

# Electro-induced hydrophilicity of hydrogen plasma bombarded Ag/TiO<sub>2</sub> nanostructure

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## Abstract

Electro-induced hydrophilicity of the Ag/TiO<sub>2</sub> nanostructure has been reported in this study. In this work hydrogen plasma bombarded Ag/TiO<sub>2</sub> nanostructure was created using a sequential process including chemical vapor deposition and plasma bombardment. X-ray diffraction and X-ray photoelectron spectroscopy were used to analyze structure and chemical states of the sample. The prepared Ag/TiO<sub>2</sub> heterostructure has enhanced visible-light-induced hydrophilicity comparing to pure TiO<sub>2</sub>. The electro-induced hydrophilicity of the samples was also examined by creating the comb like electrodes on the prepared Ag/TiO<sub>2</sub>. A super-hydrophilic surface was achieved by applying an electric bias voltage on the electrodes.

**Key words:** Nanostructures, Thin films, plasma, X-ray diffraction, Surface properties.

## 1. Introduction

Because of their photo-catalytic activity, chemical stability and mechanical hardness, titanium dioxide (TiO<sub>2</sub>) nanoparticles received much attention in recent years. Photocatalytic reactions of TiO<sub>2</sub> nanoparticles proceed under UV light radiation with photon energy greater than its band gap (3.20 eV) [1]. Antibacterial activity and self-cleaning property of the TiO<sub>2</sub> nanoparticles have been also studied [2,3]. It is very interesting that

TiO<sub>2</sub> nanoparticles show enhanced hydrophilicity beside their photocatalytic activities, even though the mechanisms are completely different [4].

One challenge, which has been studied [5-8], is shifting the materials absorption spectra from UV into the visible light region so the majority of the solar spectrum can be used as a light source. The large surface area of the porous nano-particulate films leads to increase light absorption efficiency and electron-hole generation [9]. On the other hand, system efficiency is limited by recombination of the electron-holes at the surface boundaries [10]. In recent years, the effects of dopants and deposited metals on photocatalytic activity of TiO<sub>2</sub> have been widely investigated [11-14]. It has been shown that usage of Ag in TiO<sub>2</sub> structure prevents the fast recombination of electron-hole pairs [11]. The recombination rate decreases by trapping the photo-generated carriers in Ag/TiO<sub>2</sub> composite.

In this study we have reported fabrication of Ag nanoparticles embedded in TiO<sub>2</sub> matrix with enhanced hydrophilicity. Formation of Ag/TiO<sub>2</sub> was carried out by a hydrogen bombardment system. Wettability of the fabricated Ag/TiO<sub>2</sub> nanostructure was measured under visible light. Also hydrophilicity of the obtained nanostructure under an applied electric bias voltage was examined in this work. The oxidation and reduction potentials of silver nanoparticles are low. Such behavior leads to an easy reduction and oxidation reaction within the Ag/ TiO<sub>2</sub> suitable for electrochemical application. We believe that electro-induced hydrophilicity of the Ag/TiO<sub>2</sub> nanoparticles can be attributed to the electrochemical activity of the Ag nanoparticles which leads to formation of OH<sup>-</sup> and increasing the wettability.

## 2. Experimental details

Fabrication process was started by cleaning the substrate by the standard Radio Corporation of America (RCA) method (NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub> : H<sub>2</sub>O solution with volume ratio of 1:1:5), rinsed in deionized water. Using an atmospheric pressure chemical vapor deposition (CVD) system TiO<sub>2</sub> layer was deposited on 2×2 cm<sup>2</sup> soda lime glass substrate at a temperature of 300°C [15]. TiCl<sub>4</sub> was used as the main precursor to form titanium dioxide. Argon gas was used for delivery of the solution from a bubbler into the chamber. Ar flow rates during the deposition were kept at 200 sccm.

