# NANO LETTERS

## Nanocrystalline TiO<sub>2</sub>-Catalyzed Photoreversible Color Switching

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**Supporting Information** 

**ABSTRACT:** We report a novel photoreversible color switching system based on the photocatalytic activity of  $TiO_2$  nanocrystals and the redox-driven color switching property of methylene blue (MB). This system rapidly changes from blue to colorless under UV irradiation and recovers its original blue color under visible light irradiation. We have identified four major competing reactions that contribute to the photoreversible switching, among which two are dominant: the decoloration process is mainly driven by the reduction of MB to leuco MB by photogenerated electrons from  $TiO_2$  nanocrystals under UV irradiation, and the recoloration process operates by the  $TiO_2$ -induced self-catalyzed oxidation of LMB under visible irradiation. Compared with the conventional color switching systems based on photoisomerization of chromophores, our system has not only low toxicity but also significantly improved switching rate and cycling performance. It is envisioned that this photoreversible system may promise unique opportunities for many light-driven actuating or color switching applications.



**KEYWORDS:** TiO<sub>2</sub> nanocrystals, photoreversible, color switching, reduction–oxidation reaction, methylene blue

he development of new materials for actuators that reversibly change color in response to external stimuli, such as electric or magnetic field, mechanical stress, temperature change, or chemical reaction, has attracted a great deal of attention for their important applications in sensing devices, display and signage technologies, and security features.<sup>1-5</sup> A particularly intriguing possibility is offered by light-responsive materials, which can be remotely controlled and rapidly changed in a clean and noninvasive manner without the need of direct contact with the actuators. $^{6-10}$  The common photoresponsive materials, however, mainly operate based on the photoisomerization of constitute chromophores, such as azobenzene, which undergo cis-trans isomerization upon alternating irradiation with ultraviolet (UV) and visible light.<sup>6,11</sup> In addition to photoisomerization, the chromophores also experience competing thermal back relaxation and sometimes other side reactions which, although slow, are unavoidable and give rise to serious problems such as lack of stability and controllability,<sup>10,12,13</sup> leading to low efficiency both in color switching rate and cycling performance.

Methylene blue (MB, tetramethylthionine chloride,  $C_{16}H_{18}ClN_3S$ ) is a heterocyclic aromatic dye that is brightly blue colored in an oxidizing environment. Upon reduction, however, it changes to leuco methylene blue (LMB), which is colorless.<sup>14</sup> The relationship between the oxidized form (MB) and its stable reduced leuco form (LMB) is summarized in Figure 1. Photochemical reduction of MB to LMB using semiconductors in photoelectrochromism—an area once very attractive in the field of solar to electrical energy conversion—had been widely studied in the 1970s.<sup>15</sup> Composite systems containing a semiconductor material such as TiO<sub>2</sub> (Degussa P25), MB, and a sacrificial electron donor (SED) were also



Figure 1. Schematic illustration of the photoreversible color switching between MB (blue) and LMB (colorless) catalyzed by  $TiO_2$  nanocrystals. The chloride ion is omitted in the molecular structure of MB. Reactions 1–4 are shown here.

developed previously as oxygen indicators in food and pharmaceutical industries to ensure freshness and quality control of the products.<sup>16–18</sup> In this case, blue MB is transformed into colorless LMB upon UV irradiation, where the holes photogenerated from  $TiO_2$  oxidize SED, and the remaining photogenerated electrons reduce MB to LMB (Reaction 1 in Figure 1). Recoloration occurs when the system is exposed to oxygen, inducing back electron transfer from

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Figure 2. (a) TEM image, (b) XRD, and (c) UV-vis spectrum of  $TiO_2$  nanocrystals prepared by a high temperature hydrolysis reaction using P123 as a capping ligand. Inset in (c): a digital photograph of a concentrated aqueous dispersion of the  $TiO_2$  nanocrystals in a glass vial.



**Figure 3.** Photoreversible color switching of the  $TiO_2$  nanocrystals/MB/water mixture in response to UV and visible light irradiation: (a) UV-vis spectra showing the decoloration process under UV irradiation; (b) UV-vis spectra showing the recoloration process under visible light irradiation. Inset: digital photographs showing the reappearance of the color after visible light irradiation for various lengths of time. (c) UV-vis spectra of the sample in 11 cycles of repeated UV and visible irradiation. (d) The absorption intensity at ~664 nm recorded after each UV and visible irradiation for continuous 11 cycles.

