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# "Dark Deposition" of Ag Nanoparticles on TiO<sub>2</sub>: Improvement of Electron Storage Capacity To Boost "Memory Catalysis" Activity

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Supporting Information

ABSTRACT: "Memory catalysis" (MC) studies have received appreciable attention recently because of the unique talent to retain the catalytic performance in the dark condition. However, the MC activity is still low owing to the relatively limited electron storage capacity of the present materials. Here, a TiO2@Ag composite was synthesized by a "dark-deposition (DD)" method, which is based on the electron trap effect of TiO<sub>2</sub>. Unlike traditional photodeposition (PD), an exploration of the morphology and chemical compositions of as-prepared samples shows that DD can inhibit the growth of Ag nanoparticles and the formation of Ag<sub>2</sub>O, which greatly improve the electron storage capacity. We further demonstrated that the maximum electronic capacity was in the order of TiO<sub>2</sub>@Ag-DD (1  $\mu$ mol/ mg) > TiO<sub>2</sub>@Ag-PD (0.35  $\mu$ mol/mg) > TiO<sub>2</sub> (0.11  $\mu$ mol/mg).



Moreover, the enhanced MC activity was confirmed by various degradation experiments. Especially, the use of  $TiO_2@Ag-DD$  as a round-the-clock catalyst for the degradation of multicomponent pollutants has also been achieved. This strategy opens a door for enhancing the MC activity and reveals that the coupling of photocatalysis and MC may provide a new opportunity for the continuous removal of pollutants in day and night. It also may be extended to other fields, such as energy storage and continuous disinfection.

KEYWORDS: TiO<sub>2</sub>, Ag nanoparticles, memory catalysis, photocatalysis, dark deposition

# 1. INTRODUCTION

Most studies of photocatalysis are focused on the removal of contaminants under continuous irradiation.<sup>1,2</sup> However, when the illumination is stopped, the production of photongenerated carriers within the semiconductor is subsequently ceased, thereby making it catalytically inactive immediately. Thus, maintaining the catalytic performance without illumination has been a vital issue for more widespread applications of photocatalysis. Recent studies have confirmed the distinctive "memory catalysis" (MC) effect of photocatalysts, which can exhibit catalytic performance in the dark.<sup>4,5</sup> Li et al.<sup>4</sup> have provided an excellent example of this field, where PdO/TiO2 still retained short-lived catalytic activities after the light was switched off. They concluded that this phenomenon arose from the release of electrons trapped by PdO, which can react with O<sub>2</sub> to produce <sup>•</sup>OH radicals for conducting MC reaction. To date, several materials including TiO<sub>2</sub>/WO<sub>3</sub>,<sup>6,7</sup> TiO<sub>2</sub>/ CuO,<sup>8</sup> TiO<sub>2</sub>/SnO<sub>2</sub>,<sup>9</sup> I-doped TiO<sub>2</sub>,<sup>10</sup> Bi,<sup>11</sup> Se nanorod,<sup>12</sup> and C<sub>3</sub>N<sub>4</sub><sup>13</sup> have been found to exhibit MC effect. However, the current MC activities of these materials are still very low.

Recent studies have demonstrated that Ag and Au nanoparticles (NPs) possess a capacitive nature, which can trap electrons and discharge them to suitable electron acceptors.<sup>14,15</sup> Kamat et al.<sup>14</sup> explored the charge and discharge behavior of  $M/TiO_2$  (M = Ag, Au, and Pt) and demonstrated that  $Ag/TiO_2$  has the largest electron storage capacity among them. Choi et al.<sup>15</sup> also proved that Ag/TiO<sub>2</sub> could store electrons under UV illumination and then utilized them for reducing metallic ions in the dark. Hence, the capacitive nature and discharge behavior of Ag may also render its application for the MC reaction. As MC activity is mainly dependent on the number of trapped electrons during the preirradiation process, enhancing the storage capacity is the key to promote MC activity, which depends on the size and valence state of Ag NPs. Smaller-sized NPs were found to induce higher electron capacity within a certain size range.<sup>14</sup> Unfortunately, traditional

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photodeposition (PD) methods are unable to control the size and valence state of Ag NPs well. Lin et al.<sup>16</sup> observed that the size of Ag NPs increased with extending the illumination time and Li et al.<sup>17</sup> also made a similar conclusion. Moreover, a similar phenomenon was also observed in Pt NPs,<sup>18</sup> which could be ascribed to the cocatalytic effect of metal NPs.<sup>19</sup> Note that traditional PD methods usually lead to the coexistence of Ag and AgO or Ag<sub>2</sub>O in the composite,<sup>20,21</sup> which is unfavorable for electron storage. Although there are several alternatives, such as impregnation,<sup>22</sup> atomic-layer deposition,<sup>23</sup> electrodeposition,<sup>24</sup> and chemical reduction,<sup>25</sup> these methods need rigorous operation conditions or expensive equipment. Thus, it is desirable to develop a new and facile strategy, which can effectively inhibit the growth of Ag NPs and the formation of Ag<sub>2</sub>O.

Actually, TiO<sub>2</sub> also has the ability of storing electrons because photogeneration electrons can be trapped at Ti<sup>3+</sup> sites under anaerobic conditions.<sup>26</sup> Although the phenomenon that TiO<sub>2</sub> can store electrons has been discovered, to the best of our knowledge, the utilization of this nature of TiO<sub>2</sub> as a method to control the size and valence state of Ag NPs has not been studied. In addition, the mechanistic understanding of MC and more possible applications for environmental purification are still limited. Choi et al.<sup>15</sup> synthesized Ag/ TiO<sub>2</sub> by PD methods and proved that it can be used for postillumination removal of metallic ions. However, they determined that this "electron storage effect" only worked well for Cr<sup>6+</sup> reduction and that its activities are still very low. Therefore, improving MC activity and finding more suitable applications have become a vital problem. This study aims to find a facile strategy to control the size and valence state of Ag NPs for improving the MC activity, revealing the MC mechanism of TiO2@Ag and probing more extensive applications for environmental remediation.