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Oxygen was also introduced into the chamber by a separate inlet with flow rate of 400sccm. In this process 200 nm crystalline TiO<sub>2</sub> nano-structured layer was formed on the substrate. As contact metal for electro-induced activity, 300nm thickness of Ag layer was deposited on the TiO<sub>2</sub> coated substrate. Ag layer was then patterned by standard photolithography to obtain desired comb-like electrodes with spacing between the electrodes of 500 $\mu$ m and line width of 100 $\mu$ m. Photolithography was performed using a mercury lamp as UV light source, Shipely 1813 positive resist as photoresist. Ag electrodes were used for applying the voltage within the sample. Subsequently, a thin layer of Ag with a thickness of 20 nm was deposited on the prepared samples. Deposition of Ag layers were carried out by a physical vapor deposition system at a base pressure of  $3 \times 10^{-6}$  Torr and at temperature of 200°C. Deposition rate was kept at 3Å/s. System vacuum was performed by a rotary mechanical pump and diffusion pump. The prepared samples were then placed in the DC plasma bombardment system in the presence of H<sub>2</sub> at a pressure of 7 Torr. Hydrogen plasma was applied on the samples with a power density of 3W/cm<sup>2</sup> at a temperature of 350°C for 30 minutes to form Ag nano-islands. In the plasma bombardment process, accelerated ions of plasma transfer kinetic energy to the surface and the Ag grains are formed during plasma treatment.

Morphological investigation of the nanostructures was studied by a field emission scanning electron microscopy (FESEM). Phase formation and crystalline properties of the samples were characterized by an x-ray diffractometer 'XRD' (Philips PW 1130.90) in the  $2\theta$  range from 20° to 100° operating at 40 kV accelerating voltage and 40mA current. XRD analysis was carried out by Cu K $\alpha$  (1.54Å) x-ray source in grazing geometry.

The components of the structure were determined by X-ray photoelectron spectroscopy (XPS) using Gammatdata-scienta ESCA 200 hemispherical analyzer equipped with an Al K $\alpha$  (1486.6 eV) X-ray source.

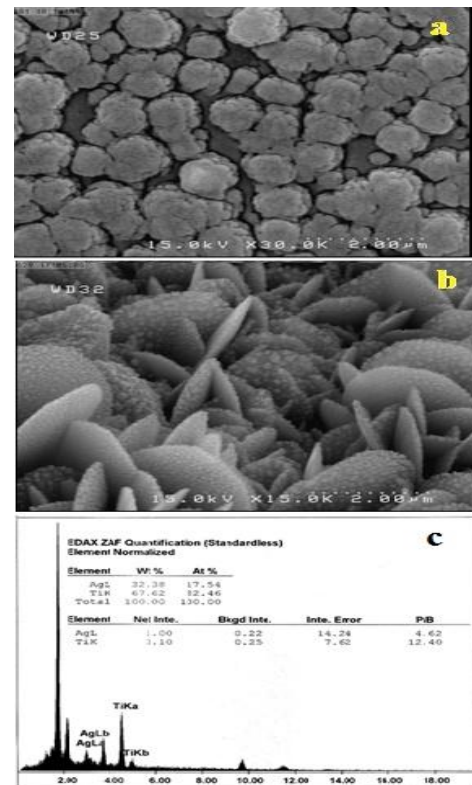
The wettability of the samples was evaluated by measuring the contact angle of distilled water. The picture of water drop on the surface was captured by a digital camera and imported to the measurement software (TESCAN Measurement) to measure the angle between the distilled water curve

and the sample surface. Contact angle was measured under a mercury lamp with maximum radiation at 365 nm wavelength as the UV source and halogen lamp as a visible light source. Irradiation power density of UV and visible light was 100mW/cm<sup>2</sup> at the sample position.

To investigate the effects of applied voltage on the hydrophilicity of the prepared Ag/TiO<sub>2</sub> nanostructures the contact angle measurement was carried out again by applying a voltage between the comb-like electrodes.

### 3. Results and discussion

Figure 1.a shows SEM image of the TiO<sub>2</sub> nanostructure on the glass substrate. As shown in this figure uniform cabbage-like nanostructures were formed on the substrate. Formation of Ag nanoparticles on the TiO<sub>2</sub> coated sample, after the hydrogen bombardment step, can be seen in SEM image of figure 1.b. The clearly observable spherical particles in this figure with a typical diameter ranging from 50 to 100nm are Ag

