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# Fast photo-induced color changes of Ag particles deposited on single-crystalline TiO<sub>2</sub> surface

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It is well known that surface-plasmon enhanced photo-electrochemical effect or photo-thermal effect of metallic particles on a semiconductor substrate or in a suspension may result in color changes. Such character could be potentially applicable to colorimetric sensors, optical filters, and data storage devices. However, usually the response time for color changes is too long to be practically applied. In this letter, we found that the response rate of color changes could be controlled by the annealing condition of the semiconductor substrate, and changes larger than 10% in spectra were observed after only 1-min exposure to light. Furthermore, such fast response was applied to realize wavelength-dependent “write” and “read” applications with high spatial resolution.

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Recently, using light to dynamically adjust the color of metallic particles<sup>1–17</sup> has captured great interest because of its potential applications to displays,<sup>3,6,16</sup> memories,<sup>2</sup> smart transmission windows,<sup>14</sup> etc. The mechanism of such a phenomenon has been revealed as the plasmon enhanced photothermal effect of metals<sup>2,3,6,14</sup> or the photo-electrochemical effect of metal-semiconductor composite materials.<sup>1,4,5,7–13,15–17</sup> For the photothermal effect, external incident light, always a femtosecond-pulsed laser of high intensity, is coupled to the plasmon mode to generate heat around the metallic structure. Such heat could not only heat up the surrounding medium, inducing vapor generation, but also change and even melt the structure itself, resulting in the dynamic color changes.<sup>18</sup> The advantages of this effect include high spatial resolution up to the micrometer scale<sup>2,6,14</sup> and realization independent of the substrate material or environmental medium.<sup>14</sup> Meanwhile for the photo-electrochemical effect, the external incident light, which is just incoherent, monochromatic, and of mild intensity, is coupled to the plasmon mode of metallic particles to generate hot electrons.<sup>1,4,5,7,19</sup> If the generated hot electrons could be transferred from the metallic particles to the surrounding semiconductor material, the particles would be partially oxidized and their size would be reduced, leading to color changes. Although the photo-electrochemical effect shows its obvious advantage of low intensity requirement of the incident light, its response time is too long to be applied practically. In this work, we found that the plasmon enhanced photo-electrochemical effect of metallic particles which leads to color change strongly relates with the properties of the surrounding semiconductor substrate. By annealing the semiconductor substrate, the properties such as the doping level and Schottky barrier could be manipulated, and then, under a suitable condition, the color change could be dramatically sped up.

Originally, the system is a rutile single crystal TiO<sub>2</sub> substrate on which there are some Ag particles deposited.

Photo-induced color changes of such a system, which are related to plasmon enhanced Ag oxidation on the TiO<sub>2</sub> surface, have been widely reported.<sup>5,16,17</sup> Obviously, the color change response is limited by the transfer rate of the plasmon-induced hot electrons from Ag to TiO<sub>2</sub>, which should be closely related to the properties of the TiO<sub>2</sub> substrate. In order to observe obvious spectral or color changes, dozens of minutes were required under light intensity of mW/cm<sup>2</sup> magnitude in the previous work.<sup>5</sup> In the present work, two kinds of TiO<sub>2</sub> single crystalline wafer [(110) surface and (111) surface] were used as substrates. The substrates were annealed either in vacuum or in air. It was found that the annealing condition of the TiO<sub>2</sub> single crystal substrate did dramatically influence the response rate of the photo-induced color changes of the system. In the fastest case, after only 1 min illumination of 6 mW/cm<sup>2</sup> monochromatic incoherent light, 20% change in extinction spectra was observed, about 5 times faster than the rate previously reported.<sup>5</sup> Moreover, due to such enhanced photo-induced color changes rate, using the spectral changes to “write” and “read” wavelength-dependent information in the micrometer scale was also demonstrated. These findings would be helpful in understanding and even controlling the photon-induced color changes of the metal-semiconductor system, which in turn would lead to many potential applications, such as data storage and certification/anticounterfeit technologies.