LMB to oxygen (electron acceptors) and producing a blue colored oxidized form of MB. Interestingly, very similar reactions may also occur when MB is used as a test model pollutant in semiconductor photocatalysis, where photobleaching of MB can be due to reduction to its leuco form rather than total decomposition, especially at low concentrations of dissolved oxygen.<sup>18</sup> In this case, the MB to LMB transition may lead to inaccurate estimation of the photocatalytic activity of the semiconductor catalysts.

Herein we report the design of colloidal  $\text{TiO}_2$  nanocrystals for enabling reversible and considerably fast color switching based on the photoelectrochromic reactions of MB in response to UV and visible light irradiation. With the assistance of  $\text{TiO}_2$ nanocrystals, UV irradiation can rapidly bleach the original blue color of MB, while the resulting colorless system can be switched back to blue through a relatively short exposure to visible light. The key to the reversible photoelectrochromic

switching is the prevention of photodecomposition of the dye. This goal is achieved first by synthesizing TiO<sub>2</sub> nanocrystals with small sizes and low crystallinity, which correspond to considerably low photocatalytic activity toward dye decomposition. We also use a nonionic polymer poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) (P123) as a capping ligand to bind on the nanocrystal surface for maintaining colloidal stability of  ${\rm TiO}_2$  nanocrystals and more importantly, as an effective SED to scavenge photogenerated holes, preclude photodegradation of the dye, and ensure sufficient electrons for rapid reduction of MB to LMB.<sup>19</sup> An added benefit of using P123 as SED is that alkoxy radicals generated initially by hole oxidation may further reduce MB at the TiO<sub>2</sub>/MB interface.<sup>15</sup> To further minimize the irreversible photocatalytic decomposition of MB, the solution is kept at slightly acidic condition (pH =  $\sim$ 4) to limit the formation of oxidative hydroxyl radicals (E = 2.80 V vs normal hydrogen

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electrode), which are generated by the reaction of the holes either with the hydroxyl groups on the oxide surface or with water favorably at higher pH.<sup>20–22</sup> Our unique synthesis involving a high-temperature hydrolysis reaction also enables carbon doping in  $TiO_2$  nanocrystals, which leads to considerable broad absorption in the visible range. The backward switching from colorless LMB to blue MB can thus be initiated by visible light irradiation of the  $TiO_2$  nanocrystals, and further completed by rapid self-catalytic oxidation of LMB by dissolved oxygen. The light-responsive color switching of the  $TiO_2$  nanocrystals/MB/water system can be repeated for more than 10 cycles with fully recovery, making them promising materials for possible light-driven actuating or color switching applications.

A typical synthesis of TiO<sub>2</sub> nanocrystals involves high temperature hydrolysis of TiCl<sub>4</sub> with NH<sub>4</sub>OH as a catalyst, poly(ethylene glycol)-b-poly(propylene glycol)-b-poly(ethylene glycol) (P123) as a surfactant, and diethylene glycol (DEG) as a polar solvent. Introduction of NH4OH provides water and also increases the alkalinity of the reaction system, both favoring the controlled hydrolysis of TiCl<sub>4</sub>. Heating the mixture at 220 °C for 3 h produces colloidal TiO<sub>2</sub> nanocrystals. As shown in a representative TEM image in Figure 2a, these nanocrystals are small particles with elongated shape and an average size below ~5 nm. A low-magnification TEM image is also included in the Supporting Information as Figure S2. No obvious precipitation can be found even after keeping the nanocrystals in the aqueous solution for six months, demonstrating an excellent dispersity in water. The crystalline structure of the TiO<sub>2</sub> nanocrystals was confirmed by X-ray powder diffraction (XRD) analysis (Figure 2b), with all diffraction peaks being indexed to anatase phase with cell constants of a = 3.7852 Å and c = 9.5139 Å (JCPDS card no. 21-1272). The diffraction peaks are significantly broadened, indicating low crystallinity and small sizes of the products. The absorption spectrum of TiO<sub>2</sub> nanocrystals shown in Figure 2c exhibits a strong absorption from 250 to 375 nm with a broad shoulder extending from 375 to 700 nm. The absorption shoulder in the visible range is consistent with the light-brown color of a concentrated solution of the TiO<sub>2</sub> nanocrystals (inset in Figure 2c), which is most possibly due to carbon doping from P123 and/or DEG during the high temperature hydrolysis reaction.23

