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Photocatalytic degradation of rhodamine B by dye-sensitized TiO_2 under visible-light irradiation

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Perylene tetracarboxylic diimide (PTCDI), widely used in organic photovoltaic devices, is an n-type semiconductor with strong absorption in the visible-light spectrum. There has been almost no study of the PTCDI-sensitized TiO_2 composite used to photocatalytically degrade pollutants. In this study, PTCDI- and copper phthalocyanine tetrasulfonic acid (CuPcTs)-sensitized TiO_2 composites were prepared using a hydrothermal method. The morphologies and structures of the two composites were characterized by X-ray diffraction, transmission electron microscopy, ultraviolet-visible spectroscopy, and fluorescence spectroscopy. The visible-light photocatalytic activities of the composites were evaluated using the degradation of rhodamine B as a model reaction. Results showed that dye-sensitized TiO_2 samples had a wider absorption spectrum range and higher visible-light photocatalytic activity compared to TiO_2 samples. The double dye-sensitized (or co-sensitized) TiO_2 composite with efficient electron collection exhibited higher photocatalytic activity than did the single dye-sensitized TiO_2 composite. The electron transfer processes of single and double dye-sensitized TiO_2 composites were illustrated according to band theory.

copper phthalocyanine tetrasulfonic acid, dye sensitization, perylene tetracarboxylic diimide, rhodamine B, visible-light photocatalysis

1 Introduction

As a surface modification technology, dye sensitization can be effective in broadening the range of semiconductor absorption [1]. The properties of the dye play an important role in determining semiconductor photocatalytic performance. Highly efficient dye sensitizers must meet the following requirements: (1) strong adsorption capacity, high photoabsorption efficiency, and a wide range of absorption spectrum regions; (2) long lifetime of excited states and high quantum yield; and (3) matching band structure to decrease energy loss during the process of electron transfer [2–4]. Metal phthalocyanine and perylene tetracarboxylic diimide derivatives are appropriate candidates for sensitizing TiO_2 semiconductors. As a phthalocyanine derivative, copper phthalocyanine tetrasulfonic acid (CuPcTs) is a p-type semiconductor. It can be easily adsorbed onto the surface of other semiconductors because of its sulfonic groups. CuPcTs has strong absorption capacity in the blue-green light spectrum, capturing about 50% of the energy of the whole solar spectrum. The degradation of methyl orange using CuPcTs-sensitized anatase nanocrystalline TiO_2 as a photocatalyst exhibited high photocatalytic activity [5]. Perylene tetracarboxylic diimide (PTCDI) is a cheap organic dye with strong absorption in the visible-light region and high photo- and thermal stability. PTCDI, as a typical n-type semiconductor, has higher electron affinity [lower "lowest unoccupied molecular orbital" (LUMO) level] and electron mobility due to its strong π-π stacking between the conjugated π bond. As a result, PTCDI materials are widely employed as fluorescent and near-infrared dyes and in or-

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*Corresponding author (email: shangjing@pku.edu.cn) ganic field effect transistors, photoinduced diodes, and imaging techniques [6–9]. An electron can transfer from the LUMO of PTCDI to the conduction band of TiO_2, and the hole can transfer from the valence band of TiO_2 to the highest occupied molecular orbital (HOMO) of PTCDI. Therefore, a composite of PTCDI and TiO_2 is expected to improve excitation separation efficiency and hence enhance photocatalytic activity.

Co-sensitization can effectively broaden the absorption spectrum range of a photocatalyst to visible or near-infrared regions [10]. Research has shown that co-sensitization could widen the absorption spectrum and photocurrent spectra significantly via chemical adsorption porphyrins and phthalocyanine modified TiO_2 [11]. In recent years, several researchers have reported that co-sensitized samples could effectively inhibit electron-hole pair recombination and greatly enhance light-to-electric energy conversion efficiency in studies using composites of zinc phthalocyanine and PTCDI-C7 [12] or phthalocyanines and JK2 [13] as co-sensitizers applied to a dye-sensitized solar cell (DSSC).

In this study, PTCDI and CuPcTs were selected as sensitizers. Composite samples of TiO_2/PTCDI, TiO_2/CuPcTs, and their co-sensitized samples were prepared using a hydrothermal method. The visible-light photocatalytic activity of each sensitized sample was evaluated using the degradation of rhodamine B as the model pollutant. The transfer mechanism of photogenerated charges is discussed.