The size of the TiO<sub>2</sub> single crystalline substrates purchased (111 and 110) were 1 cm × 1 cm × 0.05 cm, on which the silver particles were deposited. The product manual informed that wafers with (111) surface had been annealed at 900 °C in air for 24 h before cutting from the single crystalline rod, due to the fact that the (111) plane is not the cleavage plane of TiO<sub>2</sub> crystal. Meanwhile, the wafers with the (110) surface were directly cut without any treatment. Both obtained (111) and (110) TiO<sub>2</sub> substrates were immersed in a mixture of aqueous 1 mol/l AgNO<sub>3</sub> and ethanol (1:1 by volume) and exposed to UV light of intensity

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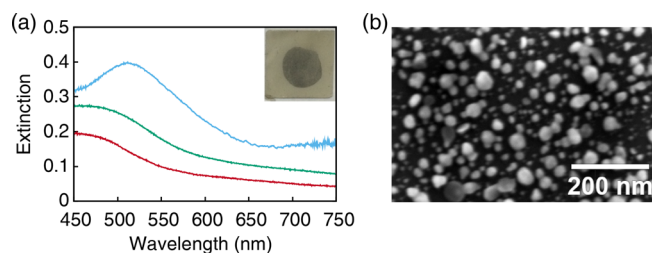


FIG. 1. (a) Visible extinction spectral changes during the deposition process of the Ag particles on the  $\text{TiO}_2$  (110) single crystal substrate ( $1\text{ cm} \times 1\text{ cm} \times 0.05\text{ cm}$ ) by UV light (325 nm;  $1.0\text{ mW/cm}^2$ ) irradiation for 1, 2, and 3 min (red, green, and blue curves). (b) SEM image of Ag particles on the  $\text{TiO}_2$  (110) substrate after UV irradiation of 3 min.

$1\text{ mW/cm}^2$  for 3 min. The electrons excited in  $\text{TiO}_2$  by the UV irradiation would reduce the Ag ions, resulting in the deposition of Ag particles on the  $\text{TiO}_2$  substrate.<sup>20</sup> Figure 1(a) shows typical changes of the extinction spectrum during the UV irradiation process. With the irradiating time increasing, a broad extinction peak around 525 nm appeared, corresponding to the plasmon resonances of the deposited poly-disperse Ag particles. Note that due to the existence of the conductive substrate, the coupling between metallic nanoparticles is different from that on insulated substrate. It deserves discussion in the future.<sup>21</sup> The SEM image of the deposited Ag particles is shown in Fig. 1(b). Similar results of this deposition process for different substrates were obtained.

The samples after Ag particle deposition were then immersed in a mixture of water and ethanol (1:1 by volume) and illuminated with monochromatic light. The monochromatic light was generated by a tungsten lamp with a narrow bandpass filter. The spectra of the incident monochromatic light for different center wavelengths are shown in Fig. 2.

