Online Detection of Reactive Oxygen Species in Ultraviolet (UV)-Irradiated Nano-TiO₂ Suspensions by Continuous Flow Chemiluminescence

Dabin Wang, Lixia Zhao,* Liang-Hong Guo,* and Hui Zhang

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, 18 Shuangqing Road, Beijing 100085, China

Supporting Information

ABSTRACT: Reactive oxygen species (ROS) play very important roles in the photocatalytic reactions of semiconductors. Using a continuous flow chemiluminescence (CFCL) system, we developed three methods for the selective, sensitive, and online detection of O₂^{•−}, •OH, and H₂O₂ generated during ultraviolet (UV) irradiation of nano-TiO₂ suspensions. TiO₂ nanoparticles were irradiated in a photoreactor and pumped continuously into a detection cell. To detect O₂^{•−}, luminol was mixed with TiO₂ before it entered the detection cell. For the detection of short-lived •OH, phthalhydrazide was added into the photoreactor to capture •OH, and then mixed with H₂O₂/K₃Cu(HIO₆)₂ to produce chemiluminescence (CL). To detect H₂O₂, an irradiated TiO₂ suspension was kept in darkness for 30 min, and then mixed with luminol/K₃Fe(CN)₆ to produce CL. The selectivity of each method for a particular ROS was verified by using specific ROS scavengers. For a given ROS, a comparison between CL and conventional method showed good agreement for a series of TiO₂ concentrations. The sensitivity of CL method was approximately 3-, 1200-, and 5-fold higher than the conventional method for O₂^{•−}, •OH, and H₂O₂, respectively. To demonstrate the utility of the methods, ROS in three different types of TiO₂ suspensions was detected by CFCL. It was found that photodegradation efficiency of Rhodamine B correlated the best ($R^2 > 0.95$) with the amount of photogenerated •OH, implying that •OH was the major oxidant in Rhodamine B photodegradation reaction. CFCL may provide a convenient tool for the studies on the reaction kinetics of ROS-participated decomposition of environmental contaminants.

Reactive oxygen species (ROS) such as hydroxyl radicals (•OH), superoxide ions (O₂^{•−}), singlet oxygen (¹O₂), and hydrogen peroxide (H₂O₂) are produced in many chemical and biological processes.¹ The roles they play differ significantly, depending on the type of ROS, the reactions they participate in, and the target molecules with which they react. Since ROS are highly reactive, they have been used to decompose hazardous chemicals.² In the area of semiconductor photocatalysis, the main mechanism of photodegradation involves light-initiated generation of ROS and their subsequent redox reactions with the chemicals.³ The general principle is that, when a semiconductor is illuminated by light with energy equal to or greater than the band gap energy of the semiconductor, electron/hole (e_{cb}[−]/h_{vb}⁺) pairs are generated in the bulk. These charge carriers migrate to the surface of semiconductor and react with oxygen or water to produce ROS. The reactivity of some ROS is high enough to decompose most organic compounds. For example, the oxidation potential of •OH is 2.7 and 1.8 V in acidic and neutral solutions, respectively.⁴ In previous studies it has been frequently observed that the photodegradation efficiency of a chemical varies over a large range, depending on the semiconductor and solution conditions. This was believed to be mainly due to the variation in the type, quantity, and lifetime of ROS produced in

semiconductor photocatalytic reactions.⁵ Therefore, identification, quantification, and kinetics evaluation of ROS are of great significance to understanding the photodegradation mechanisms, improving degradation efficiency, and eventually utilizing the technology in practical applications.

In previous studies, several analytical methods have been developed and employed for the detection of ROS generated in semiconductor photocatalysis, including electron spin resonance (ESR),⁶ ultraviolet–visible light (UV-vis) absorbance,⁷ and fluorescence.^{8,9} These methods often require a capture probe to react with ROS to form a stable and detectable product, a separation step to remove the semiconductor, followed by spectroscopic measurement. As such, they are cumbersome and time-consuming. Because spectrometric detection has an intrinsic background signal, these methods are also not sensitive enough. Their most serious drawback is the relatively long duration from sampling to measurement. Because ROS are highly reactive and have very short lifetimes (2 μs for ¹O₂, 200 μs for •OH, and from 5 s to hundreds of seconds for O₂^{•−}), their composition and concentration

Received: August 21, 2014

Accepted: October 2, 2014

Published: October 2, 2014

change almost constantly during photocatalysis.³ The conventional spectroscopic methods cannot follow the dynamic change of ROS.