2 Methods and materials

2.1 Sample preparation

2.1.1 Synthesis of PTCDI-$NH_2(CH_2)_6NH_2$

Certain amounts of perylene-3,4,9,10-tetracarboxylic acid dianhydride, zinc acetate, and 1,6-hexanediamine were added to 100 mL of quinoline solution, followed by heating, agitating, and reflux. Reflux appeared at 135 °C, while the solution turned from red to deep purple. After heating for 8 h at 170 °C, the solution was cooled to room temperature. The precipitate was then washed three times with distilled water and 2% KOH. Finally, the product was agitated at 40 °C for 1 h in 400 mL 2% KOH solution. After leaching and vacuum drying for 24 h, PTCDI-$NH_2(CH_2)_6NH_2$ powder was obtained.

The molecular structural formula of PTCDI-$NH_2(CH_2)_6NH_2$ is shown in Figure 1.

The CuPcTs (60% purity) sample material was purchased from Aldrich and used directly in the experiment.

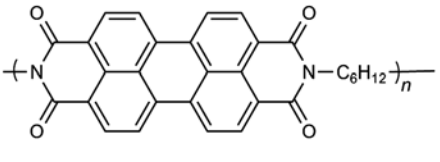

Figure 1 The molecular structural formula of PTCDI-$NH_2(CH_2)_6NH_2$.

2.1.2 Preparation of dye-sensitized samples

Preparation of single dye-sensitized samples using a hydrothermal method. The precursor of TiO_2 was prepared by dropping 10 mL tetrabutyl titanate into 20 mL ethanol solution. A certain amount of PTCDI-$NH_2(CH_2)_6NH_2$ was dissolved in 15 mL ethanol (98%). The resulting solution was dropped into the precursor. After stirring for 1 h, the solution was transferred to a hydrothermal autoclave, where it was maintained at 200 °C for 2.5 h. The obtained products were purified by centrifuging three times with ethanol, and were then dried by infrared lamp. After grinding, a sensitized sample of TiO_2/PTCDI at a 5:100 mass ratio of PTCDI to TiO_2 was obtained. TiO_2/CuPcTs samples with a loading amount of 0.7% and blank TiO_2 samples were prepared using the same hydrothermal method.

Preparation of co-sensitized samples. Three co-sensitization samples were prepared in our study. For the first sample, both PTCDI and CuPcTs were added into the precursor of TiO_2 simultaneously to obtain a TiO_2/PTCDI/CuPcTs sample. The second and third samples involved the adsorption of CuPcTs or PTCDI to TiO_2/PTCDI or TiO_2/CuPcTs samples (prepared using the hydrothermal method), respectively, to obtain (TiO_2/PTCDI)-CuPcTs or (TiO_2/CuPcTs)-PTCDI samples.

According to our previous studies, when the loading amounts of PTCDI and CuPcTs were 5% and 0.7%, respectively, the composite samples exhibited optimum activities. The detailed preparation method for the (TiO_2/PTCDI)-CuPcTs sample was as follows: a certain amount of TiO_2/PTCDI prepared using the hydrothermal method was dissolved in 50 mL ethanol, and an ethanol solution containing CuPcTs was dropped into the resulting solution. After agitating (60 °C, 30 min), centrifugal purifying, and drying (80 °C, 4 h), a (TiO_2/PTCDI)-CuPcTs sample was obtained. The preparation process for the (TiO_2/CuPcTs)-PTCDI sample was similar.

2.2 Characterization

The crystalline structures of the samples were analyzed using an X-ray diffractometer (DMAX-2400, Rigaku Corporation, Japan) and surface morphology was characterized by transmission electron microscopy (TEM, JEM-200CX, JEOL Ltd. Japan). Ultraviolet-visible (UV-vis) diffuse reflectance spectra were obtained on a UV-3100 spectrophotometer (SHIMADZU, Japan) with a wavelength range of 200–800 nm, fluorescence spectra were obtained using a FL4500 fluorescence spectrometer (Hitachi, Japan), and infrared spectra were obtained using a DRA-2CO diffuse reflectance Fourier infrared transform spectrometer (DRIFTS) (Thermao Scientific).