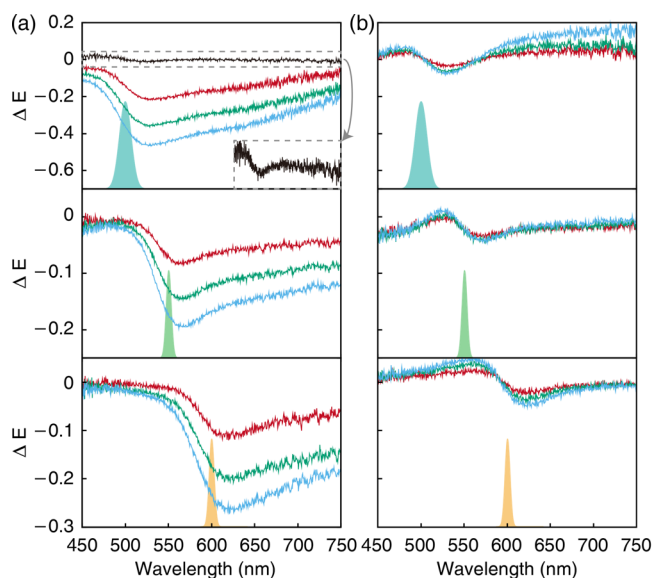


FIG. 2. Differential extinction spectra  $\Delta E(\lambda) = [E(t, \lambda) - E(0, \lambda)]/E(0, \lambda)$  of Ag particles on the  $\text{TiO}_2$  single crystal substrate illuminated with monochromatic visible light (top panel: 500 nm,  $5\text{ mW/cm}^2$ ; middle panel: 550 nm,  $15\text{ mW/cm}^2$ ; bottom panel: 600 nm,  $15\text{ mW/cm}^2$ ) for (a) (110) surface and (b) (111) surface, respectively. The red, green, and blue curves correspond to 1-min, 2-min, and 3-min illuminations, respectively, with a water environment; the black curve corresponds to 5-min illumination without the water environment. The Gaussian-like profiles shown insets are the transmission spectra of band-pass filters for 500, 550, and 600 nm.

The intensity of the incident light depends on its center-wavelength, i.e., for a center wavelength of 500 nm, it is about  $5\text{ mW/cm}^2$  and for 550 nm and 600 nm, it is about  $15\text{ mW/cm}^2$ . In Fig. 2, two typical results corresponding to the  $\text{TiO}_2$  substrate with the (110) surface and the  $\text{TiO}_2$  substrate with the (111) surface are shown. For both the (110) surface [Fig. 2(a)] and the (111) surface [Fig. 2(b)], the photo-induced color changes were both observed but with a different response rate. The extinction was reduced around the wavelength of the incident light. For example, after the illumination of 550 nm monochromatic light on the sample with the (111) surface for 3 min, the extinction change appeared around 550 nm; and after the illumination of 600 nm monochromatic light on the same sample, the center-wavelength of the change of the extinction spectrum shifted to around 600 nm. Qualitative understanding of this photo-induced multicolor changes effect has been reported<sup>5</sup> and has been briefly mentioned in the introductory part of this paper (Fig. S1). Moreover, if the incident light is polarized, the extinction is also different between vertical and parallel polarization after illumination (see [supplementary material](#), Fig. S2).

In the past, the research studies were mainly concentrated on the influence of the plasmonic properties of the metallic particles. Clearly, this complicated process should be related not only with the silver particles, but also strongly with the properties of the semiconductor substrate. Indeed, as shown in Fig. 2, different  $\text{TiO}_2$  single crystal substrates showed remarkable different rates of the multicolor changes. After 3 min illumination of 500 nm monochromatic light (top panels of Fig. 3), the extinction change of the  $\text{TiO}_2$  substrate with the (110) surface reached about 40% while that of the  $\text{TiO}_2$  substrate with the (111) surface was only about 7%. A longer illumination time [see Figs. 3(a) and 3(b)] resulted in saturation of the extinction changes around 70% for the  $\text{TiO}_2$  substrate with the (110) surface, about 7 times larger than that of the  $\text{TiO}_2$  substrate with the (111) surface. For illumination with monochromatic light of other wavelengths, the results (see the middle and bottom panels of Fig. 2) lead to similar conclusions, indicating that by controlling the property of the semiconductor substrate, the photo-induced color changes can be speeded up, namely the effect can be enhanced. Recalling the  $900^\circ\text{C}$  annealing of the  $\text{TiO}_2$  substrate with the (111) surface, it is suggested that the annealing affects the properties of the  $\text{TiO}_2$  substrate and thus would play an important role on the photo-induced color changes.

To verify such inference, a series of comparative tests were conducted on the  $\text{TiO}_2$  substrates with (110) and (111) surfaces annealed at  $450^\circ\text{C}$  for 1 h with and without air, respectively. The results for the 500 nm monochromatic light illumination are shown in Fig. 3. Figure 3(a) shows the results of the  $\text{TiO}_2$  substrate with the (110) surface. The black line corresponds to the case of the  $\text{TiO}_2$  substrate with the (110) surface without annealing for comparison, which is in consistence with the results shown in Fig. 2(a). After annealing the  $\text{TiO}_2$  substrate with the (110) surface in air, the color change response rate dramatically decreased. With 10 min illumination, the extinction around the illumination wavelength changed from 70% to less than 20%. For the  $\text{TiO}_2$  substrate with the (111) surface, to avoid any