In principle, chemiluminescence (CL) is well-suited for the detection of ROS, since the luminescence is produced by a redox chemical reaction between a CL probe and an oxidant including ROS. Because of its ultralow background, CL is currently considered to be one of the most sensitive optical detection methods. Furthermore, light emission is generated almost instantly when the CL reactants are mixed. Therefore, CL is capable of following the dynamic process of ROS generation and reaction in semiconductor photocatalysis. Over the years, many CL probes have been synthesized and tested. Among them, luminol is a popular probe that has been found to emit light when reacting with ROS.¹⁰ The Nosaka group^{11,12} and the Reitberger group¹³ developed batch CL methods for the detection of $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ produced in TiO_2 suspensions. The photoirradiated TiO_2 solution was withdrawn at appropriate time intervals, and mixed with the reaction reagent in a luminometer, where the CL intensity was measured with a photon-counting photomultiplier tube. This approach only detected the $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ concentration at discrete time intervals and, thus, did not directly reflect the dynamic process in nano- TiO_2 suspensions.

Based on the above analysis, in the present work, our objective has been to develop new analytical methods for the sensitive, selective, and dynamic detection of ROS generated during semiconductor photocatalytic reactions. Continuous-flow chemiluminescence (CFCL) offers the benefits of high sensitivity and online detection. Therefore, we first built a simple and yet effective CFCL apparatus. By stringently selecting the CL probe, oxidants and timing of signal detection, selective detection of a particular ROS was achieved. The CFCL methods were demonstrated to be able to provide useful information about the ROS involved in photocatalytic degradation reactions of several TiO_2 nanophotocatalysts.

EXPERIMENTAL SECTION

Chemicals and Materials. Three types of commercialized nano- TiO_2 powders (including anatase, rutile, and Degussa P25), phthalhydrazide (Phth), terephthalic acid (TA), 2-hydroxyterephthalic acid (TAOH), 5-amino-2,3-dihydro-1,4-phthalazinedione (Luminol), 3-bis(2-methoxy-4-nitro-5-sulfo-phenyl)-2H-tetrazolium-5-carboxanilide (XTT), *p*-hydroxyphenylacetic acid (POPHA), and horseradish peroxidase (HRP) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Rhodamine B was obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). 5-Hydroxy-2,3-dihydro-1,4-phthalazinedione (5-OH-Phth) and bis-(hydrogenperiodato)cuprate(III) [$\text{K}_5\text{Cu}(\text{HIO}_6)_2$] ($\text{Cu}(\text{III})$) were synthesized according to refs 14 and 15, respectively.

Chemiluminescence Instrumentation. A continuous flow chemiluminescence (CFCL) apparatus for the online detection of ROS generated from UV irradiation of a semiconductor nanoparticle suspension was built in our lab (Scheme 1). The apparatus mainly comprised of a photoreactor, a computer-controlled CL analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China), and three peristaltic pumps (Longer Precision Pump Co., Baoding, Hebei, China). The photoreactor is a cylindrical quartz container (100 mL) irradiated with a 500-W xenon light source (Trusttech Co., Beijing, China). Two glass containers (200 mL) are used for chemical reagents. The three containers

Scheme 1. CFCL Experimental Setup for Online Detection of $\text{O}_2^{\bullet-}$, $\bullet\text{OH}$, and H_2O_2 ^a

^aLegend: (1) light source, (5) chemiluminescence analyzer ((a) detection cell, (b) PMT, (c) electronics, (d) computer), (6, 7, 8) peristaltic pumps; for $\text{O}_2^{\bullet-}$ detection: (2) TiO_2 suspension, (3) TiO_2 suspension or free radical scavenger, (4) luminol; for $\bullet\text{OH}$ detection: (2) TiO_2 suspension and Phth, (3) H_2O_2 , (4) $\text{K}_5\text{Cu}(\text{HIO}_6)_2$; for H_2O_2 detection: (2) TiO_2 suspension, (3) $\text{K}_3\text{Fe}(\text{CN})_6$, (4) luminol. The volume of the spiral detection cell (a) and the flow rate are 0.5 mL and 2.2 mL/min, respectively.

are connected separately to the peristaltic pumps through Tygon pump tubing (i.d. = 1 mm). Fluids are pumped into a spiral detection cell in the CL analyzer, and CL intensity is measured with a photomultiplier tube (PMT). In addition, details of the detection of ROS by conventional methods were also provided in the Supporting Information.