We examined the response of the TiO<sub>2</sub> nanocrystals/MB/ water system to irradiation of UV and visible light. Upon irradiation with UV light under a 300 W Hg lamp equipped with a 365 nm filter (~ $8.2 \times 10^2 \,\mu w/cm^2$ ), the blue color of the nanocrystal dispersion disappeared completely in a short period of 10 s. To capture the change of absorption with irradiation time, we recorded the spectra under UV light with a decreased intensity (~0.5  $\times$  10<sup>2</sup>  $\mu$ w/cm<sup>2</sup>). As shown in the timedependent UV/vis spectra in Figure 3a,b, the absorption peak of the mixture at ~664 nm decreased in intensity with longer irradiation and eventually disappeared completely after 2.5 min of UV exposure. The absorption spectra of the colorless system fully recovered after 15 min of irradiation under visible light, in consistent with the recoloration of the solution from colorless to blue (inset in Figure 3b). Throughout the process, the system remains a transparent dispersion without any aggregation. To evaluate the potential of the color switching system for practical applications, the decoloration and recoloration processes were repeated for 10 times by sequentially irradiating the TiO2 nanocrystals/MB/water

mixture with UV light for 10 s and then visible light for 15 min. As shown in Figure 3c, the recorded spectra nearly overlapped. Figure 3d plots the intensity of the main absorption peak at ~664 nm against 10 cycles of UV and visible light irradiation, further demonstrating the complete reversibility of color switching. Compared with previous reports,<sup>4,24</sup> our photoreversible color switching system was able to minimize the photodecomposition and demonstrated only a slightly reduced reversibility in 10 decoloration-recovering cycles. On the other hand, photodecomposition, although minimal, still occurred, which led to reduced reversibility over many cycles of reactions. Full recoloration can also occur if the UV-irradiated system was kept under laboratory ambient light, however with a substantially longer recovering time of 150 min (Figure S3). Again, decoloration and recoloration can be cycled more than 10 times. In addition, recoloration occurring under dark conditions needed much longer time (240 min, Figure S4). It is therefore clear that visible light irradiation can significantly promote the recoloration rate of the system (Figure S5).

Compared with the color switching system based on photoisomerization of chromophores, our  $TiO_2$  nanocrystals/MB/water system exhibits superior performance in terms of switching rates, reversibility, and repeatability. Additional advantages of our system for practical application may also include low toxicity, low cost, and low environmental impact, as both titania particles and MB have already been widely used in cosmetic, medical, and other industries.<sup>25,26</sup> Compared with organic chromophores, semiconductor titania nanocrystals also have superior photostability, orders of magnitude longer excited state lifetimes, electronic states, and associated optical properties that can be engineered by controlling the size, shape, and other characteristics during synthesis.<sup>27</sup>

To confirm the MB/LMB transition, liquid chromatography-mass spectroscopy (LC-MS) was used to analyze the mixture after UV irradiation (colorless) and the completely recovered sample after visible light irradiation (blue), with aqueous solutions of pure TiO<sub>2</sub> nanocrystals and MB in water as control samples. The results are shown in Figure 4. A series of peaks were observed in the LC-MS chromatogram for aqueous TiO<sub>2</sub> nanocrystals dispersion (Figure 4a), which were analyzed by mass spectroscopy and indexed to fragments



**Figure 4.** LC-MS chromatograms of aqueous solutions of (a)  $\text{TiO}_2$  nanocrystals, (b) MB, (c)  $\text{TiO}_2$  nanocrystals, and MB mixture after UV irradiation of 10 s (colorless state), and (d) mixture of  $\text{TiO}_2$  nanocrystals and MB after recoloration by visible irradiation (recovered blue state).

derived from surface bound P123 (Figure S6). Typical LC-MS chromatogram of MB dissolved in water displays three peaks (Figure 4b), which can be indexed to m/z of 256, 270, and 284 by mass spectroscopy (Figure S7), corresponding to azure A, azure B, and MB<sup>+</sup> (losing one Cl<sup>-</sup>), respectively.<sup>28,29</sup> Interestingly, the colorless and recolored samples displayed superimposable LC-MS chromatograms (Figure 4c, d), making it reasonable to conclude that negligible photodecomposition of MB occurred during the color switching process.