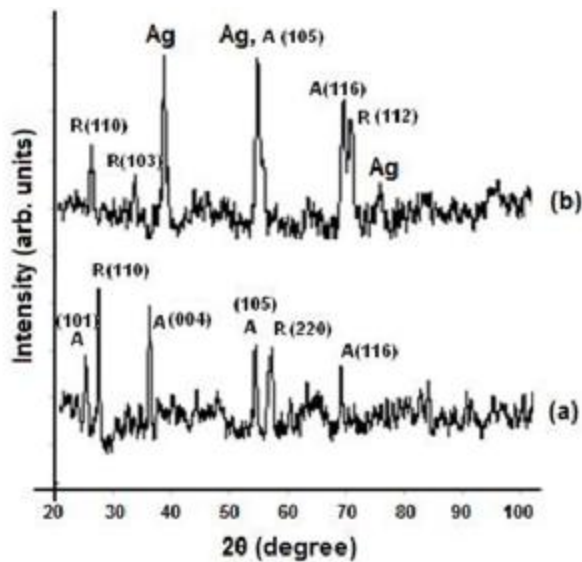


**Figure 1.** SEM images of the prepared TiO<sub>2</sub> nanostructures before (a) and after (b) the formation of Ag nano-particles. Part b demonstrates a magnified view showing the cabbage like TiO<sub>2</sub> coated by Ag nanoparticles. Part c is EDX analysis of the sample showing the presence of Ag nanoparticles on the TiO<sub>2</sub>.

nanoparticles on cabbage like TiO<sub>2</sub>. Part c of this figure is energy dispersive x-ray (EDX) analysis of the sample showing the presence of Ag nanoparticles on the TiO<sub>2</sub>.

To verify the structural characteristics of the Ag/TiO<sub>2</sub> nanostructure XRD analysis was carried out. Figure 2 shows the XRD results of the prepared nanostructures. Curve (a) of this figure is the XRD result of the TiO<sub>2</sub> coated

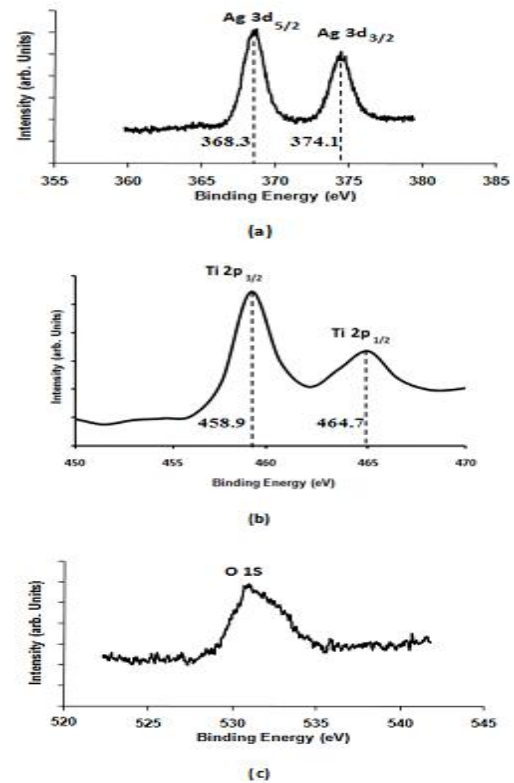
sample. The appeared peaks in this figure are associated with the crystalline planes of anatase and rutile phases of TiO<sub>2</sub>. Part b of this figure shows the XRD result of the sample after the formation of Ag nanoparticles. Some peaks associated with the crystalline planes of Ag can be seen in this figure indication the formation of Ag crystalline structure in the TiO<sub>2</sub> matrix. Peaks shift is clearly observed in the XRD results. We have reported in our previous work [16] that TiO<sub>2</sub> structure changes in the plasma treatment process. It may be due to atomic diffusion and recrystallization.



**Figure 2.** XRD patterns of the prepared TiO<sub>2</sub> nanostructures before (a) and after (b) the formation of Ag nano-particles. The peaks corresponding to anatase and rutile phases of TiO<sub>2</sub> are denoted by A and R, respectively. Numbers in parentheses indicate the orientation of crystal planes.

To investigate the chemical state of the Ag/TiO<sub>2</sub> nanostructure XPS analysis was utilized. Figure 3 shows high-resolution XPS spectra of Ag, Ti and O core level of the prepared Ag/TiO<sub>2</sub>. As can be seen from part a of this figure, the Ag(3d<sub>5/2</sub>) and

Ag(3d<sub>3/2</sub>) bands of the sample were found at binding energies of about 368.3 and 374.1 eV, respectively. The energy splitting value is 5.8 eV for the 3d doublet of Ag and can be attributed to formation of nonmetallic Ag nanoparticles [17], indicating the formation of Ag-Ti and Ag-O bonds. Such peak shift was reported in previous works [18].