Photocatalytic Degradation of Rhodamine B. Photocatalytic activity of three types of TiO_2 nanoparticles was evaluated by their photocatalytic degradation efficiency of Rhodamine B. Rhodamine B (1 mg/mL) was added into 80 mL of a TiO_2 suspension in the photoreactor. At a given time interval of UV irradiation, a 4-mL aliquot was withdrawn and centrifuged. The concentration of residual Rhodamine B in the supernatant was determined on the UV-vis spectrophotometer.

RESULTS AND DISCUSSION

Previous studies have confirmed that several types of ROS, such as $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, H_2O_2 , and $^1\text{O}_2$ are usually generated in UV-irradiated TiO_2 suspensions simultaneously.^{3,16} The most commonly used CL probe, Luminol, is not selective to any particular ROS. Therefore, we developed three CL methods for the selective detection of $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, and H_2O_2 , respectively, by taking advantage of the continuous flow system, as described below.

CFCL Method for the Dynamic Monitoring of $\text{O}_2^{\bullet-}$. Among the four types of ROS, the lifetimes of $\bullet\text{OH}$ and $^1\text{O}_2$ are very short (200 μs for $\bullet\text{OH}$, 2 μs for $^1\text{O}_2$), whereas that of $\text{O}_2^{\bullet-}$ is relatively long (5 s to hundreds of seconds), and H_2O_2 is very stable.^{17,18} In our CFCL apparatus, ~ 10 s are needed for the TiO_2 nanoparticle suspension to flow from the photoreactor to the detection cell. Therefore, only $\text{O}_2^{\bullet-}$ and H_2O_2 may reach the detection cell. Experiments confirmed that, without an oxidant such as ferricyanide, Luminol produced very little CL when reacting with micromolar H_2O_2 . Hence, if the nanoparticle suspension is mixed with Luminol immediately prior to entering the detection cell, the only ROS that reacts with the probe to produce CL would be $\text{O}_2^{\bullet-}$.

Figure 1a shows that, without UV irradiation, the CL signal of Luminol in a P25 nano- TiO_2 suspension was very weak. However, once the UV lamp was turned on, CL intensity sharply increased and continued to increase with time until 800

Figure 1. Online detection of (a) $\text{O}_2^{\bullet-}$, (b) $\bullet\text{OH}$, and (c) H_2O_2 generated in UV-irradiated nano-P25 suspension. Red line represents data for the TiO_2 suspension; black line represents data for the blank solution. Reagents used: (a) 0.1 mg/mL P25, 1 μM Luminol; (b) 0.005 mg/mL P25, 1 μM Phth, 0.1 mM H_2O_2 , and $\text{K}_5\text{Cu}(\text{HIO}_6)_2$; (c) 0.01 mg/mL P25, 0.01 M $\text{K}_3\text{Fe}(\text{CN})_6$, and 10 μM Luminol.

s later, when a plateau was reached. The CL intensity of the UV-irradiated P25 suspension is ~ 10 times higher than that of nonirradiated P25 suspension, but the blank solution did not change much upon irradiation. In addition, when another TiO_2 suspension (0.1 mg/mL) was pumped into the detection cell through separate tubing, the CL signal did not change, indicating that TiO_2 has no effect on CL reaction. Obviously, the CL generation is related to nano- TiO_2 photocatalytic reactions.

