



Original Research Paper

Photo-stability of TiO₂ particles coated with several transition metal oxides and its measurement by rhodamine-B degradation

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ABSTRACT

Titanium dioxide is the best white pigment, but it does not have good photo-stability if it is not properly coated. As a change from the conventional coating with silicon or aluminum oxide, its photo-stability after coating with zirconium, cerium as well as some other transition metal oxides was investigated. The function of the coated film was to capture electrons and holes of the TiO₂ particles produced by the ultraviolet irradiation that otherwise could produce free radicals on the TiO₂ surface. A new more efficient, easier and more accurate method that used rhodamine-B degradation was used to evaluate the photo-stability of the coated TiO₂ particles. TiO₂ particles coated with the oxides of zirconium, cerium, cobalt or nickel had excellent weather durability, even with only a small amount of coating.

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1. Introduction

Titanium dioxide pigment is widely used in the paint, paper and plastics industries due to its excellent optical properties, and because it is non-toxic and chemically inert. However, the products (such as paint film) are easily pulverized due to the high photo-catalytic activity of titanium dioxide particles under ultraviolet irradiation. The organic substrates in the paint layer are easily oxidized and decomposed due to the photo-catalytic activity of TiO₂ particles. This limits many applications of TiO₂ particles [1,2]. Therefore, the surface coating of TiO₂ particles for improving photo-stability is necessary and important. Silicon oxide and aluminum oxide coatings on TiO₂ particles have been widely used for shielding the photo-catalytic effect [3,4]. Recently, the better photo-stability of TiO₂ particles coated with mixed oxides of silicon, aluminum, and some transition metal, such as zirconium, was reported [5–7], but the effect of zirconium oxide on particle photo-stability was not discussed. However, it was implied that oxides of transition metal, such as zirconium on the TiO₂ particle surface may bring higher photo-stability.

There are two mechanisms proposed to explain the improved photo-stability of coated TiO₂ particles. One is the atomic oxygen mechanism [8–10], which is based on the assumption that when TiO₂ absorbs ultraviolet light, the O²⁻ anions of TiO₂ gets converted into atomic oxygen [O] and the electrons released in this process lead to the reduction of Ti⁴⁺. [O] has high reactivity, and can oxidize

many kinds of organic compounds in contact with the TiO₂ particles. The reactions are,



According to the atomic oxygen mechanism, the gaseous O₂ does not play a role for the photo-catalytic effect of TiO₂ particles.

The second mechanism is that the photo-catalytic effect is due to the electron excitation from the photon absorption that results in the formation of a pair of negatively charged electron and positively charged hole. The electron reacts with oxygen and water on the particle surface, and the hole reacts with hydroxyl groups, to generate free radicals of high reactivity [11–13]. The reactions are,



In the electron-hole mechanism, the presence of gaseous O₂ plays a key role for the photo-catalytic effect of TiO₂.

For the analysis of photo-stability, the evaluation of the photo-catalytic activity of coated TiO₂ particles is important. However, there has been no easy method to do this. The evaluation method often used is isopropanol or methyl orange degradation under ultraviolet irradiation [14,15]. In the isopropanol degradation method, TiO₂ particles are dispersed in isopropanol at a concentration of 100 g/L. Isopropanol is oxidized to acetone under ultraviolet

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irradiation by photo-catalysis by TiO₂ particles. The amount of acetone produced is measured by gas chromatography–mass spectrometry (GC–MS) and used to characterize the photo-catalytic activity, which is taken to be inversely related to photo-stability. However, the degradation of isopropanol is less than 10% after 100 h under irradiation of 1000 W xenon light. In the methyl orange degradation method, the N=N chromophore of methyl orange is oxidized, which leads to the fading of the orange color. The absorbance is measured by a spectrometer to characterize the photo-catalytic activity, and a lower absorbance indicates a higher reactivity. However, this method also requires a very long measurement time. Furthermore, the color of methyl orange is sensitive to the pH, with the orange turning to red for pH < 3.1 and to yellow for pH > 4.4, such that the method needs a series of complex operations.