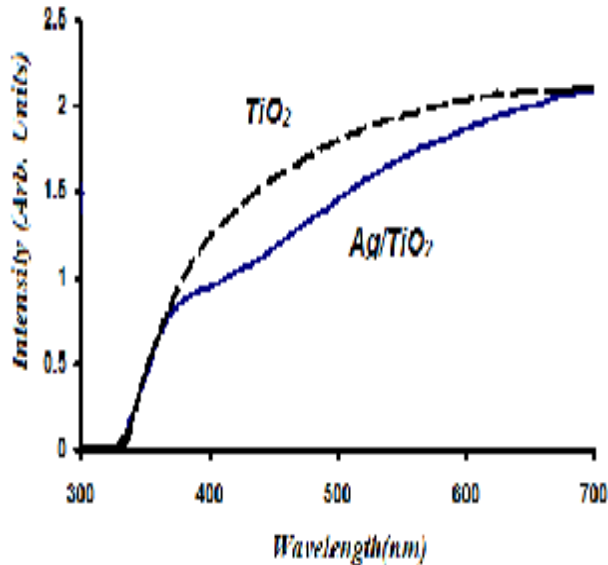


**Figure 3.** XPS spectra of a: Ag (3d), b: Ti(2p) and c: O(1s) core level of the Ag/TiO<sub>2</sub> nanostructure

The spectra of the Ti (2p) and O (1s) regions are shown in part b and c. The bands centered at binding energies of 464.7 and 458.9 eV were attributed to the Ti (2p<sub>1/2</sub>) and Ti (2p<sub>3/2</sub>) indicating a predominant state of Ti<sup>4+</sup>, respectively [18]. The slitting between bands which is found to be 5.8 eV in this result shows a bit difference comparing with the normal state of Ti<sup>4+</sup> in the anatase TiO<sub>2</sub> [19]. Part c of this figure shows XPS spectra of the O(1s) core level of the sample.

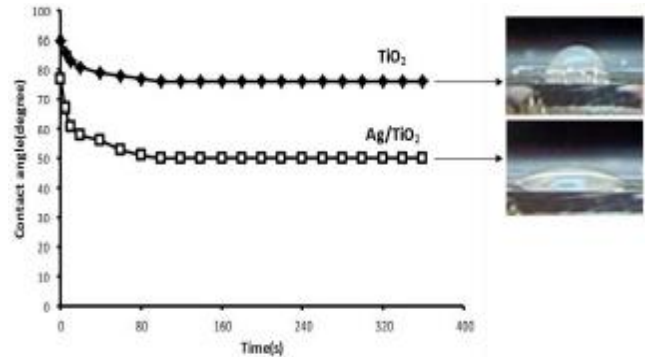
The photo-absorption ability of the Ag/TiO<sub>2</sub> nanostructure was compared with pure TiO<sub>2</sub>. Figure 4 represents the achieved results. As shown in this figure the transmission intensity of the Ag/TiO<sub>2</sub> decreases at wavelengths below the 600

nm. It shows that, increasing the visible light absorption leads to enhancement in photo induced hydrophilicity of the Ag/TiO<sub>2</sub> under the visible.



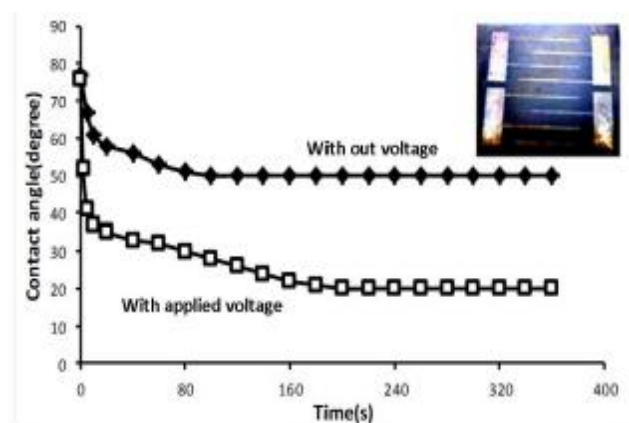
**Figure 4. a):** Transmission spectra of prepared TiO<sub>2</sub> and Ag/TiO<sub>2</sub> showing the photo-absorption of Ag/TiO<sub>2</sub> in the visible range.

