# Photocatalytic activity enhancement of TiO<sub>2</sub> porous thin film due to homogeneous surface modification of RuO<sub>2</sub>

Peng Liu and Weiying Li<sup>a)</sup> State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, People's Republic of China

Jingbo Zhang<sup>b)</sup> and Yuan Lin

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

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Ruthenium dioxide ( $RuO_2$ ) was uniformly modified on TiO<sub>2</sub> porous thin film by impregnation of Ru-contained dye on the film followed by sintering it at 450 °C to burn off organic matters and form ruthenium oxide, which is named as impregnation method. The homogenous modification of metal oxide inside porous thin film can be realized by the impregnation method, and the modification amount of  $RuO_2$  can be easily adjusted by the iteration numbers of impregnation and sintering. Appropriate amount of uniformly modified  $RuO_2$  was found to obviously enhance photocatalytic performance of TiO<sub>2</sub> to degrade eosin Y. The photocatalysis enhancement was attributed to the shallow hole traps on the surface of nanoparticles formed by  $RuO_2$ , and these traps can retard recombination of hole with electron.

#### I. INTRODUCTION

With the rapid development of society and industrialization processes, the kinds and amount of organic pollutants in industrial effluents increase sharply, which causes a great challenge to the traditional water treatment process. Therefore, photocatalytic oxidation technology, as a very effective, nontoxic, energy-saving, nonsecondary pollution procedure for the degradation of a variety of organic contaminants, has drawn a considerable attention.<sup>1,2</sup> Nanocrystalline semiconductor TiO<sub>2</sub>, which is an abundant, nontoxic, chemically stable, effectual photocatalyst, has been found to have extensive applications to solve these environmental problems, such as decomposition of inorganic and organic pollutants and toxic material in both liquid and gas phase systems.<sup>3,4</sup> However, only the ultraviolet light ( $\lambda < 387$  nm), which occupies 4% of solar light energy, can be absorbed by pure anatase  $TiO_2$  to generate electron-hole pairs.<sup>5</sup> For this reason, the practical photocatalytic application of TiO<sub>2</sub> is limited. On the other hand, the photogenerated electron-hole pairs, which play the most important role during the photodegradation process, are liable to recombine, thus leading to the low efficiency of photocatalyst.<sup>6,7</sup> Therefore, to enhance photocatalytic activity, it is paramount to extend the photoresponse of  $TiO_2$  to the visible region and to reduce the recombination of electron-hole pairs.

Recently, to overcome the deficiencies of  $TiO_2$  mentioned earlier and then to improve its photocatalysis

performance, many works have been attempted. These works include doping TiO<sub>2</sub> with noble metals such as Pt, Ag, Au<sup>8-10</sup> and with nonmetals such as N, S, C etc.,<sup>11-13</sup> and sensitizing TiO<sub>2</sub> with dye molecules and other compounds.<sup>14,15</sup> According to the literature, the modification of TiO<sub>2</sub> by doping with no matter metal or nonmetal atoms is almost conducted by adding certain amount of dopants to the solution for preparation of TiO<sub>2</sub>. That is to say, the dopants are distributed not only on the particle surface but also within TiO<sub>2</sub> crystals. However, as we all know, the photodegradation process takes place mostly on the surface of semiconductor photocatalyst because the electron-hole pairs are photogenerated by the direct irradiation of light. The interfacial electron transfer reaction of charge carriers on the surface of photocatalyst is prerequisite for a photodegradation reaction.<sup>16</sup> Therefore, the dopants inside TiO<sub>2</sub> crystals are void for photodegradation. It is meaningful to develop a surface modification method for enhancing photocatalytic activity of catalysts.

Ruthenium and ruthenium dioxide (RuO<sub>2</sub>) have been considered as effective catalysts and bottom electrode materials.<sup>17–20</sup> Different methods have been carried out to modify ruthenium, ruthenium oxide, or their nanoparticles on the porous thin films, such as electrochemical deposition,<sup>21,22</sup> chemical reduction,<sup>17</sup> Cu underpotential deposition,<sup>18</sup> sputtering<sup>23,24</sup>, and metalorganic chemical vapor deposition.<sup>25</sup> The simpler modification method is to dip the porous film in the ruthenium trichloride solution followed by the thermal oxidization process.<sup>26</sup> However, it is difficult to control the distribution of the ruthenium oxide formed on the surface of pores by this simple

1532 CAMPRIDEL JOURNAL Mater. Res., Vol. 26, No. 12, Jun 28, 2011 http://journals.cambridge.org Downloaded: 11 Mar 2015

Address all correspondence to these authors.