2.3 Photocatalysis experiment

The visible-light photocatalytic activities of the samples described above were evaluated by degrading rhodamine B. A 500-W xenon lamp was employed as a light source (CHF-XM, Beijing Changtuo Technology Company). A cutoff filter was placed outside the parallel light tube, eliminating light below 450 nm. The light intensity was 80 mW/cm^2 at the surface of the reaction solution, as measured by a FZ-A radiometer (Beijing Normal University). A sample of 50 mg was added to 200 mL rhodamine B solution (5 mg/L), which was then sonicated for 5 min and agitated for 30 min in the dark before the xenon lamp was turned on. The solution was filtered and then monitored at 553 nm using a Unico 2100 visible spectrophotometer.

3 Results and discussion

3.1 Surface and structure characteristics of samples

The UV-vis diffuse reflectance spectra of PTCDI, CuPcTs, and sensitized samples are shown in Figure 2. PTCDI had strong absorption at 200–600 nm, while the absorption region of CuPcTs was very wide. There were two absorption bands: the first was the Q band at around 550 nm, and the other was the B band, close to 370 nm [14]. These characteristics well satisfy basic requirements of dye sensitization, i.e., that the dye must have strong light-harvesting ability. Absorption was detected in the UV region below 400 nm, corresponding to the band gap transition of TiO_2 (Figure 2(a)). The composite TiO_2/PTCDI sample showed absorption in the visible-light region between 400 and 700 nm, besides the characteristic absorption of TiO_2. The absorption of the (TiO_2/PTCDI)-CuPcTs sample exhibited further enhancement in both the UV and visible-light regions. Figure 2(b) shows that TiO_2/CuPcTs also had absorption in the visible-light region at 500–800 nm, besides the characteristic absorption of TiO_2, while (TiO_2/CuPcTs)-PTCDI had strong absorption at 400–800 nm. Thus, this result indicates that co-sensitized samples can make their absorption spectra complementary, can broaden the range of the absorption spectrum effectively, and can enhance greatly light-harvesting capabilities.

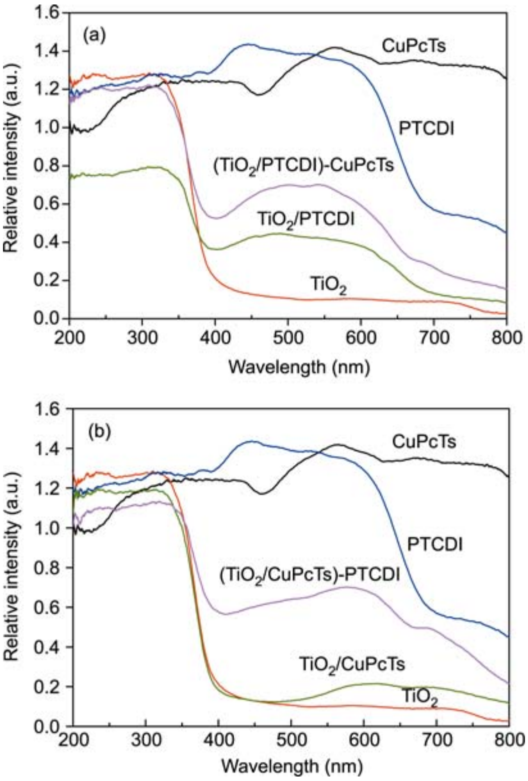

Figure 2 The UV-vis diffuse reflectance spectra. (a) PTCDI, CuPcTs and TiO_2, TiO_2/PTCDI, (TiO_2/PTCDI)-CuPcTs; (b) TiO_2, TiO_2/CuPcTs, and (TiO_2/CuPcTs)-PTCDI.

The X-ray diffraction (XRD) patterns of the sensitized samples are illustrated in Figure 3. The crystalline structure of TiO_2 prepared at 200 °C by the hydrothermal method is anatase, and the crystal size is about 10 nm according to Scherrer's equation. The XRD patterns of TiO_2/PTCDI and TiO_2/CuPcTs are basically the same as that of TiO_2. Therefore, the loading of dye does not appear to change the crystalline structure or size. It is assumed that the dye molecules did not enter the crystal lattice, and that the link between dye molecules and TiO_2 is achieved through van der Waals force or by hydrogen bonds.