Here, "dark deposition" (DD) was proposed in this work. Because of the nonpersistent illumination and the uniformity of the Ti<sup>3+</sup> site, the trapped electrons can reduce Ag<sup>+</sup> into metallic Ag NPs in situ without growth and aggregation, thereby greatly improving the electron storage capacity. As expected, the result shows that Ag NPs in TiO<sub>2</sub>@Ag prepared by DD (TiO<sub>2</sub>@Ag-DD) have a smaller size (roughly 10 nm) with uniform distribution and exist almost without AgO or Ag<sub>2</sub>O in the composite, which has maximum electron capacity (about 1  $\mu$ mol/mg), higher than TiO<sub>2</sub> (about 0.11  $\mu$ mol/mg) and TiO<sub>2</sub>@Ag prepared by PD (TiO<sub>2</sub>@Ag-PD) (roughly 0.35  $\mu$ mol/mg). Moreover, the enhanced MC activities were demonstrated by various degradation experiments such as methyl orange (MO) photodegradation coupled with Cr<sup>6+</sup> dark reduction, MO-methylene blue (MB) photodegradation coupled with dark degradation, etc. All experimental results show that TiO<sub>2</sub>@Ag-DD exhibited a much preferable performance in both the photocatalytic process and the MC process compared with TiO<sub>2</sub> and TiO<sub>2</sub>@Ag-PD. Especially, multicomponent dye degradation under natural conditions (from 04:30 p.m. to 08:30 p.m. local time) and the influence of various inorganic ions are also studied in detail, considering the more practical applications. This study not only provided a new and facile strategy to improve the electron storage capacity of materials but also revealed that TiO<sub>2</sub>@Ag can be used as a capacitor-like catalyst for the MC reaction. Furthermore, this strategy may be extended to other fields, such as energy storage and continuous disinfection.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** All chemicals used, including commercial  $\text{TiO}_2$  (P25), anatase  $\text{TiO}_2$  (A-TiO<sub>2</sub>), silver nitrate (AgNO<sub>3</sub>), ethanol, potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), sodium bromate (NaBrO<sub>3</sub>), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), diphenylcarbazide (DPC), acetone, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), ammonium molybdate tetrahydrate (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, potassium iodide (KI), sodium hydroxide (NaOH), 5,S-dimethyl-1-pyrroline N-oxide (DMPO), MO, and MB, were analytical grade reagents and purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water (D.I. water) was prepared by the ULUPURE purification system.

**2.2.** TiO<sub>2</sub>@Ag Prepared by DD (TiO<sub>2</sub>@Ag-DD). A commercial TiO<sub>2</sub> (P25, 100 mg) was added into ethanol aqueous solution (100 mL, 10 %, v/v) in a quartz beaker and then sonicated for 30 min in the dark with continuous stirring. Under continuous UV irradiation for 5 h (300 W Xe lamp) under N<sub>2</sub> atmosphere, the TiO<sub>2</sub> suspension solution gradually turned blue. Then, when the light was turned off, a certain amount of AgNO<sub>3</sub> aqueous solution was added. After 30 min of sufficient dark reaction, the precipitates were washed with D.I. water several times and dried at 70 °C for 8 h.

**2.3.** TiO<sub>2</sub>@Ag Prepared by PD (TiO<sub>2</sub>@Ag-PD). A typical PD method was employed to prepare TiO<sub>2</sub>@Ag-PD.<sup>27</sup> Briefly, TiO<sub>2</sub> was added into ethanol aqueous solution (10 %, v/v). Then, a certain amount of AgNO<sub>3</sub> was added and then sonicated for 30 min in the dark with continuous stirring. After irradiation with a 300 W Xe lamp for 60 min, the precipitates were washed with D.I. water several times and dried at 70 °C for 8 h. Moreover, PD of Ag on TiO<sub>2</sub> (labeled as TiO<sub>2</sub>@Ag-PN) was also carried out under N<sub>2</sub> atmosphere by a similar method.

To identify the effect of the crystalline structure, the deposition of Ag on pure anatase  $TiO_2$  (A- $TiO_2$ ) was also performed using the above two different deposition methods (A- $TiO_2@Ag$ -PD and A- $TiO_2@Ag$ -DD) because commercial P25 is a mixture of rutile  $TiO_2$  and A- $TiO_3$ . The experimental condition was the same as that of P25.

**2.4.** MO Photodegradation Coupled with  $Cr^{6+}$  Dark Reduction (the L-MO/D- $Cr^{6+}$  System). The prepared catalyst (20 mg) was added into the MO aqueous solution (10 mg/L, 50 mL) in a quartz glass reactor. Then, the reactor was placed in a dark place with stirring for 30 min to reach an adsorption-desorption equilibrium between the catalysts and MO. After illumination with a 300 W Xe lamp for a period of time, the lamp was turned off, and subsequently,  $K_2Cr_2O_7$  was added into the suspension with continuous stirring during the whole reaction period. The samples were taken intermittently and separated through centrifugation (4000 rpm, 10 min) for further analysis.

**2.5. MO–MB Photodegradation Coupled with Dark Degradation (the LD-MO–MB System).** The photodegradation period is the same as that of the L-MO/D-Cr<sup>6+</sup> system. During the dark reaction period, the light is just turned off without adding any chemical reagent.

2.6. MO Dark Degradation with the Addition of Various Radical Initiators. The photodegradation period is the same as that of the L-MO/D- $Cr^{6+}$  system. MC was carried out by adding various radical initiators such as  $H_2O_2$ ,  $Na_2S_2O_8$ , and  $NaBrO_3$  (L-MO/D- $H_2O_2$ , L-MO/D- $Na_2S_2O_8$ , and L-MO/D- $NaBrO_3$  systems).

Unless otherwise indicated, all of the degradation experiments were carried out in a sealed reactor.