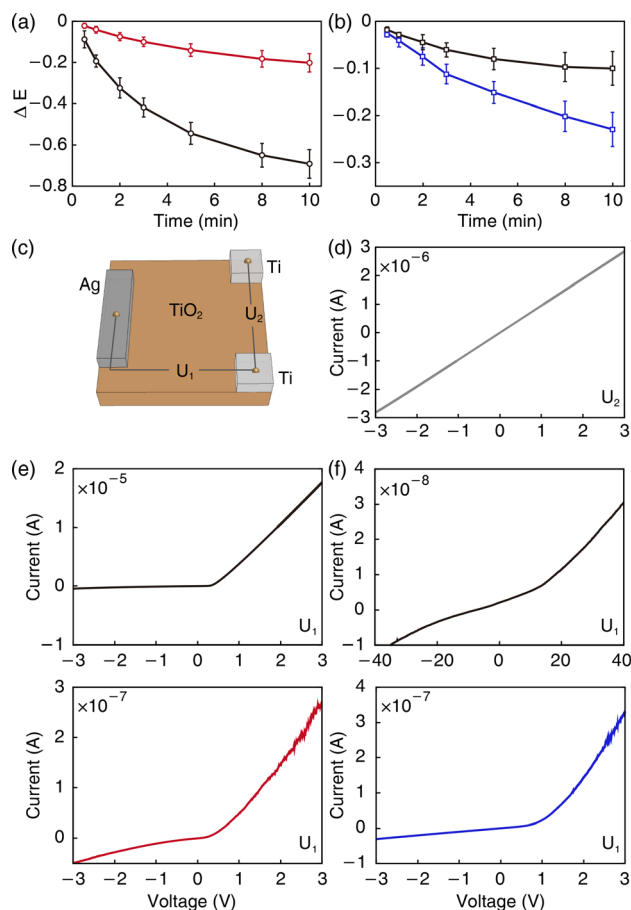


FIG. 3. Differential extinction  $\Delta E = [E(t, 500 \text{ nm}) - E(0, 500 \text{ nm})]/E(0, 500 \text{ nm})$  of Ag particles with the illuminating light of 500 nm at different times on the TiO<sub>2</sub> single crystal substrate for (a) (110) surface and (b) (111) surface, respectively. (a) Red curve: annealed in air at 450 °C for 1 h. (b) Blue curve: annealed in vacuum at 450 °C for 1 h. The black curves in both plots are for the samples unannealed. (c) Schematic configuration of the electrical transport measurement. (d) I-V characteristics of Ti/TiO<sub>2</sub>/Ti samples ( $U_2$ ). (e) and (f) I-V diagrams for the Ag/TiO<sub>2</sub>/Ti samples ( $U_1$ ). (e) Top panel: (110) surface unannealed; bottom panel (110) surface annealed in air at 450 °C for 1 h. (f) Top panel: (111) surface unannealed; bottom panel: (111) surface annealed in vacuum at 450 °C for 1 h.

degradation effects of pre-annealing treatment in air, it was annealed in vacuum. As expected, the photo-induced color change on the TiO<sub>2</sub> substrate with the (111) surface annealed in vacuum [shown as blue line in Fig. 3(b)] was sped up about 3 times faster than that of the TiO<sub>2</sub> substrate with the (111) surface [shown as the black line in Fig. 3(b)].

To further show the effects of the annealing process in detail, the electrical transport properties of the Ag-TiO<sub>2</sub> junction of different TiO<sub>2</sub> substrates under different annealing conditions were measured and the results are shown in Figs. 3(c), 3(e), and 3(f). The Ag-TiO<sub>2</sub> junction is surely important to the photo-induced colors changes effect. Due to the fact that it is difficult to directly measure the properties of the Ag particle-TiO<sub>2</sub> junction, several millimeter size Ag thin films was deposited on the top of the TiO<sub>2</sub> single crystal substrate by electron-beam evaporation to form the Ag-TiO<sub>2</sub> junction. It is assumed that the properties of the Ag thin film (35 nm) are similar to that of the Ag particles, and all the property changes of the junction would originate from different TiO<sub>2</sub> substrates. A schematic configuration of the electrical transport measurement is shown in Fig. 3(c). One electrode is the

