Boosted CO₂ reduction using ultra-thin TiO₂ photocatalyst films on nanocavities

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Abstract: We created an ultra-thin film photocatalytic light absorber (UFPLA) with 2~22-nm-thick TiO₂ films. The UFPLA structure conquered the intrinsic trade-off between optical absorption and charge carrier extraction efficiency and therefore boosted CO₂ reduction efficiency.

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Energy crisis and climate change are emerging global challenges for the 21st century. Photocatalytic conversion of carbon dioxide (CO₂)-to-hydrocarbon (CTH) fuels and chemicals, involving simultaneous greenhouse gas reduction, solar energy conversion and valuable fuel/chemical production, represents a viable and sustainable process to address these challenges [1]. Studies on photocatalytic CO₂ conversion have explored CO₂ reduction by water (H₂O) over semiconductor catalysts such as titania (TiO₂) [2, 3]. But the photoconversion efficiency is still too low to meet practical applications, mainly due to lack of materials with sufficient light absorption.

One promising scheme to enhance the optical absorption without sacrificing the catalytic activity in nanostructured catalysts would be to employ light trapping strategies on photocatalysts. Recently, planar thin film

interference in lossy ultra-thin layers attracted intensive interests [4, 5]. In this work, we will select the ultra-thin-film TiO₂ system as an example to implement this light trapping mechanism to enhance the optical absorption of ultra-thin TiO₂ films (down to ~2 nm). As illustrated in **Fig. 1a**, the ultra-thin film photocatalysis light absorber (UFPLA) is comprised of an aluminum (Al) reflector layer and an absorptive/photocatalytic TiO₂ ultra-thin film on top of the system that can interact with the external environment. We first modeled the optical absorption of this nanocavity system as the function of the thickness of TiO₂ films. One can see from **Fig. 1b** that strong resonant absorption peaks over 90% from 270 nm to 325 nm can be obtained in the optimized TiO₂ film thickness region of 12~19 nm. To validate this theoretical prediction, we prepared five ultra-thin TiO₂ films (with the thickness of 2 - 22 nm) on top of 150-nm-thick bare Al films and captured a photograph under the light at 365 nm (the inset in **Fig. 1c**). One can see that the reflection at 365 nm is lower for thicker TiO₂ films on Al reflectors. Their measured optical absorption spectra are shown in **Fig. 1e**, confirming the monotonically decreasing reflection at 365 nm (see the white dotted line). One can see that the optimized absorption peak occurred at the thickness of ~17 nm at the wavelength of ~310 nm, agreeing well with the theoretical prediction shown in **Fig. 1b**.

However, in most energy harvesting and conversion applications, there is a well-known trade-off between optical absorption and the carrier transportation efficiency: i.e., photo-generated carriers cannot be extracted efficiently if the film thickness is larger than the diffusion length of carriers because of carrier recombination. Therefore, a stronger optical absorption may unnecessarily result in an enhanced energy conversion efficiency. To reveal more details of optical absorption, the spatial absorption distributions at the absorption peak wavelength within 17-nm, 7-nm and 2-nm TiO₂ films were modeled using the finite element method (**Fig. 1d**). One can see that

Fig. 1 (a) Schematic of a two-layered UFPLA comprised of sequential photocatalytic/absorptive TiO₂ thin films and a bottom aluminum (Al) reflector layer. (b) Modeled and (c) measured total absorption spectra of TiO₂/Al as a function of the thickness of TiO₂. (d) shows the spatial absorption distribution in UFPLAs with different TiO₂ films. (e) shows the measured optical absorption spectra of different TiO₂ layers normalized by their thicknesses.

the optical absorption within the 17-nm-thick film is stronger at the top surface which decreases significantly towards the bottom side; while the optical absorption within thinner films are higher and more uniform along the vertical direction. To further reveal this thickness-dependent absorption (i.e., carrier generation), we normalized the optical absorption spectra with the film thickness (i.e., corresponding to the optical absorption per volume), as shown in **Fig. 1e**. One can see that thinner films generally produced more carriers over a given area, which should be another important factor in addition to the overall optical absorption.

To demonstrate the photocatalytic performance of these TiO₂ thin-films boosted by UFPLAs, CO₂ reduction over these five samples by H₂O were measured at 298 K. The product type and the product formation rate normalized to unit mass of TiO₂ catalyst after 4 hours of Xenon light irradiation are plotted in **Fig. 2a**. It shows that

the major product, methane, accompanied with minor amount of methanol and medium amount of formic acid were formed. To validate the high efficiency of UFPLAs in photocatalytic CTH, we employed the state-of-the-art TiO₂ catalyst (Aeroxide® P25, 0.02 g) to perform the same experiment for comparison. The reaction on Aeroxide® P25 catalyst produced sole methane product at a rate of $8.44 \times 10^{-4} \text{ mmol g}^{-1} \text{ h}^{-1}$. The thin-film TiO₂ catalysts in the UFPLAs were all much more active than Aeroxide® P25, although the activity monotonically decreased with increasing TiO₂ film thickness on the nanocavities. In particular, 2 nm- and 7 nm-thick-TiO₂ films had approximately 928 and 816 times higher productivity than that of the Aeroxide® P25 catalyst. However, the inconsistency between the product formation rates of UFPLAs in CTH reactions in **Fig. 2a** and the normalized optical absorption shown in Fig. 1e indicated that the light absorption is not the sole factor that affects the ultimate photocatalytic reaction efficiency.

The photocatalytic activity is closely correlated to the efficient charge carrier generation/transportation in the UFPLAs, which are reflected by the optical absorption intensity and charge carrier lifetime. The key fundamental question is how many photo-generated carriers can efficiently get involved in the photoreaction with CO₂ and H₂O molecules. According to ref. [6], the diffusion length of photo-generated carriers in TiO₂ films is very short (e.g. ~10 nm for holes in n-TiO₂ films). In this scenario, femtosecond transient absorption spectroscopy (fs-TAS) has been carried out to investigate the carrier dynamics for these TiO₂ films. As shown in **Fig. 2b**, we extracted the decay kinetics at 860 nm and plotted them as a function of TiO₂ thickness. The kinetic traces can be fitted bi-exponentially with less than 200 fs and ps time constants. The fs and ps time components can be assigned to surface and deep trapped states, respectively [7]. Interestingly, upon increasing the thickness of the TiO₂, the lifetime of the carriers decreases significantly. As can be clearly seen, decay time changes from 162 fs (fast) and 1311 ps (slow) to 123 fs (fast) and 377 ps (slow), respectively, as the TiO₂ thickness changes from 2 nm to 22 nm (as shown in **Fig. 2c**). This would mean that the photo-generated carriers within thinner TiO₂ films have longer lifetime, indicating the higher probability to flow to the surface and participate in photocatalytic reactions. Consequently, the 2~7-nm-thick samples are more efficient in normalized productivity per unit mass (**Fig. 2a**) due to the more efficient volume photogenerated carriers (**Fig. 1e**) and longer carrier lifetime (**Fig. 2c**).

In conclusion, the UFPLAs containing TiO₂ thin film catalysts were developed to target for photocatalytic CO₂ reduction with water to hydrocarbon fuels [8]. The structure overcomes constrains in weak light harvesting and low electron-hole pair separation efficiency in the current nano-structured semiconductor catalyst materials. This discovery indicates the potential to improve thin film catalyst photocatalytic performance using nanophotonic-managed light harvesting capabilities.

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