<sup>&</sup>lt;sup>a)</sup>e-mail: liweiying@tongji.edu.cn

<sup>&</sup>lt;sup>b)</sup>e-mail: jbzhang@iccas.ac.cn

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method. Usually, the modified oxides aggregate to form some islands at different sizes and shapes. This makes trouble to study the properties due to the modification of metal oxide.

In this study, we developed an approach to modify homogenous  $RuO_2$  on the surface of nanoparticles inside  $TiO_2$  porous thin film by monolayer adsorption of Rucontained dye and followed by sintering at 450 °C. As a comparison,  $TiO_2$  film with inhomogeneous modification of  $RuO_2$  was prepared by dropwise adding appropriate concentration of ruthenium trichloride trihydrate solution on the  $TiO_2$  porous thin film. To evaluate the effect of homogeneous modification on the photocatalytic activity of  $TiO_2$  porous thin film, both kinds of  $RuO_2$ -modified films were used as the photocatalyst to degrade eosin Y.

### **II. EXPERIMENTAL SECTION**

#### A. Preparation of porous TiO<sub>2</sub> thin films

The TiO<sub>2</sub> colloidal paste was prepared by the hydrothermal method according to the procedure in literature.<sup>27</sup> Then the paste was spread onto fluorine-doped tin oxide (FTO) glass substrate (20  $\Omega/\Box$ ; Hake New Energy Co., Ltd, Harbin, China) by the doctor-blade method. After drying in air at room temperature, the film was sintered at 450 °C for 30 min.

## B. Modification of ruthenium oxide on the TiO<sub>2</sub> nanoporous thin film

Two methods were used to modify ruthenium oxide on TiO<sub>2</sub> nanoparticles. Adsorption of Ru-contained dye followed by sintering at 450 °C (hereafter, named as impregnation method) was described as following. The asprepared TiO<sub>2</sub> porous film was dipped into absolute ethanol solution containing 0.5-mM cis-di(thiocyanato)-N,N'-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II) complex (N3; Solaronix, Aubonne, Switzerland) for 24 h. Then, the film was rinsed with ethanol and dried in air. After adsorption of dye, the thin film was sintered at 450 °C for 30 min to burn off organic matters of dye and oxidize the left ruthenium cations on the film. The modification amount can be easily adjusted by repeating the above procedure comprising adsorption and sintering processes. For comparison, dropping method was also used to modify TiO<sub>2</sub> nanoporous film, where certain amount of ruthenium trichloride trihydrate solution was dropwise added on the surface of the as-prepared  $TiO_2$ film, and then, the film was sintered at 450 °C for 30 min.

#### C. Characterization of the films

The surface morphologies of  $TiO_2$  films with and without ruthenium oxide modification were observed on a scanning electron microscope (SEM; S-4300, Hitachi, Toronto, Ontario, Canada) operated at an acceleration voltage of 15 kV, equipped with an energy dispersive x-ray spectroscope (EDX). The crystallographic characterization of the film was determined on an x-ray diffractometer (D/max 2500; Riguku, The Woodlands, TX) by Cu K $\alpha$  irradiation. To analyze binding energy of the samples, the x-ray photoelectron spectra (XPS) were recorded by an electron spectroscope for chemical analysis (ESCA) Microprobe system (LAB2201-XL, VG Scientific, London, UK) using a Mg Ka excitation source. The amount of dye loaded into the film was determined by completely dissolving a known area of the TiO<sub>2</sub> film into a known volume of NaOH (pH=10.5) aqueous solution and measuring its optical absorbance at the absorption maximum of N3 dye with a spectrophotometer (UV3010; Hitachi, Tokyo, Japan).