The results of TEM measurements show that the TiO_2 particles prepared using the hydrothermal method are spherical, with a particle size of about 10 nm. The TiO_2/PTCDI sample agglomerated slightly compared with TiO_2 particles, while the TiO_2/CuPcTs sample is relatively dispersed.

The infrared spectra of TiO_2 (a), TiO_2/PTCDI (b), and PTCDI (c) samples are shown in Figure 4.

The characteristic absorption peaks of amide are at 1702 and 1664 cm^{-1} (curve (c)) [16]. An absorption band at 400–800 cm^{-1} corresponds to stretching vibration of the Ti–O bond (curve (a)), and the absorption bands at 1600 and 3000 cm^{-1} represent the vibrations of adsorbed water [15].

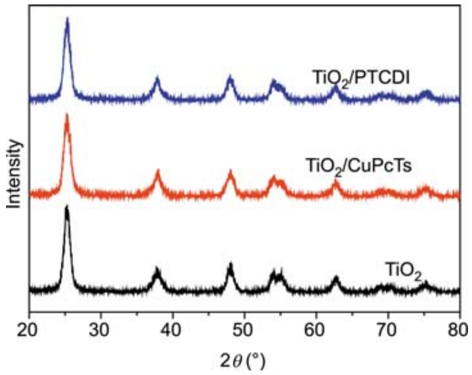

Figure 3 The XRD patterns of TiO_2, TiO_2/PTCDI and TiO_2/CuPcTs samples.

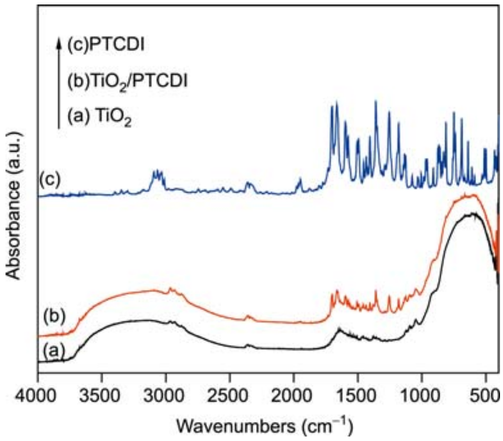

Figure 4 The infrared spectra of TiO_2 (a), TiO_2/PTCDI (b) and PTCDI (c) samples.

Besides the Ti–O stretching vibration band at 400–800 cm^{-1}, there are characteristic amide absorption peaks at 1700 and 1662 cm^{-1}(curve (b)), indicating that the PTCDI molecules have adsorbed to the TiO_2 surface. Due to the strong background absorption of TiO_2 and the small loading amounts of CuPcTs, no obvious CuPcTs characteristic absorption peaks were observed in the infrared spectrum of the TiO_2/CuPcTs sample.

3.2 Photocatalytic activity analysis

The blank test indicated that no rhodamine B photolysis occurred at the light intensity used in the present study, and there was basically no adsorption in the selected rhodamine B concentration range. The activities of single dye-sensitized and co-sensitized samples are illustrated in Figure 5. As can be seen in Figure 5, photocatalytic degradation of rhodamine B was achieved by using pure TiO_2 due to the fact that rhodamine B can be decomposed under visible-light irradiation through self-sensitization [17]. Figure 5(a) shows that all sensitized samples presented higher visible-light photocatalytic activities than did TiO_2 samples. The activity of (TiO_2/PTCDI)-CuPcTs prepared by the absorption method using TiO_2/PTCDI as a substrate performed better than TiO_2/PTCDI did, while the activity of TiO_2/ PTCDI/CuPcTs was less than that of TiO_2/PTCDI, but still slightly more than that of blank TiO_2. As can be seen from Figure 5(b), the TiO_2/CuPcTs sample presented the best photocatalytic activity. The four sulfuric groups in the CuPcTs molecule can be easily electrostatically attracted with Ti^{4+} under hydrothermal reaction conditions, which resulted in good adsorption and dispersion of the CuPcTs molecules in TiO_2. Therefore, the transfer of electrons from the excited states of the dye to the TiO_2 conduction band was favorable in the TiO_2/CuPcTs sample. The photocatalytic activity of (TiO_2/CuPcTs)-PTCDI was reduced after adsorbing PTCDI, but was still higher than that of the TiO_2/PTCDI/CuPcTs sample.