In this work, an evaluation method of photo-stability was also designed that used rhodamine-B degradation under ultraviolet irradiation. Rhodamine-B is often used for evaluation of photo-catalytic activity of catalytic titanium dioxide particles. However, the catalytic titanium dioxide particles have much higher photo-catalytic activity than the pigmentary particles used in paints. The evaluation with catalytic titanium dioxide particles is very quick and the effect of oxygen is not obvious [16,17]. For pigmentary titanium dioxide particles, the effect of oxygen becomes obvious and it was carefully considered in this research. The photo-stability of TiO₂ particles coated with zirconium oxide, cerium oxide as well as some other transition metal oxides and the effect of coating amount were investigated.

2. Materials and methods

2.1. Reagents

Commercial TiO₂ particles from the industrial sulfate process, in which TiO₂ particles were produced by the hydrolysis of TiOSO₄ and subsequent calcination, were used in the experiments. The TiO₂ particles used had the rutile structure and a mean diameter of 300 nm, with a surface area of 6.81 m²/g. All chemicals used in the experiments were analytical reagent (AR) grade.

2.2. Coating process

Experiments were carried out in a flask with the temperature and pH measured online with a thermometer and pH meter. TiO₂ particles at a concentration of 500 g/L (250 g TiO₂ particles + 500 g water) were dispersed in deionized water by continuous ultrasonic treatment for 30 min. Then, 0.4 mol/L Zr(SO₄)₂ solution and 4.5 mol/L NaOH solution were simultaneously titrated into the TiO₂ suspension. The TiO₂ suspension was stirred vigorously and its pH controlled by the rate of adding the NaOH solution with the rate of adding the Zr(SO₄)₂ solution kept constant. The temperature was controlled by a constant temperature bath. After titration, the suspension was aged for 2 h with stirring. Then, the coated TiO₂ particles were filtered and washed repeatedly, and dried at 105 °C for 24 h.

Preliminary work with a zirconium oxide coating on TiO₂ particles showed that when the temperature was set at 40 °C and the pH at 11, a dense, uniform and continuous film was obtained. The coated amount in this study was varied from 0.5 to 3 wt%.

TiO₂ particles coated with cerium oxide, cobalt oxide and nickel oxide were obtained with the same procedure. The coating reagents used were Ce(SO₄)₂·4H₂O, CoSO₄·7H₂O, and NiSO₄·6H₂O. The coating conditions were a temperature of 60 °C and pH of 9.

2.3. Characterization

The morphology and structure of the transition metal oxide coated TiO₂ particles were examined with a high resolution transmission electron microscope (HRTEM, JEM-2011, JEOL Co., Tokyo, Japan). Samples for HRTEM analysis were dispersed in ethanol with ultrasonic treatment for 30 min.

2.4. Photo-stability evaluation

The photo-stability of the coated TiO₂ particles was evaluated by rhodamine-B degradation. The coated TiO₂ particles were dispersed in 4 mg/L rhodamine-B solution at a concentration of 0.5 g/L. The suspension was put in a test tube at a controlled temperature and irradiated with xenon light (1000 W). The xenon light use is for the simulation of the nature light. After the test time, the suspension was taken out and centrifuged for 30 min, and the color intensity of the suspension supernatant was measured with a ultraviolet spectrophotometer. The characteristic absorbance of rhodamine-B at 554 nm was used to characterize the concentration of rhodamine-B, which was inversely related with the degradation of rhodamine-B.

3. Results and discussions

3.1. The effect of gaseous oxygen on the photo-catalysis by TiO₂ particles

The effect of the presence of gaseous oxygen on rhodamine-B degradation was studied. Four samples: (a) rhodamine-B solution, (b) rhodamine-B solution with gaseous oxygen added, (c) rhodamine-B solution containing uncoated TiO₂ particles, and (d) rhodamine-B solution containing uncoated TiO₂ particles with gaseous oxygen added, were used. Gaseous oxygen addition was performed by keeping a set volume of air in the tube (air/liquid volume ratio is 2:1). The four samples were sealed in tubes, irradiated with xenon light, and the absorbance of the solution with time was measured.

Fig. 1 shows the change of solution absorbance with time. Rhodamine-B showed a little degradation with time. As compared with sample (a), rhodamine-B with gaseous oxygen added showed more degradation, which showed that gaseous oxygen enhanced the degradation. When uncoated TiO₂ particles were introduced, the rhodamine-B solution showed much more degradation, which showed that the uncoated TiO₂ particles had high photo-catalytic activity. Sample (d), with uncoated TiO₂ particles and gaseous oxygen, degraded sharply with time. It was completely degraded in 6 h, which showed that the oxygen enhanced the photo-catalytic activity.