Intensity-modulated photovoltage spectroscopy (IMVS) was performed on the dye-sensitized solar cells (DSSCs) based on the TiO<sub>2</sub> porous thin film or the ruthenium oxidemodified TiO<sub>2</sub> thin films. A light emitting diode (LED, 470 nm) was used as the light source. The light intensity was modulated with a sine-shaped voltage supplied by a 1255B frequency response analyzer (FRA; Solartron, Hampshire, UK) between 0.1 Hz and 10 kHz. The DC light generated by the LED, with the intensity up to  $2 \text{ W m}^{-2}$ , was used as the superimposed constant illumination in the measurements. The amplitude and phase shift of the voltage response with respect to the modulation of the light intensity were measured with FRA. The FRA and data acquisition were controlled by a personal computer. IMVS complex plane plots were recorded for the DSSCs under open-circuit conditions. DSSC with a sandwich cell structure was fabricated with a dye-sensitized nanocrystalline TiO<sub>2</sub> thin film together with a Pt counter electrode and electrolyte composed of 0.5M LiI, 0.05M I2, and 0.5M 4-tertbutylpyridine in 3-methoxypropionitrile. Dye sensitization was performed by immersing the resulting films in a 0.5-mM ethanol solution of N3 for 24 h. A Pt counter electrode was prepared by spreading a 5-mM H<sub>2</sub>PtCl<sub>6</sub> aqueous solution on a FTO glass substrate, followed by heating at 390 °C for 15 min. For IMVS measurements, the light was directed on the Pt counter electrode of DSSC with active area of  $0.20 \text{ cm}^2$ .

#### D. Photodegradation experiment

The photodegradation experiments of eosin Y (Kanto, Tokyo, Japan) were conducted in an open beaker with 100 mL capacity at room temperature, and the beaker was opened to air to ensure enough oxygen in the solution. The TiO<sub>2</sub> film or ruthenium oxide-modified TiO<sub>2</sub> film was laid at the bottom of the beaker, immersed by 15-mL aqueous solution containing eosin Y with the initial concentration of 36  $\mu$ M, which was exposed to illumination of a 125-W high-pressure Hg lamp ( $\lambda > 320$  nm). Before the irradiation, the solution with TiO<sub>2</sub> film was placed in darkness to establish adsorption–desorption equilibrium. The concentration of dye after adsorption–desorption equilibrium was treated as  $C_0$ . The change in the concentration of dye based on  $C_0$  was detected by measuring absorbance of the dye solution taken out regularly from the reactor beaker.

#### **III. RESULTS AND DISCUSSION**

The SEM surface morphology of TiO<sub>2</sub> thin film is shown in Fig. 1. We can observe spherical aggregates of nanoparticles (typically 40 nm in diameter) that are homogeneous in size and shape, to form a porous, high surface area film. The film thickness is about 4  $\mu$ m. After modification of ruthenium cations, SEM image of the modified TiO<sub>2</sub> thin films (not shown) does not illustrate any remarkable difference between them and the pure TiO<sub>2</sub> film. EDX measurement accompanied with SEM observation determined Ru element amount of 0.62% (molar percentage) in the modified TiO<sub>2</sub> thin film with four iterations of adsorption, which proves that ruthenium cations have been successfully modified on the porous TiO<sub>2</sub> thin films. X-ray diffraction spectrum of the



FIG. 1. Morphology of the  $TiO_2$  nanoporous thin film by scanning electron microscope.



FIG. 2. X-ray diffraction patterns of the ruthenium dioxide ( $RuO_2$ )-modified TiO<sub>2</sub> thin film with four times impregnation.

ruthenium oxide-modified  $\text{TiO}_2$  thin film shown in Fig. 2 indicates ruthenium cations modification does not affect the anatase crystalline structure of  $\text{TiO}_2$  film.

To distinguish the existing form of ruthenium cations after modification, we carried out XPS analysis, which is an important tool for examining surface electronic states of materials. In the XPS of ruthenium cation-modified TiO<sub>2</sub> prepared by the impregnation method as shown in Fig. 3, the elements of Ti and O can be detected and their binding energies are 458.6 and 529.8 eV, respectively. The binding energy of Ru 3d<sub>3/2</sub> is unfortunately overlaid with that of C 1s, thus its peak can not be clearly recognized. The peak corresponding to C 1s looks unsymmetrical and one peak at 286.0 eV can be separated from it. The separated peak is identified as Ru  $3d_{3/2}$ . At the same time, the binding energy of 280.1 eV is assigned to Ru 3d<sub>5/2</sub>. All of these results indicate the existing form of ruthenium cation is Ru<sup>4+</sup>, and it exists as RuO<sub>2</sub> on the surface of TiO<sub>2</sub> nanoparticles. The same measurements and analyses were conducted on the ruthenium cation-modified TiO<sub>2</sub> prepared by the dipping method indicating ruthenium cation also exists as  $Ru^{4+}$  on the film.