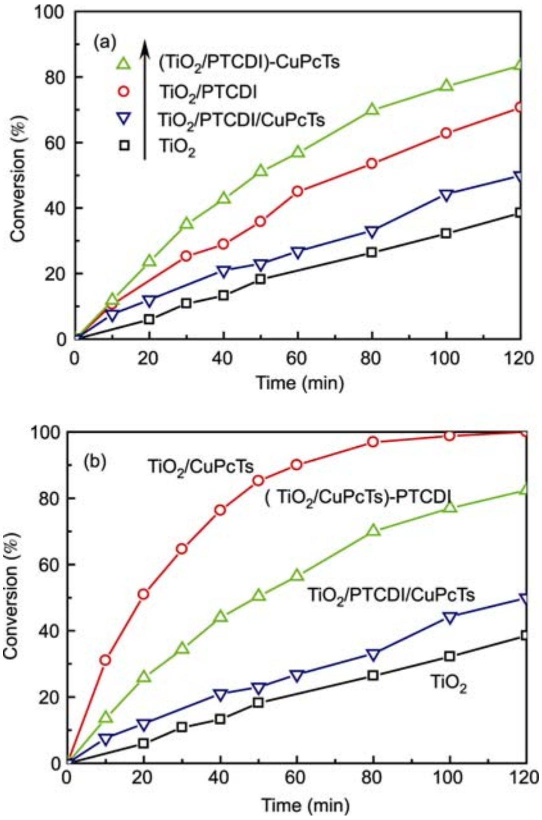

Figure 5 Comparison of the activity of samples, (a) (TiO_2/PTCDI)-CuPcTs, TiO_2/PTCDI/CuPcTs, TiO_2/PTCDI and TiO_2; (b) (TiO_2/CuPcTs)-PTCDI, TiO_2/PTCDI/CuPcTs, TiO_2/CuPcTs and TiO_2.

The fluorescence spectra of sensitized samples are illustrated in Figure 6, which shows that the order of fluorescence intensity was TiO_2/PTCDI > TiO_2/PTCDI/CuPcTs > (TiO_2/PTCDI)-CuPcTs and TiO_2/PTCDI/CuPcTs > (TiO_2/ CuPcTs)-PTCDI > TiO_2/CuPcTs. The results indicate that other electron transfer processes occurred in addition to the electron transfer between the dye and TiO_2 in single dye-sensitized samples. These processes reduced the probability of energy release in the form of fluorescence radiation, resulting in decreased fluorescence intensity. That is, electron transfer may also occur between the two dyes in co-sensitized samples.

Differences between the photocatalytic activities (Figure 5) and fluorescence intensities (Figure 6) of co-sensitized and single dye-sensitized samples can be explained by the mechanisms governing photogenerated electron transfer in (TiO_2/PTCDI)-CuPcTs and (TiO_2/CuPcTs-PTCDI) samples, as shown in Figure 7. The valence band (VB) and conduction band (CB) of TiO_2 are located at 2.9 and −0.3 eV (vs. NHE), respectively [18]; the VB and CB of PTCDI are located at 1.2 and −1.0 eV (vs. NHE), respectively [19]; and the VB and CB of phthalocyanines are located at 1.2 and −1.0 eV (vs. NHE), respectively [20]. Due to the matching energy level (the CB levels both of PTCDI and CuPcTs are higher than that of TiO_2), electrons could be transferred from