It is concluded that the gaseous oxygen remarkably affects the photo-catalytic effect of TiO₂ particles. This result was consistent with the electron–hole mechanism. Therefore, it is analyzed that the slight degradation of rhodamine-B containing uncoated TiO₂ particles but without gaseous oxygen added was contributed from the dissolved oxygen already present in the solution, and the formed free radicals due to the holes react with hydroxyl groups.

3.2. Photo-stability measurement using rhodamine-B degradation

Photo-stability was investigated by rhodamine-B degradation measurements. Rhodamine-B is tetraethyl-rhodamine, which is a dye of peachblow. Its color is due to the chromophoric group of phenylamino with the characteristic absorbance at 554 nm. The photo-catalytic action of TiO₂ particles destroys the chromophoric group, which results in the fading of the color of the rhodamine-B solution. The degradation of rhodamine-B is a process of two steps

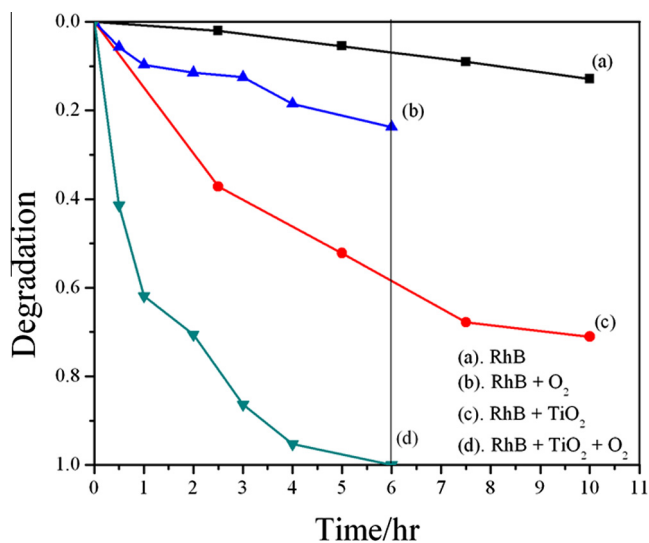


Fig. 1. Degradation of rhodamine-B in solutions containing TiO₂ particles and gaseous oxygen.

including N-de-ethylation and oxidization due to ·OH formed in the photo-catalytic effect. Rhodamine-B is de-ethylated in a step-wise manner, and the de-ethylated N is then oxidized into NH⁴⁺ with the main structure of rhodamine-B oxidized into CO₂ and H₂O [18–20]. Thus, the characteristic absorbance of the solution can be used to reflect the photo-stability of the TiO₂ particles.

Since the linear relationship between its concentration and absorbance is in the absorbance range 0.2–0.8, the concentration of the rhodamine-B solution was set at 4 mg/L, at which the absorbance of the rhodamine-B solution was about 0.7. The absorbance in the most of the measurements were kept in the range of 0.2–0.8. The concentration of TiO₂ particles in rhodamine-B solution was 0.5 g/L, which allowed the degradation measurement to be performed in an acceptable time.

There are some literature reports reported that the degradation of rhodamine-B solution without TiO₂ particles is negligible [16,17], but our experiments showed that a little degradation occurred. This is shown in Fig. 1 and was confirmed by repeated experiments. This discrepancy is due to that the particles in these literatures were catalytic titanium dioxide particles, which had very high photo-catalytic activity, and compared to this high photo-catalytic activity, the degradation of rhodamine-B solution without TiO₂ particles is negligible. While in our researches, the TiO₂ particles had much lower photo-catalytic activity, so the degradation of rhodamine-B is obvious. Fig. 1 shows that a higher concentration of oxygen (gaseous oxygen added) gave more degradation of rhodamine-B. This can cause a systematic error in the measurement, and should be reduced. However, too small a quantity of oxygen in the rhodamine-B solution would result in a longer measurement time. Therefore, a certain quantity of gaseous oxygen addition in the rhodamine-B solution was more efficient. Taking into account the acceptable experimental uncertainty and measurement time, based on a series of experiments about different air/liquid volume ratios, a ratio of 2:1 was used for the sample preparation in measurements.