The large surface area of porous film is favorable for the adsorption of pollutant, which is recognized as the prerequisite procedure for photodegradation. However, at the same time, the large surface area makes more opportunities for the recombination of electron and hole, which will decrease the photocatalytic activity. The RuO<sub>2</sub>-modified TiO<sub>2</sub> thin films prepared by the impregnation method and the dropping method were used as photocatalysts to degrade eosin Y in aqueous solution at room temperature. Before degradation, the blank experiment without photocatalyst was carried out to check the stability of eosin Y under irradiation of high-pressure Hg lamp. Without TiO<sub>2</sub> film, the irradiated solution showed about 15% of self-degradation within 60 min for eosin Y.



FIG. 3. Wide-scan x-ray photoelectron spectrum of the  $RuO_2$ -modified  $TiO_2$  thin film with four times impregnation and its Ru 3d spectrum (inset).

J. Mater. Res., Vol. 26, No. 12, Jun 28, 2011 Downloaded: 11 Mar 2015 This value was used to correct the following photodegradation results of TiO<sub>2</sub> films. Figure 4 shows the photocatalytic degradation curves of the left dye concentration as a function of irradiation time for the pure TiO<sub>2</sub> thin film and RuO<sub>2</sub>-modified TiO<sub>2</sub> thin films with different modification amounts prepared by different methods. The loaded amount of RuO<sub>2</sub> can be controlled by the iteration numbers of adsorption and sintering processes. The adsorption amount of dye and the modification amount of  $RuO_2$  on porous TiO<sub>2</sub> thin film were measured after each iteration and are listed in Table I. The modification amount of RuO<sub>2</sub> almost increases linearly with the times of adsorption. This means modification of RuO<sub>2</sub> does not affect readsorption of dye on the porous film. As a pure  $TiO_2$  film was used as a photocatalyst, within 60 min, 73% of eosin Y was degraded. For a porous TiO<sub>2</sub> film with one time modification of  $RuO_2$ , the degradation percentage is 80% within 60 min, whereas for a porous TiO<sub>2</sub> film with four times modification, 90% of eosin Y was degraded. All of RuO<sub>2</sub>-modified TiO<sub>2</sub> films show obviously higher degradation efficiency than the pure TiO<sub>2</sub> thin film,



FIG. 4. The photocatalytic degradation of eosin Y by the pure  $\text{TiO}_2$  film ( $\Box$ ), the RuO<sub>2</sub>-modified TiO<sub>2</sub> thin films prepared by the dropping method ( $\blacklozenge$ ) and by the impregnation method with twice dye adsorption ( $\bigstar$ ), four times dye adsorption ( $\blacklozenge$ ), and six times dye adsorption ( $\blacktriangledown$ ).

TABLE I. The adsorption amount of dye and the modification amount of Ru cations on the pure  $TiO_2$  and the ruthenium dioxide (RuO<sub>2</sub>)-modified  $TiO_2$  thin films ( $TiO_2 + xRuO_2$ , x represents the iteration numbers of impregnation).

Film	The modification amount of Ru/mol $\rm cm^{-2}$	The adsorption amount of dye/mol $cm^{-2}$
Pure TiO <sub>2</sub>	_	$4.0  imes 10^{-8}$
$TiO_2 + 1RuO_2$	$4.0  imes 10^{-8}$	$4.2 \times 10^{-8}$
$TiO_2 + 2RuO_2$	$8.2  imes 10^{-8}$	$3.8  imes 10^{-8}$
$TiO_2 + 3RuO_2$	$12.0 \times 10^{-8}$	$3.6 \times 10^{-8}$
$TiO_2 + 4RuO_2$	$15.6  imes 10^{-8}$	$3.3  imes 10^{-8}$
$TiO_2 + 5RuO_2$	$18.9 \times 10^{-8}$	$3.7 \times 10^{-8}$
$TiO_2 + 6RuO_2$	$22.6 \times 10^{-8}$	$3.8  imes 10^{-8}$