**2.7. Analysis.** The DPC method was used to measure the concentration of  $Cr^{6+,28}$  The concentrations of MO and MB were determined by the characteristic optical absorption at 465 and 664 nm, respectively, with a UV-vis spectrophotometer.  $H_2O_2$  was determined by the  $I_3^-$  method titration.<sup>29</sup> •OH and •O<sub>2</sub><sup>-</sup> were tested by electron spin resonance (ESR). Detailed experimental steps are provided in the Supporting Information.

**2.8. Characterization.** All of the characterization methods used in this experiment include X-ray diffraction (XRD, Rigaku, Smartlab), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, England), transmission electron microscopy (TEM, JEOL, JEM-2100F), UV–vis diffuse-reflectance spectroscopy (DRS, Cary 300,

# Scheme 1. Mechanism and Process of (a) DD and (b) PD



Figure 1. (a) XRD pattern of as-prepared samples. High-resolution XPS spectrum of (b) Ag 3d and (c) O 1s. UV–vis DRS spectra of  $TiO_2@Ag-DD$  (d) and  $TiO_2@Ag-PD$  (g) (1–4) corresponding to the increase in Ag content (0.1–0.7%) and 5–7 corresponding to 1, 1.2, and 2%, respectively; the Ag content was calculated from the amount of AgNO<sub>3</sub> (assuming that all Ag<sup>+</sup> is successfully deposited on  $TiO_2$ ). TEM (e,h) and scanning TEM (f,i) images of samples. (e,f)  $TiO_2@Ag-DD$ ; (h,i)  $TiO_2@Ag-PD$ .

Varian), photoluminescence (PL) (Hitachi F-7000), ESR (JES FA200), electrochemical measurements (CHI 660C electrochemical analyzer, CHI Inc., USA), surface photovoltage (SPV) spectroscopic measurement, and total organic carbon (TOC) analysis (TOC-VCPH/CPN, Shimadzu). The detailed description is provided in the Supporting Information.

## 3. RESULTS AND DISCUSSION

3.1. Mechanism and Process of DD. In addition to metal NPs, some other semiconductors can also trap electrons, such as TiO<sub>2</sub> and WO<sub>3</sub>, under anaerobic conditions.<sup>30,31</sup> The stored electrons can be used for the reduction of heavy metal ions in a postirradiation process.<sup>26</sup> On the basis of this principle, DD was proposed in this study. Under anaerobic conditions,  $TiO_2$ suspension solution (Figure S1a) could be charged and turn to blue (Figure S1b), which is characteristic of trapped electrons.<sup>32</sup> After turning off the light, the electrons trapped at the Ti3+ site can reduce Ag+ into metallic Ag NPs in situ; meanwhile, the blue TiO<sub>2</sub> suspension solution changed to orange (Figure S1c) and the color gradually deepened with the increase of Ag content (Figure S2). Ti<sup>3+</sup> also turned back to Ti<sup>4+</sup> because of the consumption of electrons. Ethanol was used as the sacrificial agent of the hole  $(h^+)$  in the reaction solution. To exclude the influence of ethanol for Ag NP

deposition, a control experiment was carried out (Figure S3). The original TiO<sub>2</sub> suspension added with ethanol and AgNO<sub>3</sub> in the dark condition could not cause successful deposition of Ag NPs. The result clearly reveals that the reduction of Ag<sup>+</sup> occurs from the release of stored electrons rather than the influence of ethanol. As the stored electrons are certain and there is no further generation of electrons, Ag NPs will uniformly cover the  $\mathrm{TiO}_2$  surface with a smaller size and will not grow further (Scheme 1a). On the contrary, a large number of electrons are produced continuously during the PD process. Once small Ag particles are formed, electrons will transfer into Ag particles quickly, leading to the growth of particles because of the cocatalytic effect of metal NPs (Scheme 1b).<sup>19</sup> Hence, Ag NPs on TiO<sub>2</sub>@Ag prepared by the DD method should have a smaller size compared with those prepared by the PD method, thereby storing more electrons.

**3.2. Size and Valence State of Ag NPs.** To compare the size and valence state of Ag NPs prepared by different methods, composition and morphology investigations of asprepared samples were carried out. XRD patterns of all samples exhibit similar diffraction peaks, which can be ascribed to the mixture of rutile  $TiO_2$  (little) and A-TiO<sub>2</sub> (main constituent)

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(Figure 1a).<sup>33</sup> However, no obvious characteristic peak of Ag can be detected in the TiO2@Ag-PD and TiO2@Ag-DD materials, which may be caused by the relative low content. Intriguingly, weak diffraction peaks at  $2\theta$  values of  $33.6^{\circ}$  and  $38.39^{\circ}$  in TiO<sub>2</sub>@Ag-PD materials appeared, which can be ascribed to the (100) and (011) planes of Ag<sub>2</sub>O (JCPDS no. 72-2108), respectively (Figure 1a, right panel).<sup>34</sup> This implied that not only Ag NPs but also Ag<sub>2</sub>O are formed during the PD process. Further insights into the chemical compositions and the valence of Ag were obtained by XPS analysis. The survey spectra in Figure S4 reveal the existence of Ag, O, Ti, and adventitious C in both TiO2@Ag-PD and TiO2@Ag-DD materials. Figure 1b shows the high-resolution XPS spectra for Ag 3d3/2 and Ag 3d5/2. These binding energies at 367.4 and 373.6 are ascribed to metal Ag, whereas the binding energies at 366.7 and 372.2 are consistent with the values reported for  $Ag_2O.^{19,34}$  The ratio of  $Ag^0/Ag^+$  in TiO<sub>2</sub>@Ag-DD is far greater than that of TiO2@Ag-PD (Table S1). The result demonstrated that Ag NPs prepared by the DD method are mainly in the form of metallic Ag compared with that by the PD method. Also, the O 1s peak at about 529.3 eV is assigned to  $Ag_2O_1^2$ which further confirms its existence in TiO<sub>2</sub>@Ag-PD (Figure 1c). As only metallic Ag NPs have electron storage ability, the appearance of Ag<sub>2</sub>O during the PD process is averse to MC. Note that TiO2@Ag-PD was prepared in air atmosphere. Nevertheless, TiO2@Ag-DD was prepared in N2 atmosphere. Thus, to exclude the influence of air during the preparation process, the PD of Ag on TiO<sub>2</sub> was also carried out under N<sub>2</sub> atmosphere (TiO<sub>2</sub>@Ag-PN). As shown in Figure S5a, the ratio of  $Ag^0/Ag^+$  in TiO<sub>2</sub>@Ag-PN is increased compared with that in TiO<sub>2</sub>@Ag-PD, indicating that Ag<sub>2</sub>O more easily forms in air atmosphere during the PD process. However, the ratio of Ag<sup>0</sup>/ Ag<sup>+</sup> in TiO<sub>2</sub>@Ag-PN was still much lower than that in TiO<sub>2</sub>@ Ag-DD (Table S1). This means that it is impossible to completely inhibit the formation of Ag<sub>2</sub>O by simply removing air and that the DD method is more superior than the PD method. XRD patterns of TiO2@Ag-PD and TiO2@Ag-PN exhibit similar diffraction peaks, which suggest that air has no influence on the crystalline structure of the final sample (Figure S5b).