It was also noticed that the dispersion of the TiO₂ particles and their settling during the irradiation process also led to experimental uncertainty due to the different contact states between the particles and rhodamine-B in the solution. This was minimized by keeping the sample tubes on a shaking table for keeping the particles well dispersed in the solution. In addition, ultraviolet irradiation could increase the temperature of the solution rapidly and the

degradation of rhodamine-B was highly dependent on temperature. To prevent this, the temperature of the sample was controlled at 25 ± 1 °C to minimize the error from temperature fluctuation.

By using the rhodamine-B method, easily observable measurements of degradation could be made in a convenient time. The degradation was about 50% after 1 h ultraviolet irradiation of the uncoated TiO₂ particles dispersed in the rhodamine-B solution. As compared to the use of isopropanol degradation, the rhodamine-B method was more efficient and accurate, and the ultraviolet spectrophotometer measurement for the rhodamine-B method was easier.

3.3. Morphology and photo-stability of coated TiO₂ particles

3.3.1. Coating with zirconium oxide

ZrO₂-coated TiO₂ particles with coated amounts of 0.5, 1, 2, and 3 wt% are shown in Fig. 2. A continuous and dense film was coated on the particle surface. The thickness of the film increased with coated amount, as shown in Fig. 2c–e. However, when the coating amount was too small, i.e., 0.5%, it was difficult to see the film.

By using the method of rhodamine-B degradation under ultraviolet irradiation, the photo-stability of the coated TiO₂ particle samples was measured. The result is shown in Fig. 3. The photo-stability of the coated TiO₂ particles was obviously increased with increased coated amount. After 3 h ultraviolet irradiation, the uncoated TiO₂ particles caused the rhodamine-B to degrade by nearly 90%, while the TiO₂ particles coated with 3 wt% zirconium oxide caused it degrade about 40%. Rhodamine-B degradation in the absence of TiO₂ particles was about 10%. This showed that the zirconium oxide film coating significantly reduced the photo-catalytic effect of TiO₂ particles.

3.3.2. Coating with cerium oxide

TiO₂ particles coated with different amounts of cerium oxide were investigated. HRTEM photos of cerium oxide coated TiO₂ particles with the coated amounts of 0.2, 0.5, 1 and 2 wt% are shown in Fig. 4. There was no obvious film with the coating amounts of 0.2 and 0.5 wt%. A thin film of about 1–2 nm thickness was observed with the coating amounts of 1 and 2 wt%. There was no obvious change in film thickness, which may be due to the high viscosity of the slurry in the coating process.

The measurement of the photo-stability of the cerium oxide coated TiO₂ particles is shown in Fig. 5. All the cerium oxide coated TiO₂ particles had good photo-stability. The degradation was only 30% after 2 h ultraviolet irradiation and less than 50% after 6 h, which showed that the cerium oxide coating had brought about a remarkable improvement in photo-stability. On the other hand, the photo-stability of the four samples was about the same. This may be because it was hard to form a film or because the photo-stability of cerium oxide coated TiO₂ particles film was not sensitive to the coating amount.

3.3.3. Coating with other transition metal oxides

TiO₂ particles coated with other transition metal oxides, including cobalt oxide and nickel oxide at 60 °C, pH 9 and with a coating amount of 0.5 wt% were also investigated. Since the coating amount was only 0.5 wt%, it was difficult to see the film, as were also the cases with ZrO₂ and CeO₂ coated particles with coated amounts of 0.5% in Figs. 2b and 4b. EDS mapping was used to examine the surface coating. This showed that all the ZrO₂, CeO₂, CoO and NiO coatings with coated amounts of 0.5 wt% were uniformly distributed on the TiO₂ particle surface. For comparing the photo-stability difference due to different metal oxide coatings, the measurements with the ZrO₂, CeO₂, CoO and NiO coated TiO₂ particles at the same coating amount of 0.5 wt% are shown in Fig. 6. CeO₂ and CoO coated particles showed better photo-stability