To further understand the recoloration process, the colorless  $TiO_2$  nanocrystals/LMB/water system were irradiated with visible light by passing a series of bandpass filters (fwhm 25 nm) for a defined period of time (30 min), and the corresponding UV-vis spectra are shown in Figure 5a.



**Figure 5.** (a) UV–vis spectra of recoloration process of a colorless  $TiO_2$  nanocrystals/LMB/water mixture upon irradiation using visible lights passing through different bandpass filters (fwhm 25 nm). Each irradiation lasts 30 min. (b) UV–vis spectra of a blue colored  $TiO_2$  nanocrystals/MB/water mixture initially purged with nitrogen for 20 min then followed by visible light irradiation for different amounts of time.

Interestingly, all of the light with bandpass filters at different wavelengths, such as 370, 400, 450, 500, 550, 600, 650, and 700 nm, leads to enhanced recoloration rate than the case of laboratory ambient conditions. A particular surprise is the enhanced recoloration rate from LMB to MB by using a bandpass filter of 370 nm, which seems to be contradictory to the observation of decoloration of MB by UV exposure. In fact, this is due to the UV driven photooxidation of LMB in the presence of abundant dissolved oxygen (Reaction 2), which has

been reported previously by following a photooxidative quenching mechanism:<sup>30</sup> LMB  $\rightarrow$  LMB\*; and then 2LMB\* +  $O_2 \rightarrow 2MB + 2OH^-$ , where \* denotes an electronically excited state. The important role of oxygen in this reaction has been confirmed by the fact that irradiation of LMB by using a bandpass filter of 370 nm, in the absence of oxygen resulted in no significant change in its color and absorption spectrum (Figure S8). Note that, when the system was irradiated with broad UV light produced by a powerful Hg lamp, the TiO<sub>2</sub> nanocrystals were excited, leading to predominant reduction of MB to LMB and subsequently no observance of backward photooxidation of LMB.

The enhanced recoloration rate by visible light can be attributed to self-catalyzed oxidation of LMB that is initiated by TiO<sub>2</sub> nanocrystals, which have an absorption shoulder in visible region. Although further exploration is required to understand their exact role in this recoloration process, it is reasonable to believe that the TiO<sub>2</sub> nanocrystals absorb visible light energy and then excite the LMB to LMB\*, which then reacts with dissolved oxygen to produce MB, in a way similar to the abovementioned photooxidative quenching mechanism under UV irradiation. When a small amount of MB molecules are produced, they strongly absorb visible light, transfer the energy to LMB molecules, and further promote their oxidation to MB, leading to a self-catalyzed oxidation reaction (Reaction 3) and subsequently rapid conversion of LMB to MB. Note that the self-catalyzed oxidation of LMB by MB under visible light is proposed for the first time by this work. In order to confirm this reaction mechanism, we prepared a LMB solution by reducing MB with ascorbic acid under visible light by following a procedure reported by Lee and Mills.<sup>30</sup> While the solution remained colorless under extended visible light irradiation, a small addition of MB solution to the system instantly initiated the recoloration process which proceeds to completion within seconds (Figure S9).

Clearly, the oxygen dissolved in the system again plays a key role in the conversion of LMB to MB under visible light. In the absence of oxygen, photooxidation of LMB cannot occur (Figure S8).<sup>19</sup> Instead, a reverse reaction of reduction of MB (Reaction 4) may take place. When an aqueous mixture containing TiO<sub>2</sub> nanocrystals and MB was purged with nitrogen to remove the dissolved oxygen, visible irradiation led to gradual disappearance of blue color, as shown in the time-dependent UV-vis spectra in Figure 5b, suggesting reduction of MB by photoelectrons generated from TiO<sub>2</sub> nanocrystals by visible irradiation due to their considerable absorption in visible region. We believe this process may also operate when oxygen is present, but it is much slower than the self-catalyzed oxidation of LMB to MB, leading to overall fast recoloration. Conversely, purging oxygen through the LMB solution by bubbling air can significantly enhance the recovering rate from LMB to MB, further demonstrating that oxygen dissolved in the system plays a key role in the recovering process (Figure S4b and 5d).