indicating RuO<sub>2</sub> modification increases photocatalytic efficiency of the  $TiO_2$  thin film. With increasing in the iterations of modification, the highest degradation efficiency occurs for the RuO<sub>2</sub>-modified TiO<sub>2</sub> thin film with four times impregnation, where almost all of eosin Y was degraded after 100 min irradiation. The over-modification of  $RuO_2$  (six times impregnation), however, decreases the degradation efficiency. There is an adequate modification amount for the impregnation method. For comparison, the RuO<sub>2</sub>-modified TiO<sub>2</sub> thin film with same amount of RuO<sub>2</sub> as that of film with four times impregnation was prepared by the dropping method. Its photocatalytic performance is obviously worse than that of the film with same modification amount but prepared by the impregnation method and just a little better than that of the pure  $TiO_2$  thin film (Fig. 4). The difference between two kinds of modified films prepared by different methods is the distribution of RuO<sub>2</sub> on the surface of TiO<sub>2</sub> nanoparticle as shown in Fig. 5. The impregnation method leads to a homogenous distribution of RuO<sub>2</sub> on the particles and in the porous film, while RuO<sub>2</sub> will aggregate on the surface of TiO<sub>2</sub> particle for the dropping method.

As already pointed out in literatures,  $^{28,29}$  photocatalytic degradation reaction of organic pollutants usually follows the first-order kinetics. The kinetics of photodegradation reaction can be described by the Langmuir–Hinshelwood model by which the apparent rate constant can be determined. Figure 6 shows the linear relationship of ln ( $C_0/C$ ) and irradiation time for the photocatalytic results shown in Fig. 4. The good linear relationship confirmed that the photodegradation process for all of catalysts follows the first-order kinetics. The photodegradation apparent rate constant is enhanced with increasing in the modification amount on the porous films, and attaches a maximum for the film with four times modification, then decreases after over loading of RuO<sub>2</sub>. For the different



FIG. 5. Schematic of  $RuO_2$ -modified  $TiO_2$  porous thin films prepared by (a) the impregnation method and (b) the dropping method.

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FIG. 6. Relationship between irradiation time and  $\ln(C_0/C)$  of photocatalytic degradation data shown in Fig. 4.

modification methods, under the same loading amount, homogeneous modification based on the impregnation method exhibits higher degradation apparent rate constant than the inhomogeneous modification based on the dropping method.

The basic degradation mechanism is usually explained as follows according to literatures.<sup>29,30</sup> Electron-hole pairs, generated by irradiating TiO<sub>2</sub> nanoparticles, transfer to the surface of particles. After separated with electron, hole reacts with water to produce hydroxyl and superoxide radicals. These radicals can initiate a series of chemical reactions and act as a strong oxidizing agent to mineralize the pollutants. Therefore, the effective separation and the low recombination of electron-hole pairs are very important to decide the photodegradation efficiency. Adequate RuO<sub>2</sub> homogenously distributed on the surface of TiO<sub>2</sub> particles can serve as a shallow trap of holes to favor the separation of electron-hole pairs and retard the recombination of holes with electrons, thus improving photodegradation activity.<sup>31,32</sup>

IMVS recorded the photovoltage response of electrode under the light modulated by a low intensity sine signal. As the IMVS measurement enables to distinguish the photovoltages under different modulating frequencies, the interfacial processes at different rates between electrode and electrolyte can be determined. IMVS is a useful method to study lifetime of electrons, which relates to the electron recombination process. To demonstrate the effect of RuO<sub>2</sub> on this recombination in TiO<sub>2</sub> porous thin film, IMVS of pure TiO<sub>2</sub> and RuO<sub>2</sub>-modified TiO<sub>2</sub> thin films was measured on the mode of DSSC fabricated by the dye-sensitized porous nanocrystalline film and platinized FTO electrode, between which redox electrolyte was sandwiched. Figure 7 shows IMVS complex planes of the TiO<sub>2</sub> and RuO<sub>2</sub>modified TiO<sub>2</sub> thin films. The response mainly appears in the fourth quadrant of the complex plane and displays one semicircle, i.e., it is a single time constant process in IMVS