As we know, ROS production by nanophotocatalysts can be greatly affected by some experimental factors including ionic species, and pH, etc. We found that a P25 suspension in NaOH solution produced far greater CL than the one in Na_2CO_3 solution, indicating that more $\text{O}_2^{\bullet-}$ radicals were generated in the former case (see Figure S-1a in the Supporting Information). This is probably because carbonate ions can be oxidized by the photogenerated holes (h^+) of P25 to carbonate radicals, which compete with O_2 for the photoexcited electrons in the reduction reaction and thus inhibit $\text{O}_2^{\bullet-}$ formation.¹⁹ Medium pH is another parameter that has significant impact on the ROS production.²⁰ Figure S-1b in the Supporting Information depicts the dependence of CL intensity on the pH of the P25 suspension adjusted by HCl or NaOH solution in the pH range of 3–13. Overall, CL signal/blank ratio (I/I_0) was higher in alkaline solutions than in acidic solutions, and pH 11 was the optimum value for the production of photocatalyzed $\text{O}_2^{\bullet-}$. It is worth noting that, regardless of the pH variation of TiO_2 suspensions, the pH value of the mixture that enters the CL detection cell remained at pH 10.6, because of the buffering capacity of 0.1 M carbonate. Luminol CL intensity is also susceptible to experimental conditions. The effect of Luminol concentration, and flow rate, on CL was investigated systematically (see Figures S-1c and S-1d in the Supporting Information). Based on the results, a Luminol concentration of 50 μM and flow rate of 2.2 mL/min were selected. In order to evaluate the selectivity of this CFCL method for $\text{O}_2^{\bullet-}$ detection, ROS radical scavengers were added into the nano-P25/Luminol mixture before CL measurement. CL intensity decreased dramatically with the addition of superoxide dismutase (SOD), which is a $\text{O}_2^{\bullet-}$ scavenger (see Figure S-2a in the Supporting Information), while isopropanol (a $\bullet\text{OH}$ scavenger) or NaN_3 (a $^1\text{O}_2$ scavenger) had no effect on the CL intensity (see Figures S-2b and S-2c in the Supporting Information). This confirms that the ROS involved in the Luminol CL reaction is $\text{O}_2^{\bullet-}$, not $\bullet\text{OH}$ or $^1\text{O}_2$.

CFCL Method for the Dynamic Monitoring of $\bullet\text{OH}$.

Since $\bullet\text{OH}$ is short-lived and cannot reach the CL detection cell in our system, an indirect method was developed for its detection. Phthalhydrazide (Phth) was added into the nano-

TiO_2 suspension to specifically capture photogenerated $\bullet\text{OH}$ and convert to 5-OH-Phth.¹³ The latter acts as a stable CL probe and emits strong CL when mixed with oxidants such as $\text{H}_2\text{O}_2/\text{K}_5\text{Cu}(\text{HIO}_6)_2$ in alkaline medium (1 M Na_2CO_3).²¹ Figure 1b shows the CL kinetic curve of a nano-P25 suspension. Without UV irradiation, there was little CL signal, whereas, with the lamp on, the CL intensity increased rapidly with the illumination time and reached a plateau after 1200 s. The CL intensity of the UV-irradiated P25 suspension is ~ 40 times higher than that of nonirradiated P25 suspension. As with superoxide radicals, the selectivity of this method for $\bullet\text{OH}$ was evaluated by adding different radical scavengers. As shown in Figure S-3a in the Supporting Information, CL intensity was completely inhibited by the addition of isopropanol, which is a selective scavenger of $\bullet\text{OH}$, whereas SOD and NaN_3 had no impact on CL intensity (see Figures S-3b and S-3c in the Supporting Information). This confirms that the species involved in the Phth CL generation was $\bullet\text{OH}$, not $\text{O}_2^{\bullet-}$ or $^1\text{O}_2$.

The CL intensity was greatly affected by Phth concentration, oxidant H_2O_2 and $\text{K}_5\text{Cu}(\text{HIO}_6)_2$ concentration, as well as the pH of the TiO_2 suspension. All these parameters were investigated separately (see Figure S-4 in the Supporting Information) and the optimized values are 20 μM Phth, 50 μM H_2O_2 , 0.1 mM $\text{K}_5\text{Cu}(\text{HIO}_6)_2$, and pH 9. It is now generally accepted that ROS are generated on the TiO_2 surface during UV irradiation. At pH 9, the TiO_2 surface ($\text{pH}_{\text{zpc}} = 6.25$) is negatively charged, and phthalhydrazide ($\text{pK}_a = 6.5$) is ionized into an anion. The electrostatic repulsion may hinder the adsorption of phthalhydrazide on TiO_2 surface. Thus, phthalhydrazide probably does not interfere with $\bullet\text{OH}$ generation in the TiO_2 photocatalytic reaction.