Ag film itself deposited on the substrate while the other one is two Ti films deposited on the other side of the TiO<sub>2</sub> substrate. It is well known that the contact between Ti and TiO<sub>2</sub> is ohmic, as shown by the black line in Fig. 3(d). Four junctions made of TiO<sub>2</sub> single crystalline substrates with different surface planes and annealing conditions, i.e., the TiO<sub>2</sub> with the (110) surface without annealing [black line in Fig. 3(e) top panel], with annealing in air [red line in Fig. 3(e) bottom panel], the TiO<sub>2</sub> with the (111) surface without annealing [black line in Fig. 3(f) top panel], and with annealing in vacuum [blue line in Fig. 3(f) bottom panel], were measured. Most current-voltage (I-V) curves show rectification indicating Schottky contact. Two important conclusions could be derived from the results. First, the series resistance of the TiO<sub>2</sub> single crystalline substrate changed obviously, which is attributed to the amount of oxygen in the substrate changed during the annealing treatment. For the TiO<sub>2</sub> substrate with the (110) surface, the resistance of the TiO<sub>2</sub> substrate changed from  $\sim \text{M}\Omega$  to  $\sim 100 \text{ M}\Omega$  after annealing in air.<sup>22</sup> For TiO<sub>2</sub> substrate with the (111) surface, the resistance of the TiO<sub>2</sub> substrate changed from  $\sim 10 \text{ G}\Omega$  to  $\sim 0.1 \text{ G}\Omega$  after annealing in vacuum.<sup>22</sup> Considering the fact that the resistance of a semiconductor is related to the defects inside,<sup>23</sup> the oxygen environment during the annealing treatment could affect the amount of oxygen defects inside the TiO<sub>2</sub> substrate. The less the O<sub>2</sub> pressure is during annealing treatment, such as annealing in the vacuum, the larger the amount of oxygen defects would be inside the TiO<sub>2</sub>, and thus the decreasing the resistance.<sup>22,24</sup> Second, not only the series resistance of the TiO<sub>2</sub> substrate changed, but also the properties, such as the height and the width of the Schottky barrier of the Ag-TiO<sub>2</sub> interface, changed obviously with different annealing conditions.<sup>24–26</sup> For the TiO<sub>2</sub> substrate with the (110) surface annealed in vacuum, the contact between the Ag and TiO<sub>2</sub> even changed from Schottky contact to ohmic contact.<sup>24</sup> This observation is understandable and consists with previous observation as it has been reported<sup>24–26</sup> that the barrier properties of the metal-TiO<sub>2</sub> interface strongly related to the amount of oxygen defects inside the TiO<sub>2</sub>. Here, it is important to emphasize that because the observed photo-induced color changes happen on the interface of TiO<sub>2</sub> and silver particles, the reaction rate should mainly depend on the properties of the interface<sup>22</sup> rather than the bulk properties (such as the resistance) of the substrate. When the barrier is high, it should be difficult for the plasmons induced hot electrons emitting to the TiO<sub>2</sub> substrate, leading to a low reaction rate. On the contrary, a low Schottky barrier corresponding to the samples with high concentrations of oxygen defects, could speed up the reaction, as our experimental results shown. Therefore, according to the results shown in Figs. 2 and 3, it can be qualitatively concluded that by annealing the TiO<sub>2</sub> single crystal substrate in vacuum or air, the response rate of the Ag-TiO<sub>2</sub> composite photo-induced color change effect of the system could be modified, i.e., either increase or decrease. The results of the electrical transport experiments on the TiO<sub>2</sub> single crystal substrate revealed that, variation of the response rate may be related to the property changes of the Ag-TiO<sub>2</sub> contact, such as the height of Schottky barrier, while such properties could be adjusted by the condition of annealing treatment.