In addition to the valence of Ag, the size of Ag NPs also plays a vital role in electron storage. Because of the difficulty in determining the exact size of these Ag NPs, the UV-vis DRS was used to characterize it indirectly. As the mean diameter of the Ag NPs increased, the surface plasmon resonance peak (SPRP) will show a red shift.<sup>35</sup> Figure 1d presents the optical absorption spectra of TiO2@Ag-DD with various ratios. The absorption band edge of TiO<sub>2</sub> is about 410 nm. A new peak at 460 nm appeared in these spectra when Ag NPs were deposited on the surface of TiO<sub>2</sub>, which can be attributed to the SPRP of Ag NPs.<sup>36</sup> With the increase of Ag content, the position of the peak does not change significantly but has a slight blue shift. This suggests that there is no growth of Ag NPs with the increase of the Ag content. Generally, excess electrons can increase the plasma frequency of the metal.<sup>37</sup> Therefore, a slight blue shift of the SPRP of Ag NPs may arise from excess electrons stored within the Ag NPs. A higher silver content provides a greater possibility of capturing the electrons from  $TiO_2$ , which renders the slight blue shift of the SPRP of Ag NPs. From Figure 1e,f, it can be observed that Ag NPs (about 10 nm in average) were sparsely distributed on the surface of TiO<sub>2</sub> and without the aggregation phenomenon. However, the situation of TiO2@Ag prepared by the PD

method is exactly the opposite. The SPRP showed a significant red shift when the Ag content gradually increased, indicating the growth of Ag NPs, which greatly reduces their electronic storage capacity (Figure 1g). The TEM image (Figure 1h) also showed that a relatively large size of Ag NPs (about 20 nm) was obtained by the PD method and that they have an obvious agglomeration (Figure 1i). The PD experiment was also carried out in different reaction times (Figure S6). A similar red-shift phenomenon appeared but was more prominent, indicating the growth of Ag NPs over time, which confirmed the mechanism of PD discussed above. It is necessary to point out that because the speed of deposition by DD is fast, contrast experiments cannot be provided. Moreover, as shown in Figure S7a,b, no obvious size change can be observed in TiO<sub>2</sub>@Ag-PD and TiO2@Ag-PN, which demonstrated that air has no influence on the size of Ag NPs during the PD process. This suggests that the decrease in the size of Ag NPs results from different deposition methods, not air. It is worth noting that the absorbance of TiO<sub>2</sub>@Ag-PD in the 600-800 nm region is significantly increased compared with that of TiO2@Ag-DD (Figure 1d,g). This result implies that Ag<sub>2</sub>O gradually appeared during the PD process because its absorbance edge was greater than 800 nm (1.2 eV)<sup>38</sup> which is consistent with the XRD and XPS results. Considering that commercial P25 is a mixture of rutile TiO<sub>2</sub> and A-TiO<sub>2</sub>, to examine whether the same conclusion can be made in pure A-TiO<sub>2</sub> (Figure S8), A-TiO<sub>2</sub>@Ag-PD and A-TiO<sub>2</sub>@Ag-DD were also prepared in this study. As shown in Figure S9a and Table S1, the ratio of Ag<sup>0</sup>/ Ag<sup>+</sup> in A-TiO<sub>2</sub>@Ag-DD is far greater than that in A-TiO<sub>2</sub>@Ag-PD, indicating that Ag NPs in A-TiO2@Ag-DD are mainly in the form of metallic Ag compared with that in A-TiO<sub>2</sub>@Ag-DD. Similarly, compared to A-TiO2@Ag-PD, the size of Ag NPs in A-TiO<sub>2</sub>@Ag-DD is much smaller (Figure S9b,c). This result clearly demonstrated that the same conclusion can be made if only A-TiO<sub>2</sub> was used in this work. To sum up, TiO<sub>2</sub>(a)Ag-DD resulted in smaller-sized Ag NPs and a less amount of Ag<sub>2</sub>O exists during the deposition process compared with TiO<sub>2</sub>@Ag-PD. The detailed comparison of the two methods can be found in Table S2. Moreover, the same conclusion can also be made when pure A-TiO<sub>2</sub> was used in this work.