Hydrophilicity of the prepared samples under visible light was evaluated by measuring the contact angle of distilled water on the sample surface. Figure 5 demonstrates the results of this measurement. This figure shows the contact angle of the water drop versus time on the TiO<sub>2</sub> layer and Ag/TiO<sub>2</sub> nanostructures. Substrate temperature during the irradiation is very important. We measured the substrate temperature during the irradiation. Measurement shows a 3°C increasing in the substrate temperature. As shown in this figure the Ag/TiO<sub>2</sub> nanostructure shows a significant activity under visible light while hydrophilicity of the TiO<sub>2</sub> layer does not change considerably under visible light. It means that Ag/TiO<sub>2</sub> can be excited under visible light. Visible light absorption by surface plasmon resonance of Ag nanoparticles is thought to induce electron transfer to TiO<sub>2</sub> resulting in charge separation and thus activation by visible light [20, 22]. Therefore, Ag-TiO<sub>2</sub> nanocomposites can be a promising material for visible light induced photocatalytic applications.



**Figure 5.** Contact angle measurement of distilled water on the TiO<sub>2</sub> and Ag/TiO<sub>2</sub> nanostructures under visible light exposure.

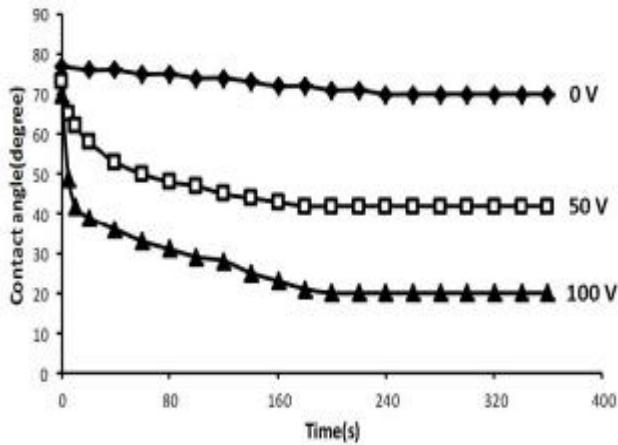
For investigation of the electro-induced activity of the fabricated structure 50 and 100V were applied on the Ag electrodes. Electric current between the electrodes was 150μA and 300μA, respectively. Figure 6 and 7 show the electro-induced wettability of the sample. Figure 6 shows a significant enhancement in visible light induced wettability of the Ag/TiO<sub>2</sub> by applying voltage between the electrodes. Inset in figure 6 is optical image of the sample containing the Ag electrodes. We believe that ionization ability of the Ag nanoparticles [23] is responsible for this enhancement. Ionization of H<sub>2</sub>O molecule on the nano-structured surface increases the



**Figure 6.** Contact angle measurement of distilled water on the Ag/TiO<sub>2</sub> nano-structure under visible light by applying 100V bias voltages on the electrodes.

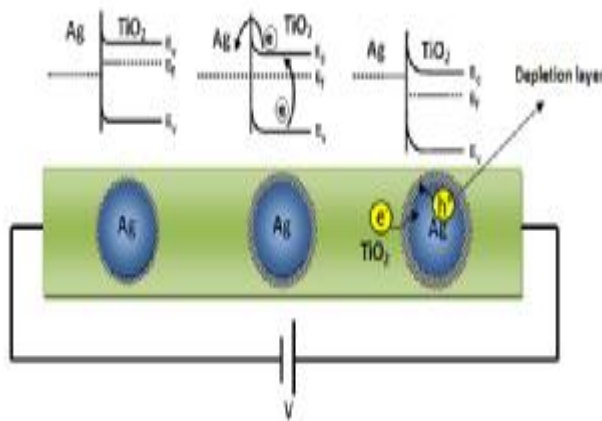
quantum efficiency of the photo-induced hydrophilicity [24]. Figure 7 represents contact angle measurement of Ag/TiO<sub>2</sub> in dark with

different applied voltage. Results confirm the electro-induced wettability of the prepared structure.