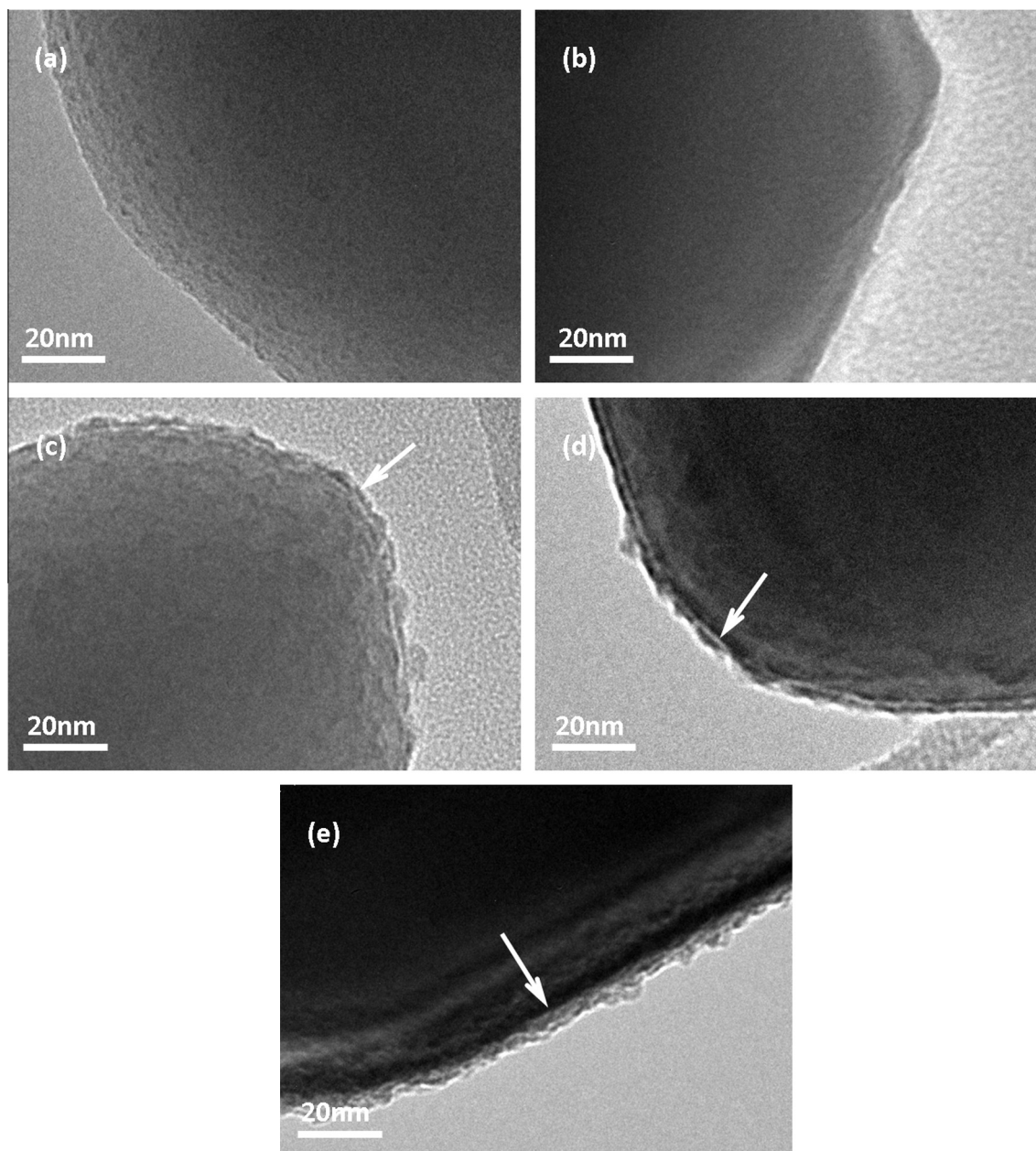


Fig. 2. HRTEM photos showing the surface morphology of ZrO₂-coated TiO₂ particles with coated amount: (a) 0 wt%; (b) 0.5 wt%; (c) 1 wt%; (d) 2 wt%; and (e) 3 wt%.

than ZrO₂ and NiO coated particles. Degradation of rhodamine-B with CoO and NiO coated TiO₂ particles was about 30%, even a little lower than the conventional coating with 3.0 wt% SiO₂ and 2.0 wt% Al₂O₃ of about 35% in our previous work. However, all these coated TiO₂ particles had good photo-stability, even with the very small coated amount.

It should be noted that some of the transition metal ions are colored. However, when the hiding and scattering power are the main points, coating with transition metal oxide is still a promising option. Because a small amount of transition metal oxide coating can bring high photo-stability, it also can be together coated with some other oxide coating, e.g. Si/Al oxide.