**3.3. Electron Storage Capacity Estimates.** To directly compare the electron storage capacity of different samples, MB titration experiments were carried out.<sup>14</sup> As a portion of the electrons was captured by Ag or TiO<sub>2</sub> during UV irradiation (under anaerobic condition), these electrons can be released to the appropriate electron acceptor in the absence of light. MB as a good electron acceptor (the absorption peak at 655 nm) can receive one electron from the catalyst to form MB<sup>-•</sup> and then rapidly convert to a colorless dye, MB<sup>2-</sup> (eqs 1–3).

$$\text{TiO}_2(e^-) + \text{MB} \to \text{TiO}_2 \to \text{MB}^{-\bullet}$$
 (1)

$$\text{TiO}_2 @Ag(e^-) + MB \rightarrow \text{TiO}_2 @Ag \rightarrow MB^{-\bullet}$$
 (2)

$$2MB^{-\bullet} \to MB^{2-} + MB \tag{3}$$

As  $MB^{2-}$  is colorless, any absorption at 655 nm cannot be observed. With continuous titration of MB, the trapped electrons in the TiO<sub>2</sub>@Ag-DD system are gradually consumed. Once all the electrons are depleted, further titration of MB will arouse an abrupt increase in the absorption at 655 nm (Figure 2). As total consumption of MB was estimated to be 10  $\mu$ mol, the electrons stored in the TiO<sub>2</sub>@Ag-DD system correspond to 20  $\mu$ mol (namely, 1  $\mu$ mol/mg). Similarly, the electrons



Figure 2. UV-vis absorption spectra of  $TiO_2@Ag$ -DD titrating with MB. "a" presents the absorption spectra of  $TiO_2@Ag$ -DD before titrating and (b-m) correspond to the incremental addition of MB (10  $\mu$ mol/mL, 0.1 mL). The experiment condition is as follows: [TiO<sub>2</sub>@Ag-DD] = 0.4 g/L, anaerobic condition.

stored in the TiO<sub>2</sub>@Ag-PD and TiO<sub>2</sub> systems are estimated to be 0.35 and 0.11  $\mu$ mol/mg, respectively (Table S3).

3.4. Behavior of Carriers in the Charge and Discharge Process. Prominent carrier separation efficiency not only improves the photocatalytic activity but also enhances the electron storage capacity. Figure 3a shows the comparison of the steady-state PL spectra of the samples. An emission peak at 410 nm is caused by the interband transitions of carriers within  $TiO_2$ , which was applied to characterize the electron-hole recombination behavior.<sup>39</sup> The results indicated that  $TiO_2@$ Ag-DD has a higher carrier separation efficiency than TiO<sub>2</sub> and TiO<sub>2</sub>@Ag-PD. Moreover, SPV spectra were recorded to further reveal the recombination behavior of carriers.<sup>40</sup> As shown in Figure 3b, the strong SPV response peak around 300-360 nm can be attributed to the electron transition from valence band to conduction band of  $TiO_2$  ( $O_{2p} \rightarrow Ti_{3d}$ ).<sup>41</sup> It should be noted that the SPV response intensity of TiO2@Ag-DD is much stronger than that of TiO<sub>2</sub> and TiO<sub>2</sub>@Ag-PD, which signifies that a higher separation efficiency of photogenerated charges is achieved on the TiO2@Ag-DD hybrid. In addition, a broad SPV response between 360 and 800 nm was observed, which can be attributed to the superposition of the localized level of surface states.<sup>42</sup>

As mentioned above, Ag NPs have a capacitive nature, which can accumulate electrons during illumination (charge process) and subsequently discharge at metal—electrolyte interfaces. Hence, to monitor such a slow discharge behavior directly, Figure 3c shows the time-dependent curves of the photocurrent decay of the illuminated electrodes (TiO<sub>2</sub>, TiO<sub>2</sub>@Ag-PD, and TiO<sub>2</sub>@Ag-DD) after switching off the lamp. The photocurrent decay on the TiO<sub>2</sub>@Ag-DD electrode is greatly retarded compared with TiO<sub>2</sub>@Ag-PD and TiO<sub>2</sub> electrodes, indicating that some of the current remains on the TiO<sub>2</sub>@Ag-DD electrode even under dark condition, which could be a direct evidence of the discharge process. **3.5. Verifying the Formation of Reactive Radicals in the MC Process.** The MC activity mainly arises from the release of trapped electrons, which trigged the generation of  ${}^{\circ}O_{2}^{-}$  and  ${}^{\circ}OH$  radicals. Therefore, it is necessary to verify the formation of reactive radicals under the dark condition. Figure 4 presents the ESR spectra of TiO<sub>2</sub> and TiO<sub>2</sub>@Ag-DD



**Figure 4.** Time evolution of DMPO $-^{\bullet}O_2^{-}$  (a,b) and DMPO $-^{\bullet}OH$  (c,d) ESR spectrum for as-prepared samples. (a,c) TiO<sub>2</sub>@Ag-DD and (b,d) TiO<sub>2</sub>.

samples. After 10 min of UV irradiation, the strong characteristic peak DMPO $-^{\bullet}O_2^{-}$  signals were clearly observed, which demonstrates the formation of  ${}^{\bullet}O_2^{-}$  radicals by both TiO<sub>2</sub> and TiO<sub>2</sub>@Ag-DD under light illumination (Figure 4a,b). When the light was turned off, the four peaks associated with  $DMPO-{}^{\bullet}O_2^{-}$  adducts could still be distinguished for TiO<sub>2</sub>@Ag-DD (Figure 4a), but they completely disappeared for TiO<sub>2</sub> (Figure 4b). This result demonstrated that  $^{\circ}O_2^{-1}$ could be produced by TiO<sub>2</sub>@Ag-DD during the dark discharge process. Similarly, we also verified the formation of <sup>•</sup>OH radicals in the dark (Figure 4c,d). Note that weak DMPO-<sup>•</sup>OH adduct signals could be observed in TiO<sub>2</sub> after shutting off the light for about 5 min (Figure 4d). However, it decayed fast and disappeared after 10 min. Interestingly, TiO2@Ag-DD tested exhibited slower decay kinetics of DMPO-OH adducts than TiO<sub>2</sub> did (Figure 4c). This result indicates that more number of electrons in TiO2@Ag-DD may still remain when illumination is stopped, providing additional •OH to mitigate the decay of DMPO-•OH, which is consistent with a previous study.<sup>12</sup>



Figure 3. (a) PL spectra (excited wavelength: 300 nm), (b) SPV spectra, and (c) photocurrent test of as-prepared samples.