The four major reactions involved in the color switching process are summarized in Figure 1. Upon UV irradiation, the  $TiO_2$  nanocrystals are excited to produce oxidative holes  $(E^{\circ}(h^+) = +2.91 \text{ V})$  and reductive electrons  $(E^{\circ}(e^-) = -0.32 \text{ V})$  which are diffused to the surface of the nanocrystals. As the holes are captured by surface bound SED molecules including both P123 and its possible derivatives, the surviving photogenerated electrons reduce blue MB to colorless LMB  $(E^{\circ}(MB/LMB) = +0.53 \text{ V})$  by following Reaction 1. The



**Figure 6.** Photoreversible color switching of a  $TiO_2$  nanocrystals/RhB/water mixture upon UV and visible light irradiation: (a) UV-vis spectra of the decoloration process under UV irradiation. (b) UV-vis spectra of the recoloration process under laboratory ambient conditions. (c) UV-vis spectra of recoloration process under visible light irradiation. (d) The UV-vis spectra of a typical  $TiO_2$  nanocrystals/RhB/water system during three cycles of repeated UV and visible light irradiation.

tight binding of SED molecules to the TiO<sub>2</sub> nanocrystal surface benefits not only the rapid electron-transfer from TiO<sub>2</sub> to MB but also the high stability of the colloidal system, both favoring a high color switching rate. While photobleaching of MB is dominant during UV irradiation, the resulting LMB can be partially oxidized simultaneously into MB by dissolved oxygen through Reaction 2.<sup>30</sup> Under strong UV irradiation, Reaction 1 is however dominant as it is driven photocatalytically by excited TiO<sub>2</sub> nanocrystals. On the other hand, the recoloration process essentially involves the oxidation of LMB by dissolved oxygen, which however is very slow (150 min) under laboratory ambient condition. Visible light irradiation can dramatically enhance the recoloration rate by photocatalytic initiation of LMB to MB transition followed by a visible light-driven selfcatalyzed LMB oxidation (Reaction 3). A competing reverse reaction (Reaction 4) may exist during recoloration, thanks to the photocatalytic activity of carbon doped TiO<sub>2</sub> nanocrystals in the visible region. However, this reaction is substantially suppressed when the solution contains abundant  $O_2$  so that the overall reaction is predominantly the oxidation of LMB to MB (Reaction 3).

As pointed out previously, the cyclability of the photoelectrochromic system is mainly attributed to the relatively low photocatalytic activity of TiO<sub>2</sub> nanocrystals toward photodecomposition of the dye and the efficient hole scavenging by surface bound P123 as SED. For comparison, a simple aqueous mixture containing Degussa P25 TiO<sub>2</sub>, MB, and P123 was irradiated by UV light under laboratory ambient conditions (Figure S10). The blue color of the system disappeared totally after UV irradiation of 15 min. But after centrifuging for 5 min to remove TiO<sub>2</sub> particles, only a very weak absorption peak of MB at  $\sim$ 660 nm was observed, which did not change in intensity even after aging for another 7.5 h, indicating irreversible decomposition of the MB molecules.

The color switching scheme can be extended to other dyes which change colors based on redox reactions. For example, as shown in Figure 6, Rhodamine B (RhB), an important representative of xanthene dyes well-studied for its good stability as dye laser materials,<sup>31</sup> also exhibited reversible color switching by UV/visible light irradiation when it was mixed with TiO<sub>2</sub> nanocrystals. Upon UV irradiation, its absorption peak at ~556 nm decreased gradually in intensity and disappeared completely after 6 min (Figure 6a). Under ambient conditions, the absorption peak gradually recovered to ~75% of the original value after 15 h (Figure 6b). Further elongating the maintaining time to 24 h did not lead to apparent change in the absorption intensity. Similar to the case of MB, the recovering rate of RhB from leuco RhB (LRhB) can be significantly enhanced by visible light irradiation, with a full recovery in 55 min (Figure 6c). The longer light-responsive time of RhB in comparison to MB is consistent with its higher chemical stability. Also, unlike the MB system which allows more than 10 times of reversible color switching, full recovery becomes difficult for the RhB system after 3 cycles of reactions (Figure 6d).