3.4. Film capture of the electron/hole

According to the electron–hole mechanism, it is analyzed that the improvement of the photo-stability of the coated TiO₂ was

due to that the coated film captures the electrons/holes produced by TiO₂ on light absorption. This will prevent the electron/hole transition onto the surface of TiO₂ that could otherwise produce highly active free radicals there.

The high photo-stability of TiO₂ coated with these metal oxides may be due to that the hybridization of different electron orbits in transition metal forms new unsaturated electron orbits, which can capture the produced electrons, and the active electron in unsaturated orbits can recombine the produced holes.

Therefore, it is inferred that orbital hybridization in the transition metal may be the key factor for achieving excellent photo-stability. The detailed mechanism will be further studied in the future.

4. Conclusions

It is confirmed that gaseous oxygen takes an important role in the photo-catalysis of TiO₂ particles. A photo-stability evaluation

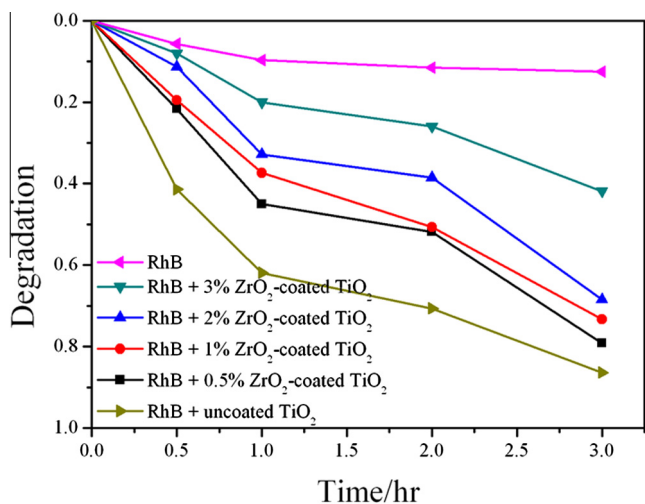


Fig. 3. Degradation of rhodamine-B by ZrO₂-coated TiO₂ particles with different coated amounts.

method was developed that used rhodamine-B degradation under ultraviolet irradiation. It is more efficient, easier and more accurate than the present methods.

Film coating of TiO₂ particles with oxides of zirconium, cerium, cobalt and nickel were performed, and it was shown that these significantly improve the photo-stability of TiO₂ particles, even with a small coated amount. A cerium or cobalt oxide coating gave better photo-stability than a zirconium or nickel oxide coating of the same coating amount. The photo-stability of zirconium oxide coated TiO₂ particles increased with coating amount. It is analyzed

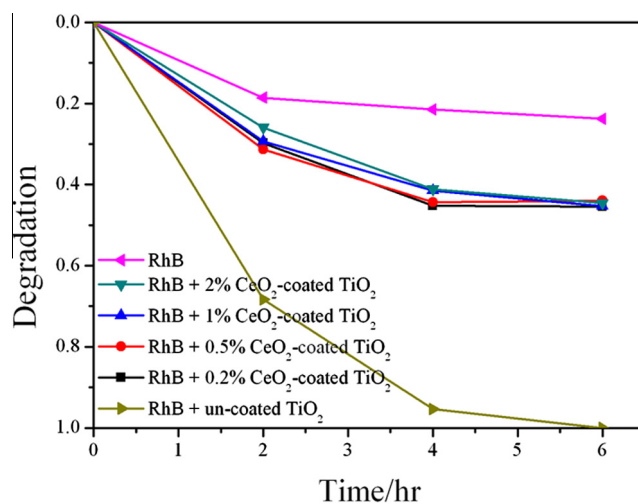


Fig. 5. Degradation of rhodamine-B with CeO₂-coated TiO₂ particles with different coated amounts.

that the layers of these oxides increase the capability of film capture on the produced electrons/holes, preventing the electron/hole transition onto the surface of TiO₂ that could otherwise produce highly active free radicals there.