**Figure 5.** (a) Time graphs of the removal of MO under UV irradiation, followed by dark reduction of  $Cr^{6+}$ . (b) Contribution of each part for dark reduction of  $Cr^{6+}$  removal. (c) Photocatalytic degradation used by tested samples under both light illumination and dark condition toward MB. (d) MB photodegradation under light irradiation with the addition of AgNO<sub>3</sub> when the light is turned off. (e) Photocatalytic degradation of MB coupled with MC under anaerobic condition. (f–h) MO photodegradation and subsequent MC with the addition of various radical initiators. (f) L-MO/D-H<sub>2</sub>O<sub>2</sub> system; (g) L-MO/D-Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system; and (h) L-MO/D-Na<sub>B</sub>PO<sub>3</sub> system. The experiment condition is as follows:  $[TiO_2] = [TiO_2@Ag-DD] = [TiO_2@Ag-DD] = 0.4 g/L, [Cr<sup>6+</sup>] = 8.2 mg/L, [AgNO<sub>3</sub>] = 0.1 M, [H<sub>2</sub>O<sub>2</sub>] = [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = [Na<sub>B</sub>PO<sub>3</sub>] = 20 mM, and [MO] = [MB] = 10 mg/L.$ 

3.6. MC Performance. MO as a model pollutant was employed to test the photocatalytic activities of as-prepared samples. The optimized mass ratios (Ag content) of TiO<sub>2</sub>@ Ag-DD and TiO2@Ag-PD are 1.2 and 1.5 wt %, hereafter abbreviated as TiO2@Ag-DD and TiO2@Ag-PD, respectively (Figure S10a,b). It is notable that the apparent rate constant  $(k_{\rm MO, light})$  of TiO<sub>2</sub>@Ag-DD is always greater than that of TiO2@Ag-PD at the same Ag content (Figure S10b), which embodies the superiority of the DD method (detailed analysis is provided in the Supporting Information). To further investigate the MC activity of the samples, various model systems were proposed. First, MO (10 mg/L) photodegradation coupled with dark reduction of Cr6+ (the L-MO/D-Cr<sup>6+</sup> system) by as-prepared catalysts (TiO<sub>2</sub>, TiO<sub>2</sub>@ Ag-PD, and TiO<sub>2</sub>@Ag-DD) was carried out and is shown in Figure 5a. Among them, the photodegradation efficiency was in the order of  $TiO_2$ @Ag-DD >  $TiO_2$ @Ag-PD >  $TiO_2$ . After 90 min of illumination, the dark reduction of Cr<sup>6+</sup> was studied by adding 8.2 mg/L Cr<sup>6+</sup> into the reaction suspension. It is noted that the dark reduction efficiency of Cr<sup>6+</sup> was much higher with TiO<sub>2</sub>@Ag-DD (72%) compared with TiO<sub>2</sub> (8.5%) and TiO<sub>2</sub>@Ag-PD (12.2%) (Figure 5a, right panel). As mentioned above, TiO2@Ag prepared by the DD method has a smaller size and a little amount of Ag<sub>2</sub>O, which greatly improves the electron storage capacity, thereby boosting dark reduction activity. As shown in Figure 5a (right panel), the time-dependent curves of  $[Cr^{6+}]$  display two obvious regions, a rapid decrease regime (regime I) and a tardy decrease regime (regime II). We hypothesize that regime II mainly results from the reduction of electrons and regime I may be rooted in adsorption of the sample or chemical reduction by degradation intermediates of MO. To further examine whether the

reduction of  $Cr^{6+}$  results from the above reasons or not, control experiments were carried out. First, the adsorption removal of  $Cr^{6+}$  was evaluated for  $TiO_2$ ,  $TiO_2@Ag-PD$ , and  $TiO_2@Ag-DD$  (Figure S11a). The removal efficiency of  $Cr^{6+}$  by adsorption is nearly identical for all samples and quickly reached adsorption equilibrium (30 min). Then, the chemical reduction by MO oxidation intermediates was also confirmed (Figure S11b). The contribution of each part for dark reduction of  $Cr^{6+}$  is also provided in Figure 5b. This result powerfully demonstrated that  $TiO_2@Ag$  prepared by the DD method has a higher electron storage capacity, thereby exhibiting more superior dark reduction activity.

Second, because the stored electrons can react with O2 to produce  ${}^{\bullet}O_2^{-}$  and  ${}^{\bullet}OH$  radicals in the dark, they can be applied to the MC reaction (the LD-MO-MB system). As shown in Figure 5c, all samples show good performance toward MB photodegradation, with TiO<sub>2</sub>@Ag-DD exhibiting the greatest activity. After 30 min of illumination, the light was shut off and the experiments were carried out in the dark condition. All tested samples, except TiO<sub>2</sub>, exhibited an obvious catalytic performance, and TiO2@Ag-DD showed the greatest MC activity. A similar situation also appeared in the LD-MO system (Figure S12a). To further demonstrate that MC activity is derived from the reaction of releasing electrons with O<sub>2</sub>, control experiments were conducted. When the lights were turned off, AgNO<sub>3</sub> (the sacrificial agent for electrons) was added into the LD-MB system, but no MC activity could be observed (Figure 5d). The result revealed that the MC activity had arisen from the release of trapped electrons on Ag NPs. However, under the anaerobic condition (purging with  $N_2$ ), all tested samples show enhanced MC activity (Figure 5e). Especially, TiO<sub>2</sub> also exhibited weak MC activity, indicating

## Scheme 2. MC Reaction Mechanism



**Figure 6.** (a) Influence of various inorganic ions during photocatalytic degradation. (b) Photodegradation of the MO–MB mixture solution. (c) Comparison of single-component and multicomponent dye photocatalytic degradation. (d) Image of the MO–MB mixture solution degradation in the outdoor environment. (e) Removal of the MO–MB mixture solution in the outdoor environment. The experiment condition is as follows:  $[TiO_2@Ag-DD] = 0.4 \text{ g/L}, [Na_2S_2O_8] = 20 \text{ mM}, \text{ and } [MB] = [MO] = 10 \text{ mg/L}.$ 

that  $\text{TiO}_2$  can only store electrons under anaerobic condition because of oxygen competition. This also shows that Ag NPs can trap electrons even in the presence of dissolved oxygen (DO). It should be noted that enhanced MC activity is mainly due to the decoloration of MB resulted from the reduction of electrons (eqs 1–3) rather than degradation (Figure S12b). It is confirmed by the TOC result that the TOC removal rate is greatly reduced in the absence of DO (Figure S12c). Therefore, MC activity mainly occurs from the active radicals generated by the reaction of stored electrons with DO. TiO<sub>2</sub>@ Ag-DD shows the greatest MC activity and is more suitable for practical applications compared with TiO<sub>2</sub>@Ag-PD.