CFCL Method for the Online Determination of H_2O_2 .

Among the four ROS species generated in TiO_2 photocatalytic reactions, H_2O_2 is the most stable one. In our method for H_2O_2 detection, the short-lived ROS species were excluded from the CL detection cell by irradiating TiO_2 for a desired duration, then keeping the suspension in darkness for 30 min.²² The suspension was then mixed with Luminol/ $\text{K}_3\text{Fe}(\text{CN})_6$ prior to the detection cell to produce CL. Figure 1c shows a plot of CL intensity of nano-P25 suspension with different irradiation times. The luminescence initially increased with the irradiation time, and then reached a plateau after 600 s. This is very similar to the kinetic curve of $\text{O}_2^{\bullet-}$, probably because H_2O_2 is the product of $\text{O}_2^{\bullet-}$ disproportionation. Although this CL method does not follow the dynamic generation of H_2O_2 , it is nonetheless quantitative. After 600 s of irradiation, the estimated H_2O_2 production was 2.95 μM , in accordance with the previous reports.^{9,23}

Comparison of CFCL with Conventional Methods.

To validate the new methods, the comparison between CL methods and these conventional techniques was investigated. P25 suspensions of a series of concentrations were irradiated, and ROS was detected with one of the CL methods (Figure 2). In parallel, the suspensions were detected by XTT absorbance, TA fluorescence, and POPHA fluorescence for $\text{O}_2^{\bullet-}$, $\bullet\text{OH}$, and H_2O_2 , respectively (see Figure S-5 in the Supporting Information). As shown in Figure 2 and Figure S-5 in the Supporting Information, for a given ROS, the detected signals all increased with P25 concentration, regardless of the method used. In addition, the rate of increase is very similar between CL and spectroscopic measurement, indicating the reliability of the developed CL methods. Based on the CL dependence on

Figure 2. CFCL methods for the detection of ROS generated during P25 irradiation: (a) detection of $\text{O}_2^{\bullet-}$ by Luminol CL; (b) detection of $\bullet\text{OH}$ by Phth/ H_2O_2 / $\text{K}_3\text{Cu}(\text{HIO}_6)_2$ CL; and (c) detection of H_2O_2 by Luminol/ $\text{K}_3\text{Fe}(\text{CN})_6$ CL. TiO_2 concentrations are given in the plots.

P25 concentration, the sensitivity of each method was estimated by calculating the limit of detection (LOD) of P25 under the UV irradiation (signal-to-noise ratio of $S/N = 3$). This should be directly related to the LOD of ROS. As shown in Table S-1 in the Supporting Information, the LOD of CL method is approximately 3-, 1200-, and 5-fold lower than the conventional method for the detection of $\text{O}_2^{\bullet-}$, $\bullet\text{OH}$, and H_2O_2 , respectively. This demonstrates the inherently high sensitivity of CL-based detection methods, in comparison with spectroscopic methods. This advantage is in addition to the capability of CL methods for the real-time monitoring of $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ generation during P25 photocatalytic reactions.

Relationship between ROS Generation and Photocatalytic Degradation Properties of Nano- TiO_2 . It is well-recognized that photogenerated ROS is the species responsible for the photocatalytic degradation of chemicals by semiconductor nanomaterials.³ For a given chemical, semiconductor nanomaterials with different shapes, sizes, morphologies, or crystal structures frequently exhibit different photodegradation efficiency or even different degradation pathways.^{24,25} The commonly accepted rationale is that the type and amount of photogenerated ROS are critically dependent on the type of semiconductor used, and subsequently dictate the degradation reactions.