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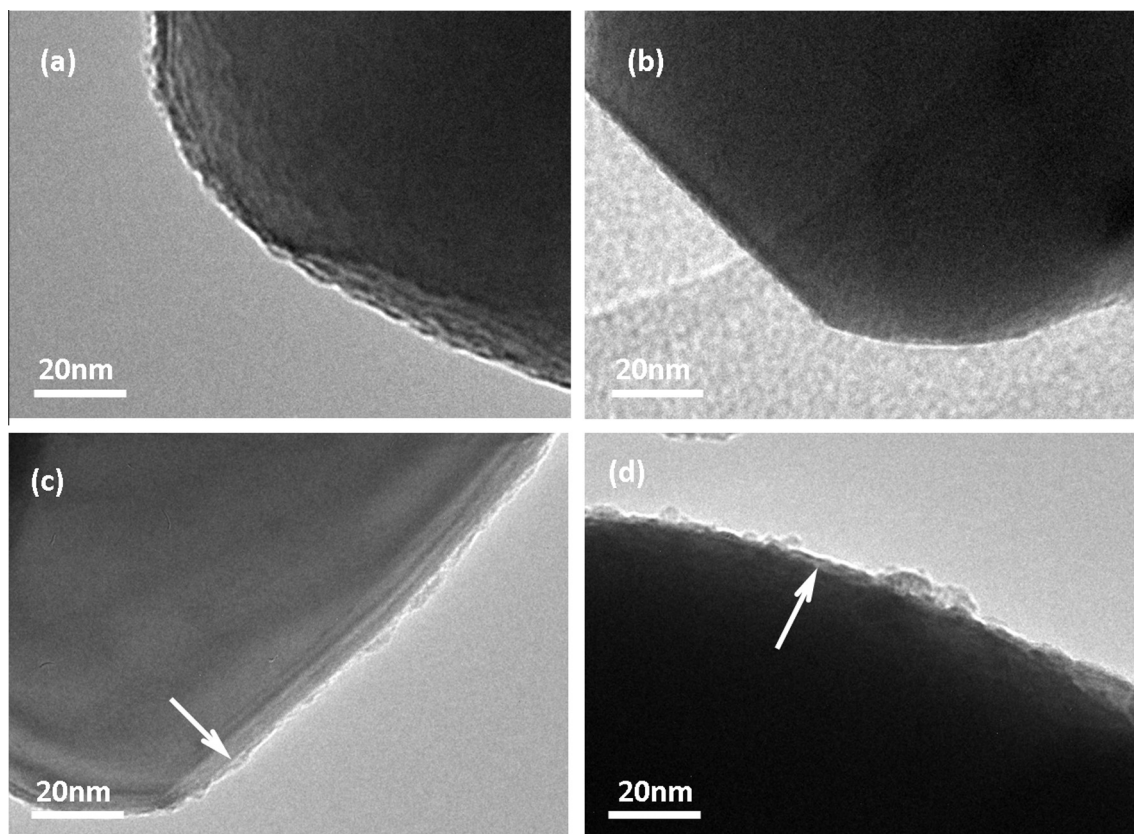


Fig. 4. HRTEM photos of the surface morphology of CeO₂-coated TiO₂ particles with coated amount: (a) 0.2 wt%; (b) 0.5 wt%; (c) 1 wt%; and (d) 2 wt%.

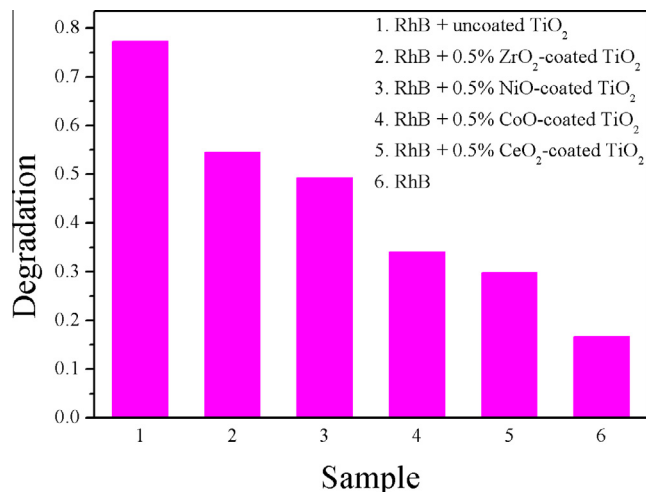


Fig. 6. Degradation of rhodamine-B with ZrO₂-coated, NiO-coated, CoO-coated, CeO₂-coated TiO₂ particles after ultraviolet irradiation for 2 h.

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