Finally, because the stored electrons can react with  $O_2$  to produce active radicals under dark condition, they may also be enabled to react with other radical initiators, thereby being applicable to MC. Herein, MC was carried out by adding various radical initiators such as  $H_2O_2$ ,  $Na_2S_2O_8$ , and  $NaBrO_3$ (L-MO/D-H<sub>2</sub>O<sub>2</sub>, L-MO/D-Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and L-MO/D-NaBrO<sub>3</sub> systems). The mechanisms of the above systems are based on the following reaction:<sup>43,44</sup>

$$H_2O_2 + e^- \to OH^- + {}^{\bullet}OH \tag{5}$$

$$S_2 O_8^{2-} + e^- \to S O_4^{2-} + {}^{\bullet}S O_4^{-}$$
 (6)

$$BrO_{3}^{-} + 2e^{-} + 2H^{+} \rightarrow {}^{\bullet}BrO_{2}^{-} + H_{2}O$$
 (7)

As shown in Figure 5f, after 45 min of illumination, the light was turned off and H<sub>2</sub>O<sub>2</sub> was added to continue the degradation of MO. As expected, TiO2@Ag-DD has the most remarkable MC activity, which may be ascribed to more electrons trapped by TiO<sub>2</sub>@Ag-DD, thereby producing more •OH for MC. The effect of  $H_2O_2$  could be excluded by control experiments as shown in Figure S13a. The addition of the same H<sub>2</sub>O<sub>2</sub> in dark conditions did not cause any change in the concentration of MO, indicating that the degradation caused by H<sub>2</sub>O<sub>2</sub> could be neglected. Strangely, we did not detect any signal of •OH radicals under such a condition (data not given). However, the concentration of H<sub>2</sub>O<sub>2</sub> is drastically reduced (Figure S13b), which could be attributed to stronger adsorption between the surface of TiO2 and H2O2, thereby forming Ti<sup>4+</sup> peroxide species.<sup>43</sup> As H<sub>2</sub>O<sub>2</sub> could not be degraded by MB and no OH radicals were detected in the solution, the MC activity may result from the formation of a surface-bound OH radical (\*OH<sub>bd</sub>), which also has a certain degree of oxidizing ability.<sup>45</sup> In the L-MO/D-Na $_2S_2O_8$  (Figure 5g) and L-MO/D-NaBrO<sub>3</sub> systems (Figure 5h), all samples exhibited outstanding MC activity, with TiO2@Ag-DD showing the greatest performance. Interestingly, in the L- $MO/D-Na_2S_2O_8$  system, the removal efficiency of MO with TiO<sub>2</sub>@Ag-DD (75.17%) in the dark is much higher than with TiO<sub>2</sub> (6.7%) and TiO<sub>2</sub>@Ag-PD (16.16%) (Figures 5g and S13c), indicating that TiO<sub>2</sub>@Ag-DD has a higher capacitance to produce more  ${}^{\bullet}SO_{4}^{-}$  radicals. In addition, the contribution of different free radicals to MO degradation is provided in Figure S13c. Among them,  ${}^{\bullet}OH$  and  ${}^{\bullet}SO_{4}^{-}$  radicals have excellent removal effect toward MO because of their strong oxidizing ability and no selectivity.<sup>46</sup> However, the oxidizing ability of  ${}^{\bullet}BrO_{2}^{-}$  is slightly weak compared with that of  ${}^{\bullet}OH$  and  ${}^{\bullet}SO_{4}^{-}$  radicals.<sup>44</sup> Therefore, from the perspective of practical applications, the L-MO/D-H<sub>2</sub>O<sub>2</sub> and L-MO/D-Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems show more superior activity.

**3.7. MC Reaction Mechanism.** The MC reaction mechanism was proposed based on the above experimental results and analysis. During the photocatalytic degradation process, excess electrons can be accumulated on metal NPs because of the capacitive nature of Ag NPs (charging). Subsequently, the trapped electrons can be discharged to suitable electron acceptors under the dark condition (discharging). The released electrons can react with  $O_2$ ,  $H_2O_2$ ,  $S_2O_8^{2-}$ , and  $BrO_3^{--}$  to produce active free radicals for the degradation of pollutants (Scheme 2). Coupling the photocatalytic and dark catalytic reaction may provide a possibility to achieve round-the-clock contaminant removal.

