscoelastic carbon nanotube fluids. *J. Am. Chem. Soc.*, 2008, **130(11)**: 3256–3257.
- [17] BOURLINOS A B, CHOWDHURY S R, HERRERA R, *et al*. Functionalized nanostructures with liquid-like behavior: expanding the gallery of available nanostructures. *Adv. Funct. Mater.*, 2005, **15(8)**: 1285–1290.
- [18] ZHANG J X, ZHENG Y P, LAN L, *et al*. The preparation of a silica nanoparticle hybrid ionic nanomaterial and its electrical properties. *RSC Advances*, 2013, **3(37)**: 16714–16719.
- [19] ZHANG J X, JIANG K M, ZHENG Y P, *et al*. The preparation of solvent-free multiwall carbon nanotubes/silica hybrid nanomaterial with liquid-like behaviour. *Funct. Mater. Lett.*, 2013, **6(2)**: 1350015–1–5.
- [20] ZHANG J X, ZHENG Y P, LAN L, *et al*. The direct synthesis of solvent-free multiwall carbon nanotubes/silica nonionic nanofluid hybrid material. *ACS Nano*, 2009, **3(8)**: 2185–2190.

水溶性 TiO₂ 离子液体纳米杂化材料的制备与应用

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摘 要: TiO₂ 纳米颗粒具有较强的氧化性, 作为光催化剂, 可以在阳光照射下减少或消除有机污染物。为提高 TiO₂ 纳米颗粒分散性和溶解性, 研究其在不同领域, 特别是环境保护领域的应用, 本实验室用两步法制备得到黄色透明的水溶性 TiO₂ 离子液体纳米杂化材料。在这个杂化体系中, 有机磺酸基团作为冠层可以提供“自溶剂”成为 TiO₂ 纳米粒子的分散体。分散实验表明: TiO₂ 离子液体纳米杂化材料表面的水溶性有机物在水中具有良好的溶解性, 容易去除, 可应用于家居装饰表面。光催化降解甲醛的研究表明: TiO₂ 离子液体纳米杂化流体具有良好的光催化性能。水溶性 TiO₂ 离子液体纳米杂化材料有望成为未来环境保护的发展方向。

关 键 词: TiO₂ 离子液体; 杂化材料; 水溶性; 光催化

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