In summary, we have demonstrated a photoreversible color switching system by integrating photocatalytic property of  $TiO_2$  nanocrystals with the redox-driven color change property of MB. This system can be rapidly switched from blue to colorless by UV irradiation and then back to original blue by visible light irradiation, and such color switching cycles can be repeated for more than 10 times. The decoloration process is dictated by

reduction of MB by electrons generated in  $TiO_2$  nanocrystals under UV irradiation, while the recoloration process is driven by visible light irradiation, which excites  $TiO_2$  nanocrystals and initiates self-catalyzed oxidation of LMB. In comparison to the previous color switching systems based on photoisomerization of chromophores, the current system has key advantages in lower production cost and environmental impact and significantly higher switching rate and cycling performance. We believe this photoreversible system can find potential use in many practical applications that require photoactuation and color switching, such as photorewritable papers, security features, and other information recording and displaying devices.

**Experimental Section.** Synthesis of  $TiO_2$  Nanocrystals. In a typical procedure, a mixture containing TiCl<sub>4</sub> (1 mL), P123 (0.6 g), NH<sub>4</sub>OH (1 mL), and DEG (20 mL) was heated to ~220 °C in air in a 100 mL flask with vigorous stirring, forming a transparent solution. The resulting mixture was kept at 220 °C for 3 h and then cooled to room temperature. A light-brown mud-like precipitate was obtained upon adding acetone and centrifuging at 11 000 rpm for 10 min. The product was washed several times with ethanol and acetone to remove residuals and then redispersed in water.

Color Switching Reactions. Typically, 1 mL of TiO<sub>2</sub> nanocrystals (~ 10 mg/mL), 100 uL of MB (2  $\times$  10<sup>-5</sup> M), and 24 mL of water were mixed in a 50 mL quartz cell. UV irradiation was performed under a UV lamp (300 W, Hg) equipped with a 365 nm filter in a commercial photoreactor system (Xujiang XPA-7). Visible light irradiation was carried out using a visible lamp (Utilitech-WL250CL4-L, 250 W, emission spectrum shown in Supporting Information, Figure S1). The concentration of MB in the system during the reactions was monitored by UV-vis spectrophotometry (HR2000CG-UV-NIR, Ocean Optics). For removing oxygen from the system, the quartz cell was sealed with a rubber cap and then continually purged with nitrogen for at least 20 min before irradiation. A control sample was made by mixing 10 mg of TiO<sub>2</sub> (Degussa P25), 100 uL of MB ( $2 \times 10^{-5}$  M), and 24 mL of water in a 50 mL quartz cell while keeping other conditions the same as the standard TiO<sub>2</sub> nanocrystals/MB/ water system.

#### ASSOCIATED CONTENT

#### **Supporting Information**

Additional experimental details, emission spectrum of the visible lamp, TEM image of  $TiO_2$  nanocrystals, plots of the percent of MB recovered from LMB, LC-MS chromatogram analyses, and UV–vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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### REFERENCES