3.8. Simulation of Practical Applications. Generally, the actual sewage water involves various inorganic ions and some of them can remarkably interfere with the photocatalytic performance of catalysts.<sup>47</sup> A certain amount of Na<sup>+</sup>, K<sup>+</sup>, Cr<sup>6+</sup>,  $H_2PO_4^-$ , Cl<sup>-</sup>, and  $NO_3^-$  ions (Table S4) was added into MO aqueous solution to study the influences on the photocatalytic performance. As shown in Figure 6a, no obvious difference can be observed when NaCl, NaH<sub>2</sub>PO<sub>4</sub>, and KNO<sub>3</sub> were added compared with the blank experiment, indicating that Na<sup>+</sup>, K<sup>+</sup>,  $H_2PO_4^-$ , Cl<sup>-</sup>, and  $NO_3^-$  ions have no bad influence on the catalytic activity. However, the photocatalytic activity decreased sharply with the addition of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, indicating that  $Cr^{6+}$  seriously affected the activity of TiO<sub>2</sub>@Ag-DD. The study by Choi et al. indicated that Cr<sup>6+</sup> serving as an external charge recombination center can block the pathways of active free radical generation.<sup>15</sup> As Cr<sup>6+</sup> can reduce the photocatalytic activity, it is not appropriate to put Cr6+ and MO into one reactor. Thus, the L-MO/D-Cr<sup>6+</sup> system is a better choice. Coupling the photodegradation of MO with dark reduction, Cr<sup>6+</sup> reaction can effectively remove both MO and Cr<sup>6+</sup> with consumption of identical photon energy. Besides, real wastewaters usually contain diverse forms of contaminants and they often tend to interact with each other, making disposal more difficult. Photodegradation of the MO-MB multicomponent solution was performed to simulate and evaluate the actual performance of TiO<sub>2</sub>@Ag-DD. As shown in Figure 6b, the typical peaks of MB and MO decreased rapidly over time and completely disappeared after 30 min. The control experiment (single-component) was conducted and is shown in Figure 6c. It can be clearly observed that singlecomponent MO was only removed by 60% within 28 min, which is far below the multicomponent system. Note that MB is adsorbed preferentially by TiO2@Ag-DD and there is no adsorption of MO in the MO-MB mixture solution (Figure 6b). The reasons may be the electrostatic adsorption between negative  $TiO_2$  (isoelectric point, IEP = 6.25, PH > IEP)<sup>19</sup> and positive MB. As MB is absorbed on the surface of  $TiO_{2}$ , it may, as a photosensitive center, enhance the photodegradation of MO, which is also similar to previous reports.<sup>48</sup> The detailed mechanism can be found in Figure S14.

To explore a more widespread practicality, using TiO<sub>2</sub>@Ag-DD as a round-the-clock work catalyst for MO–MB mixture solution, degradation in a natural environment was further carried out. First, the removal of the MO–MB mixture solution was initiated under sunlight (afternoon, 04:30 p.m. local time). Then,  $S_2O_8^{2-}$  was added into the reaction system to continue the degradation of the MO–MB mixture solution when nighttime began (06:30 p.m. local time) (Figure 6d). As shown in Figure 6e, approximately 65 and 55% of MO and MB were removed at daytime, respectively. Interestingly, the residual MO and MB continue to be decomposed at night by the MC effect of TiO<sub>2</sub>@Ag-DD. This experiment revealed that the coupling of photocatalysis and MC may provide a new opportunity for the continuous removal of pollutants in day and night.

Finally, the stability of as-prepared catalysts should be tested, which is very important for practical applications. The reusability of  $TiO_2@Ag$ -DD was tested via multiple cycles of degradation experiments. As shown in Figure S15, no obvious decay of catalytic activity was found for  $TiO_2@Ag$ -DD after five cycles whether in the photocatalytic period or in the dark catalytic period. Moreover, the XPS spectra of the sample before and after the reaction were further investigated. As shown in Figure S16, there was no obvious change of the Ti 2p and Ag 3d peaks after the reaction. This result reveals that the present  $TiO_2@Ag$ -DD could be promisingly utilized in the long-term course of both photocatalysis and MC.

## 4. CONCLUSIONS

In summary, we demonstrated that DD can greatly improve the electron storage capacity to boost MC activity compared with that by PD. Significantly, the conception of the removal of the MO-MB mixture solution during both daytime and nighttime is presented and experimentally achieved. It undoubtedly enables a new perspective in exploring a roundthe-clock photocatalyst for more applications. Experimental results demonstrate that this method (DD) can inhibit the growth of Ag NPs and the formation of Ag<sub>2</sub>O, which induces larger electron storage capacity, thereby enhancing the MC activity. The present work provides new insights into the rational design of an efficient catalyst for MC. Note that the present work is only at a preliminary research stage, whereas the practical application might be impeded by numerous issues such as short MC reaction time. Further studies may find more adequate applications. For example, bacteria usually have strong environmental adaptability and reproductive ability. The MC effect may be used to restrain the increase of bacteria at night, and the survived bacteria can be killed by the photocatalysis effect of TiO2@Ag-DD in the next daytime. Thus, coupling the photocatalytic and MC effect may provide a possibility to achieve a continuous bactericidal effect.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b06076.

Analysis method and characterization of the samples; image of original  $TiO_2$ , blue  $TiO_2$ , and  $TiO_2@Ag-DD$ ; preparation of  $TiO_2@Ag$  in dark; control experiment of original  $TiO_2$  and blue  $TiO_2$  added with AgNO<sub>3</sub> under

anaerobic and dark conditions; XPS survey spectra of TiO<sub>2</sub>@Ag-PD and TiO<sub>2</sub>@Ag-DD; XPS spectrum and XRD pattern of TiO<sub>2</sub>@Ag-PD and TiO<sub>2</sub>@Ag-PN; photodeposition of Ag NPs on TiO<sub>2</sub> in different reaction times; TEM images of TiO<sub>2</sub>@Ag-PD and TiO<sub>2</sub>@Ag-PN; XRD pattern of A-TiO<sub>2</sub>; high-resolution XPS spectrum of Ag 3d in A-TiO2@Ag-DD and TiO2@Ag-PD and TEM images of TiO<sub>2</sub>@Ag-DD and TiO<sub>2</sub>@Ag-PD; photodegradation curves of MO and reaction kinetic constant curves of as-prepared samples; time profiles of Cr<sup>6+</sup> removal by adsorption on different samples and dark reduction; photocatalytic degradation of MO coupled with MC reaction, color change of MB, and removal rate of MB; influence of H<sub>2</sub>O<sub>2</sub> for removal of MO; mechanism of MB as a photosensitive center enhancing MO photodegradation; recycling test on the TiO2@Ag-DD sample for MO photodegradation and multivariate curve resolution; XPS spectra of Ti 2p and Ag 3d of the sample before and after the reaction; atomic ratio of Ag<sup>0</sup>/Ag<sup>+</sup> calculated by XPS; comparison of size and valence state of Ag NPs by different methods; and electron storage in different samples (PDF)

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#### Notes

The authors declare no competing financial interest.

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