With the developed CFCL methods, we attempted to investigate the relationship between ROS generation of three different types of TiO_2 nanoparticles (P25, anatase, and rutile) and their photocatalytic degradation properties. Rhodamine B was chosen as the model chemical, since its photocatalytic degradation reaction with TiO_2 has been investigated extensively. Figure S-6 in the Supporting Information shows the photocatalytic degradation efficiency of Rhodamine B by the three TiO_2 nanoparticles. It follows the order of P25 > anatase > rutile, which is consistent with previous reports.²⁴ ROS generated during the UV irradiation of these TiO_2 nanoparticles was then measured selectively by one of the CFCL methods. Figure S-7 in the Supporting Information showed that $\text{O}_2^{\bullet-}$ generation is essentially the same on the three nanoparticles, $\bullet\text{OH}$ generation follows the order of P25 > anatase > rutile, and the order of H_2O_2 generation is rutile > P25 > anatase. ROS generation of the three nanoparticles was also evaluated with the conventional methods. For a given ROS, good agreement was observed between the CL and conventional method. This result provides another piece of evidence that validates the CL methods. Comparing the photodegradation efficiency with ROS generation of different TiO_2 materials, it is obvious that the degradation efficiency correlates with $\bullet\text{OH}$ generation but not the other two ROS, suggesting that $\bullet\text{OH}$ is the primary ROS responsible for the degradation of Rhodamine B.

The relationship between photodegradation efficiency and $\bullet\text{OH}$ generation was analyzed in a more-quantitative way. P25 suspensions of various concentrations and UV-irradiation durations were used as a means to change the concentration of $\bullet\text{OH}$ generated from UV irradiation. In addition, the photodegradation efficiency of Rhodamine B in these suspensions was then measured. Figure 3 depicts the

Figure 3. Relationship between the photodegradation efficiency of Rhodamine B and CL intensity of P25 suspensions: (a) a 10 $\mu\text{g/mL}$ P25 suspension with different UV-irradiation duration (2, 4, 8, 12, 16, 20 min); (b) P25 suspensions with concentrations of 0, 2, 5, 10, and 20 $\mu\text{g/mL}$ and irradiated for 10 min.

relationship between the degradation efficiency and CL intensity of P25 suspensions with various UV-irradiation duration and concentrations (which represent $\bullet\text{OH}$ concentration). Evidently, the degradation efficiency increased linearly with CL intensity, with a correlation coefficient of $R^2 > 0.95$. The combined results in Figure S-7 in the Supporting Information and Figure 3 strongly support the notion that photogenerated $\bullet\text{OH}$ in P25 suspensions plays a major role in the degradation of Rhodamine B, as reported previously.²⁶

CONCLUSIONS

In the present work, we have developed three CFCL-based methods for the online detection of $\text{O}_2^{\bullet-}$, $\bullet\text{OH}$, and H_2O_2 generated during the ultraviolet (UV) irradiation of nano- TiO_2 suspensions. The methods were shown to be selective, and more sensitive than conventional absorbance- and fluorescence-based detection. We also demonstrated that the methods could be employed to rapidly identify radicals among various ROS, which are mainly responsible for the photocatalytic degradation of chemicals. One of the unique features of the new methods is the almost-real-time detection of $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ radicals. This may provide a very convenient and low-cost tool for the studies of ROS generation kinetics in photocatalytic reactions. In principle, the methods can be expanded to the detection of ROS generated in chemical reactions such as the Fenton reaction, in which $\bullet\text{OH}$ is produced by redox reactions, not UV irradiation. Furthermore, the methods can also be applied to the online detection of chemicals which become luminescent upon reaction with ROS. In such cases, the chemical replaces Luminol in the above experiments as the CL probe. Recently, it was reported that tetrachloro-1,4-benzoquinone (TCBQ) and H_2O_2 produced CL in the absence of any CL probes.²⁷ Therefore, it is possible to investigate the reaction kinetics of TCBQ production and decomposition, or even some other chemicals, by using the CFCL methods.

ASSOCIATED CONTENT

Supporting Information

Experimental data including optimization of CL detection conditions, the selectivity and sensitivity of the CL method, ROS detection for a series of P25 concentrations by

conventional methods, and ROS detection and photocatalytic activities of three TiO₂ photocatalysts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

*Tel.: (86) 10-62849338. Fax: (86) 10-62849685. E-mail: zlx@rcees.ac.cn (L. Zhao).