- (1) Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. *Nature* **2007**, *446*, 778.
- (2) Evans, R. A.; Hanley, T. L.; Skidmore, M. A.; Davis, T. P.; Such, G. K.; Yee, L. H.; Ball, G. E.; Lewis, D. A. *Nat. Mater.* **2005**, *4*, 249.
- (3) Ohkoshi, S.; Tsunobuchi, Y.; Matsuda, T.; Hashimoto, K.; Namai, A.; Hakoe, F.; Tokoro, H. *Nat. Chem.* **2010**, *2*, 539.
- (4) Yao, J. N.; Hashimoto, K.; Fujishima, A. Nature 1992, 355, 624.
  (5) Liu, Y. D.; Han, X. G.; He, L.; Yin, Y. D. Angew. Chem., Int. Ed. 2012, 51, 6373.
- (6) Zhang, J. J.; Zou, Q.; Tian, H. Adv. Mater. 2013, 25, 378.
- (7) Pardo, R.; Zayat, M.; Levy, D. Chem. Soc. Rev. 2011, 40, 672.
- (8) Wang, M. S.; Xu, G.; Zhang, Z. J.; Guo, G. C. Chem. Commun. 2010, 46, 361.
- (9) Uno, S.; Dohno, C.; Bittermann, H.; Malinovskii, V. L.; Haner, R.; Nakatani, K. Angew. Chem., Int. Ed. 2009, 48, 7362.
- (10) Li, Y. N. A.; Urbas, A.; Li, Q. J. Am. Chem. Soc. 2012, 134, 9573.
  (11) Dong, H. L.; Zhu, H. F.; Meng, Q.; Gong, X.; Hu, W. P. Chem. Soc. Rev. 2012, 41, 1754.
- (12) Lohmann, F.; Ackermann, D.; Famulok, M. J. Am. Chem. Soc. 2012, 134, 11884.
- (13) Li, H.; Fahrenbach, A. C.; Coskun, A.; Zhu, Z. X.; Barin, G.; Zhao, Y. L.; Botros, Y. Y.; Sauvage, J. P.; Stoddart, J. F. Angew. Chem., Int. Ed. **2011**, 50, 6782.
- (14) Galagan, Y.; Su, W. F. J. Photochem. Photobiol., A 2008, 195, 378.
  (15) Yoneyama, H.; Tamura, H.; Toyoguch, Y. J. Phys. Chem. 1972, 76, 3460.
- (16) Lee, S. K.; Mills, A.; Lepre, A. Chem. Commun. 2004, 1912.
- (17) Lee, S. K.; Sheridan, M.; Mills, A. Chem. Mater. 2005, 17, 2744.
- (18) Mills, A.; Wang, J. S. J. Photochem. Photobiol., A 1999, 127, 123.
- (19) de Tacconi, N. R.; Carmona, J.; Rajeshwar, K. J. Electrochem. Soc. 1997, 144, 2486.
- (20) Takizawa, T.; Watanabe, T.; Honda, K. J. Phys. Chem. 1978, 82, 1391.
- (21) Matthews, R. W. J. Chem. Soc., Faraday Trans. 1 1989, 85, 1291.
  (22) Mills, A.; Belghazi, A.; Davies, R. H.; Worsley, D.; Morris, S. J.
- Photochem. Photobiol., A 1994, 79, 131.
- (23) Zhang, Q.; Lima, D. Q.; Lee, I.; Zaera, F.; Chi, M. F.; Yin, Y. D. Angew. Chem., Int. Ed. 2011, 50, 7088.
- (24) Ohko, Y.; Tatsuma, T.; Fujii, T.; Naoi, K.; Niwa, C.; Kubota, Y.; Fujishima, A. *Nat. Mater.* **2003**, *2*, 29.
- (25) Yin, Z. Y.; Wang, Z.; Du, Y. P.; Qi, X. Y.; Huang, Y. Z.; Xue, C.; Zhang, H. Adv. Mater. **2012**, 24, 5374.
- (26) Zhou, W. J.; Yin, Z. Y.; Du, Y. P.; Huang, X.; Zeng, Z. Y.; Fan, Z. X.; Liu, H.; Wang, J. Y.; Zhang, H. Small **2013**, *9*, 140.
- (27) Han, Z. J.; Qiu, F.; Eisenberg, R.; Holland, P. L.; Krauss, T. D. Science 2012, 338, 1321.
- (28) Warth, A.; Goeppert, B.; Bopp, C.; Schirmacher, P.; Flechtenmacher, C.; Burhenne, J. Virchows Arch. 2009, 454, 341.
- (29) Kim, S. J.; Ha, D. J.; Koo, T. S. Biomed. Chromatogr. 2014, 10.1002/bmc.3063.
- (30) Lee, S. K.; Mills, A. Chem. Commun. 2003, 2366.
- (31) Li, Y. X.; Lu, G. X.; Li, S. B. J. Photochem. Photobiol., A 2002, 152, 219.