Taking advantages of the fast photo-induced color change response by using the  $\text{TiO}_2$  substrate with the (110) surface, it is suggested that this system could even be used as a platform to directly “write” information in micron-scale on the  $\text{TiO}_2$  substrate using light of mild intensity, as shown in Fig. 4. The information to “write” in is made as a mask shown in the top panel of Fig. 4(a). The mask is just put on the top of the Ag particle coated  $\text{TiO}_2$  (110) substrate. Both the mask and the substrate with silver particles were immersed in the mixture of water and ethanol. Monochromatic light, with a center wavelength of 500 nm and an intensity of around  $14 \text{ mW/cm}^2$  was directly shined on the mask for 5 min. Shown in Fig. 4(a), the size of mask is about tens of micron and the smallest feature size is about  $2.5 \mu\text{m}$ . As shown in Fig. 4(a), the pattern “FDU” on the mask [Fig. 4(a), top panel] was faithfully replicated on the  $\text{TiO}_2$  with (110) surface [see Fig. 4(b), bottom panel]. To quantitatively show the resolution of this “write” technology, the gray scale as functions of the position on a line of the image of the mask (red dashed lines) and on the same line of the image of the replicated pattern (green dashed lines) are shown in the middle panel of Fig. 4(a). The feature size of the replicated pattern is only about  $1.3 \mu\text{m}$  larger than that of the mask, indicating the high resolution of this “write” technique based on the photo-induced color change effect. Figure 4(b) shows one of the most important advantages of this writing technique, i.e., wavelength-dependent information reading. As shown in Fig. 4(b), the mask is the logo of Fudan University. After writing the information on the  $\text{TiO}_2$  substrate with the (110) substrate covered by silver particles with 500 nm monochromatic light, the images were read under monochromatic light with different center wavelengths [from 400 nm to 800 nm, corresponding to the panels shown in Fig. 4(b) from the top to the bottom]. Obviously, the “written” information is not viewable at the wavelength far away from 500 nm, but readable at the wavelength around 500 nm.

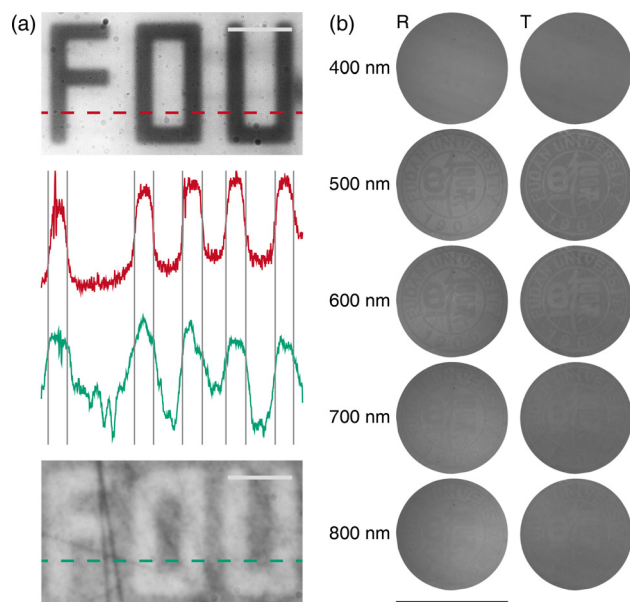


FIG. 4. (a) Images of the mask (top panel) and the replicated pattern (bottom panel). The data to the middle display slices through the two gray-scale images. Scale bar:  $10 \mu\text{m}$ . (b) Images in reflected and transmitted modes of the Fudan Logo made of Ag particles on the  $\text{TiO}_2$  single crystal substrate illuminated by light of different wavelengths. Scale bar:  $200 \mu\text{m}$ .

Therefore, due to the wavelength-dependent characteristic, this writing technique could be useful in the field of storage of confidential information.

In conclusion, the photo-induced color change effect of the system of silver particles deposited on  $\text{TiO}_2$  single crystal substrates is investigated in detail. It is found that the color change response rate is directly influenced by the properties of the  $\text{TiO}_2$  substrate, which is adjustable with different annealing treatments. A fast photo-induced color change effect, about 20% spectral change in extinction after only 1 min mild intensity ( $5 \text{ mW/cm}^2$ ) monochromatic light illumination, is observed on the sample of the  $\text{TiO}_2$  (110) surface substrate, which is several times faster than what was previously reported. Moreover, the present fast photo-induced color change effect could be applied to store confidential information at the micron-scale.

See [supplementary material](#) for figures of changes in the size distribution of Ag nanoparticles after illumination and polarized photo-induced color changes.

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