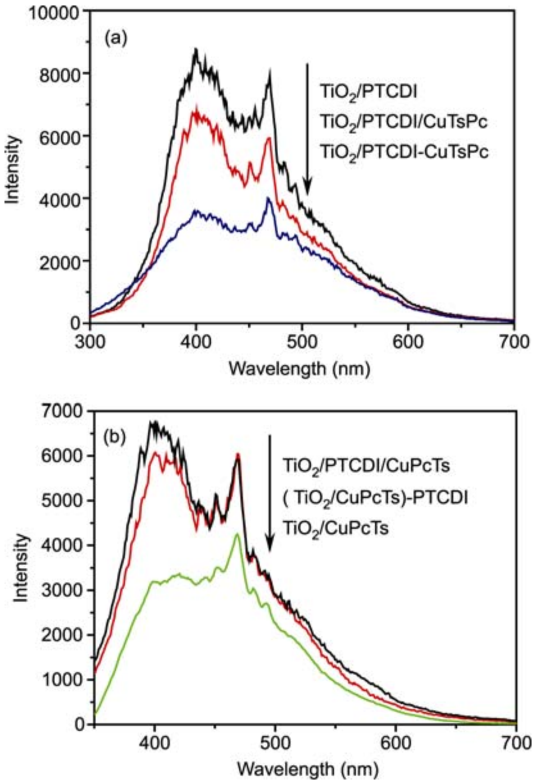

Figure 6 The fluorescence spectra of sensitized samples. (a) (TiO_2/PTCDI)-CuPcTs, TiO_2/PTCDI/CuPcTs and TiO_2/PTCDI; (b) (TiO_2/CuPcTs)-PTCDI, TiO_2/PTCDI/CuPcTs, and TiO_2/CuPcTs.

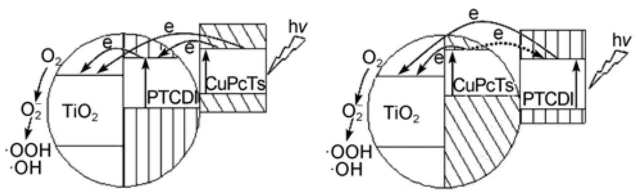

Figure 7 The mechanisms of photogenerated electron transfer in (TiO_2/PTCDI)-CuPcTs and (TiO_2/CuPcTs)-PTCDI samples.

dye excited state molecules to the CB of TiO_2. Electrons in the CB of TiO_2 could be trapped by adsorbed molecular oxygen to generate O_2^-, which could be further converted to ·OOH and ·OH radicals [21]. These highly reactive oxygen species could then attack organic pollutants and cause them to degrade. Therefore, the single dye-sensitized samples of TiO_2/PTCDI and TiO_2/CuPcTs presented superior visible-light photocatalytic activities than did TiO_2. For the co-sensitized sample of (TiO_2/PTCDI)-CuPcTs, electrons could be transferred from the excited state of the CuPcTs molecule to the CB of PTCDI, and then to the CB of TiO_2. Electron transfer from the excited state of the CuPcTs molecule directly to the CB of TiO_2 could also occur. In addition, PTCDI could also be excited and electrons transferred from PTCDI to the CB of TiO_2. These possible electron transfer processes resulted in a greater number of electrons in the CB of TiO_2 and the consequent production of more active oxygen species. The photocatalytic activity of the (TiO_2/PTCDI)-CuPcTs sample was thus enhanced significantly. Therefore, the number of electrons transferred to the CB of TiO_2 in the (TiO_2/PTCDI)-CuPcTs sample was much greater than that in TiO_2/PTCDI sample, which is attributed to the lower fluorescence intensity of the (TiO_2/PTCDI)-CuPcTs sample. For the co-sensitized (TiO_2/CuPcTs)-PTCDI sample, the higher CB of CuPcTs over PTCDI allowed for electrons on the CB of CuPcTs to be back-transferred to the CB of PTCDI. Hence, the number of electrons transferred to the CB of TiO_2 for the (TiO_2/CuPcTs)-PTCDI sample was relatively low, resulting in lower amounts of ·OOH and ·OH reactive species being generated.

Accordingly, the photocatalytic activity of the (TiO_2/CuPcTs)-PTCDI sample was lower and its fluorescence intensity was higher. The photocatalytic activity of the co-sensitized TiO_2/PTCDI/CuPcTs sample prepared using the hydrothermal method was lower than that of the single dye-sensitized sample because competitive adsorption between the two dyes may have resulted in disorder in the photogenerated electron transfer process in the TiO_2/PTCDI/CuPcTs sample.

4 Conclusions

Using PTCDI as a sensitizer can broaden the absorption spectrum range of TiO_2 and effectively enhance its visible-light photocatalytic activity. The (TiO_2/PTCDI)-CuPcTs sample prepared using the hydrothermal combing adsorption method showed electron-collection properties and exhibited better photocatalytic activity than did TiO_2/PTCDI and TiO_2 samples.

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