**Figure 7.** Contact angle measurement of distilled water on the Ag/TiO<sub>2</sub> in dark by applying different voltages showing the electro-induced hydrophilicity of the sample.

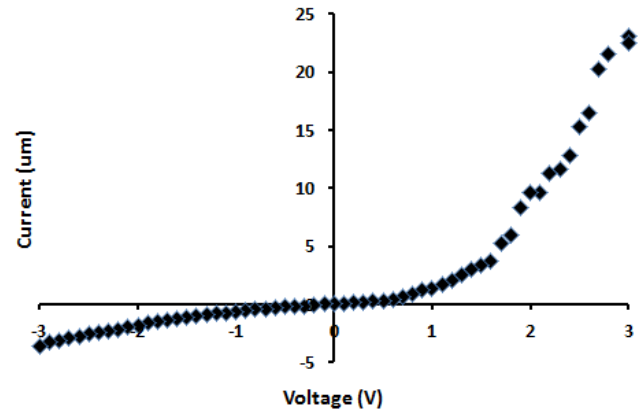
As schematically shown in Figure 8, formation of the Ag nano particles on the TiO<sub>2</sub> (as a semiconductor) allows formation of isolated Schottky barriers [25]. Schottky barriers serve as efficient electron traps to avoid electron-hole recombination leading to increase hydrophilicity of the surface. Electron-hole generation (accumulation of negative charges on the Ag nanoparticle surface and positive



**Figure 8.** Schematic of electro-induced electron-hole generation in the Ag/TiO<sub>2</sub> structure.

charges in TiO<sub>2</sub>) due to applied voltage in such Schottky nano-diodes is responsible for electro-induced hydrophilicity of the Ag/ TiO<sub>2</sub>. I-V

characteristic of the Ag-TiO<sub>2</sub> (shown in figure 9) confirms formation of Schottky junction.



**Figure 9.** Electrical characteristic of the Ag/TiO<sub>2</sub> heterojunction showing the Schottky junction related rectifying behavior.

Additionally, the deposition of metal nanoparticles onto the TiO<sub>2</sub> surface and hence the intimate interfacial contacts may lead to the formation of structural defects and trap states within the TiO<sub>2</sub> band gap [26]. Visible light absorption and visible light induced hydrophilicity of the Ag/TiO<sub>2</sub> may come from such structural defects and trap states.

#### 4. Conclusion

Ag/TiO<sub>2</sub> nanostructure was successfully grown on glass substrates. An atmospheric pressure cabbage-like nanostructure. Structural studies using CVD method was used to fabricate crystalline TiO<sub>2</sub> XRD confirmed formation of Ag and TiO<sub>2</sub> crystalline phases. XPS spectra showed the Ag(3d<sub>5/2</sub>) and Ag(3d<sub>3/2</sub>) bands of the sample at binding energies of 368.3 and 374.1 eV, which have a bit difference with typical core level of Ag(3d) (368.1 and 374.25 eV). Also the Ti (2p<sub>1/2</sub>) and Ti(2p<sub>3/2</sub>) bands are centered at binding energies of 464.7 and 458.9eV. Comparing with the typical core level of Ti (2p<sub>3/2</sub>) band at 459.1 a little shift is shown in this band. These little shifts in typical core levels of Ag (3d) and Ti(2p) indicate the diffusion of the Ag in TiO<sub>2</sub> structure. Due to this heterostructure formation photo-absorption intensity of the fabricated Ag/TiO<sub>2</sub> increased in the range of visible light wavelengths. Hydrophilicity of the Ag/TiO<sub>2</sub> was compared with the corresponding activity of pure TiO<sub>2</sub> as well. The tests under visible light showed that the

Ag/TiO<sub>2</sub> heterostructure has enhanced visible-light-induced hydrophilicity. The electro-induced hydrophilicity of the samples was also examined by creating the comb like electrodes on the prepared Ag/TiO<sub>2</sub>. Contact angle measurement in dark confirmed the pure electro-induced hydrophilicity of the sample. Enhancement in the hydrophilicity of TiO<sub>2</sub> using electric voltage encouraged us to use this approach in other applications based on catalytic activity of TiO<sub>2</sub> such as antibacterial, anti-fogging air and water purification.

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