*Tel.: (86) 10-62849338. Fax: (86) 10-62849685. E-mail: LHGuo@rcees.ac.cn (L.-H. Guo).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Basic Research Program of China (Nos. 2011CB936001, 2010CB933502) and the National Natural Science Foundation of China (Nos. 21177138, 21207146).

REFERENCES

- (1) Freinbichler, W.; Colivicchi, M. A.; Stefanini, C.; Bianchi, L.; Ballini, C.; Misini, B.; Weinberger, P.; Linert, W.; Varešlija, D.; Tipton, K. F. *Cell. Mol. Life Sci.* **2011**, *68*, 2067–2079.
- (2) Neyens, E.; Baeyens, J. *J. Hazard. Mater.* **2003**, *98*, 33–50.
- (3) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69–96.
- (4) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886.
- (5) Xu, Y. M. *Progress Chem.* **2009**, *21*, 524–533.
- (6) Wang, Z.; Ma, W.; Chen, C.; Ji, H.; Zhao, J. *Chem. Eng. J.* **2011**, *170*, 353–362.
- (7) Li, Y.; Zhang, W.; Niu, J.; Chen, Y. *ACS Nano* **2012**, *6*, 5164–5173.
- (8) Ishibashi, K.-I.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Photochem. Photobiol., A* **2000**, *134*, 139–142.
- (9) Kormann, C.; Bahnemann, D. W.; Hoffmann, M. R. *Environ. Sci. Technol.* **1988**, *22*, 798–806.
- (10) Tsaplev, Y. B. *J. Anal. Chem.* **2012**, *67* (6), 506–514.
- (11) Nosaka, Y.; Yamashita, Y.; Fukuyama, H. *J. Phys. Chem. B* **1997**, *101*, 5822–5827.
- (12) Nosaka, Y.; Nakamura, M.; Hirakawa, T. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1088–1092.
- (13) Backa, S.; Jansbo, K.; Reitberger, T. *Holzforschung* **1997**, *51*, 557–564.
- (14) Drew, H.; Pearman, F. H. *J. Chem. Soc.* **1937**, 26–33.
- (15) Jose, T. P.; Tuwar, S. M. *J. Mol. Struct.* **2007**, *827*, 137–144.
- (16) Daimon, T.; Hirakawa, T.; Kitazawa, M.; Suetake, J.; Nosaka, Y. *Appl. Catal., A* **2008**, *340*, 169–175.
- (17) Nosaka, Y.; Nakamura, M.; Hirakawa, T. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1088–1092.
- (18) Lin, J.-M. *Chemiluminescence—Basic Principles and Applications*, 1st Edition; Chemical Industry Press: Beijing, 2004; p 148.
- (19) Bonini, M. G.; Miyamoto, S.; Di Mascio, P.; Augusto, O. *J. Biol. Chem.* **2004**, *279*, 51836–51843.
- (20) Liang, H.-C.; Li, X.-Z.; Yang, Y.-H.; Sze, K.-H. *Chemosphere* **2008**, *73*, 805–812.
- (21) Miller, C. J.; Rose, A. L.; Waite, T. D. *Anal. Chem.* **2010**, *83* (1), 261–268.
- (22) Hirakawa, T.; Nosaka, Y. *J. Phys. Chem. C* **2008**, *112*, 15818–15823.
- (23) Teranishi, M.; Naya, S.-I.; Tada, H. *J. Am. Chem. Soc.* **2010**, *132*, 7850–7851.
- (24) Mahlambi, M.; Mishra, A.; Mishra, S.; Krause, R.; Mamba, B.; Raichur, A. *J. Therm. Anal. Calorim.* **2012**, *110* (2), 847–855.
- (25) Pan, J.; Liu, G.; Lu, G. Q.; Cheng, H.-M. *Angew. Chem., Int. Ed.* **2011**, *50* (9), 2133–2137.

(26) Zielinska, B.; Grzechulska, J.; Kalenczuk, R. J.; Morawski, A. W. *Appl. Catal., B* **2003**, *45* (4), 293–300.

(27) Zhu, B.-Z.; Mao, L.; Huang, C.-H.; Qin, H.; Fan, R.-M.; Kalyanaraman, B.; Zhu, J.-G. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109* (40), 16046–16051.