FIG. 7. Complex planes obtained from intensity-modulated photovoltage spectroscopy measurements of the pure TiO<sub>2</sub> film ( $\Box$ ) and the RuO<sub>2</sub>-modified TiO<sub>2</sub> nanoporous thin films with twice dye adsorption ( $\blacktriangle$ ), four times dye adsorption ( $\heartsuit$ ), and six times dye adsorption ( $\blacktriangledown$ ).

measurement, where the frequency at the apex of the semicircle is related to the time constant of the process.

The time constant  $(\tau_n, \text{ lifetime of electron})$  can be estimated from  $\tau_n = (2\pi f_{max})^{-1}$ , where  $f_{max}$  is the characteristic frequency at the minimum imaginary voltage of IMVS at the imaginary voltage, which gives an estimate of the average time before the injected electrons are recombined by holes, dye cations, or oxidization compositions of redox electrolyte. For films with comparable film thickness, dye loading, and electrolyte compositions, such as those investigated here, the lifetime of electron should enable a valid comparison of the electron recombination with hole in the films. From the measured  $\tau_n$  value, one can estimate that the recombination process of electrons is different between the TiO<sub>2</sub> and RuO<sub>2</sub>modified TiO<sub>2</sub> thin films. The lifetime of electron for the RuO<sub>2</sub>-modified TiO<sub>2</sub> thin film electrode with four times adsorption and the TiO<sub>2</sub> electrode without RuO<sub>2</sub> modification are 31.8 and 1.4 ms, respectively. The reduction of electron recombination in the RuO<sub>2</sub>-modified TiO<sub>2</sub> film is quite remarkable. Low electron recombination means an increasing in the lifetime of holes and thus ensures holes have enough time to degrade substrate, consequently improving photocatalytic performance. The reason that the RuO<sub>2</sub>-modified TiO<sub>2</sub> thin film has lower electron recombination should be related to the shallow traps for holes formed by the modification of RuO<sub>2</sub>. But overmodification of RuO<sub>2</sub> will form some surface states that can become recombination centers for electrons and holes. Therefore, the photodegradation efficiency begins to decrease over an adequate modification amount. And, for the adequate amount of RuO<sub>2</sub>, the homogenous distribution of RuO<sub>2</sub> is also a very important factor for high photocatalytic performance. Otherwise, the aggregation of RuO<sub>2</sub> even at an adequate amount will act as

1536CAMBRIDGE JOURNALS

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recombination sites to accelerate recombination of electron and hole. The adsorption of metal contained dye followed by sintering process, as a method to form homogeneous distribution of metal oxide on nanocrystalline porous thin film, will favor exact studying of the special properties due to homogeneous metal oxide modification.

#### **IV. CONCLUSIONS**

The nanoparticles colloidal paste prepared through the hydrothermal method was cast onto FTO glass substrate to form porous TiO<sub>2</sub> thin film. The impregnation method and the dropping method were used to modify RuO<sub>2</sub> on the porous TiO<sub>2</sub> films, respectively. The impregnation method is to adsorb dye of N3 on TiO<sub>2</sub> nanoporous film followed by sintering process to burn off organic matters and form ruthenium oxide. The modification amount of RuO<sub>2</sub> was controlled by the iteration numbers of adsorption and sintering processes. In the dropping method, appropriate concentration of ruthenium trichloride trihydrate aqueous solution was dropwise added to the surface of TiO<sub>2</sub> thin film, which was sintered at 450 °C to form RuO<sub>2</sub> after evaporation of solvent. Eosin Y was selected as a substrate to estimate the photocatalytic efficiency of two kinds of  $RuO_2$ -modified TiO<sub>2</sub> films. The results indicate that appropriate modification amount of RuO<sub>2</sub> can improve TiO<sub>2</sub> photocatalytic performance by retarding recombination of hole with electron. RuO<sub>2</sub>-modified TiO<sub>2</sub> prepared by the impregnation method exhibited better photocatalytic performance than that by the dropping method because of the uniform distribution of RuO<sub>2</sub> formed by the impregnation method.

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