

Supplementary Material

Preparation, characterization and photocatalytic degradation properties of TiO₂/calcium alginate composite film and the recovery of TiO₂ nanoparticle

Kongyin Zhao^{1,2*}, Lingzhi Feng^{1,2}, Zhihui Li², Yifan Fu², Xinxin Zhang², Junfu Wei^{1*}, Shuxin Wei^{1,2}

¹ *State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, Tianjin 300387, China*

² *School of Material Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China*

*Corresponding authors: tjzhaokongyin@163.com, Tel.: +086-02283955362, Fax, +086 -0228395055; jfwei@tjpu.edu.cn, Tel.: +086-02283955898.

Figure captions

Fig. S1. Schematic representation for the recovery of TiO₂.

Fig. S2. Digital photos of T/CA-10% films with different thickness. (a) 0.10mm (b) 0.20mm (c) 0.30mm (d) 0.40mm.

Fig. S3. TGA of CA film and T/CA composite films with various TiO₂.

Fig. S4. Schematic diagram of mechanical tensile properties of T/CA film.

Fig. S5. UV scanning spectrum of MO solutions before and after photocatalytic degradation.

Fig. S6. HPLC of MO solutions before and after photocatalytic degradation.

2.8. Recovery of TiO_2 from T/CA film

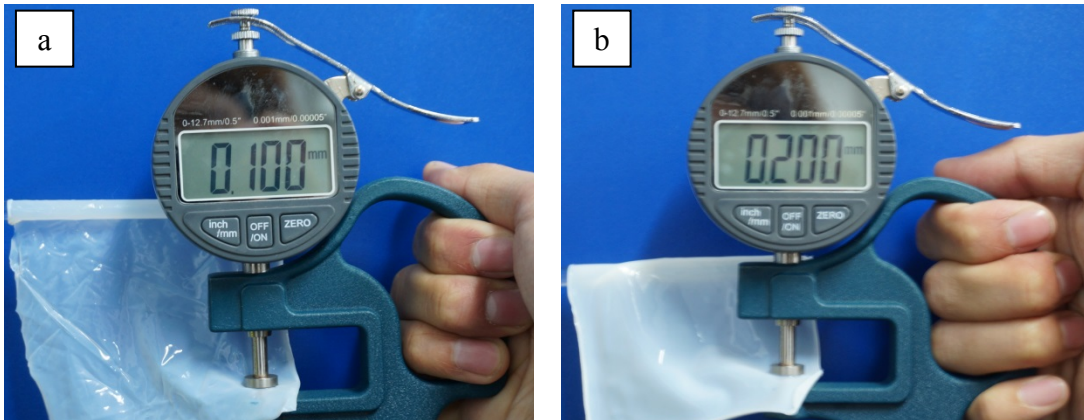
About 0.2g T/CA-10% composite film was placed in a small vial containing 10 ml 0.2 mol/L sodium citrate aqueous solutions, and then the vial was placed into the concussion incubator for 2 hours. After the composite film was completely dissolved, the mixture was centrifuged for 5min at 4000r/min. Subsequently the precipitation was rinsed with 0.1mol/L HCl and then dried at 60°C for 8 hours. Afterwards, the recovered TiO_2 powder was reused to prepare new composite film, whose degradation performance for MO was evaluated later. The schematic representation for the recovery of TiO_2 was presented in Fig. S1.



Fig. S1. Schematic representation for the recovery of TiO_2 .

3.2. Morphology of TiO_2 and T/CA composite film

Fig. S2 shows the digital photos of T/CA-10% composite film with different thickness. The T/CA-10% films were smooth and the thickness of T/CA-10% film could be easily controlled to 0.1-0.4mm. The transparency of T/CA-10% composite film decreased with the increase of the thickness.



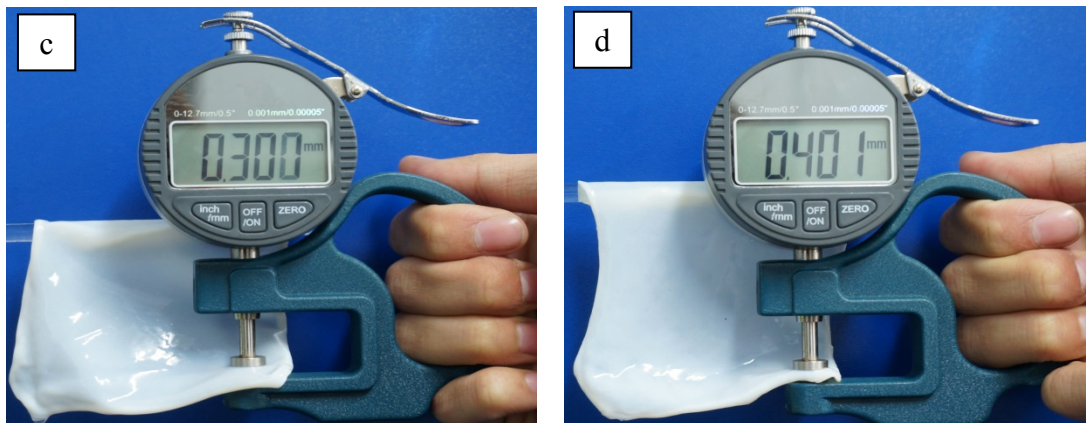


Fig. S2. Digital photos of T/CA-10% films with different thickness. (a) 0.10mm (b) 0.20mm (c) 0.30mm (d) 0.40mm.

3.5. TGA of T/CA composite film

Fig. S3. Shows the TGA of CA film and T/CA composite films prepared with different contents of TiO_2 . It is found that alginate has two pyrolysis stages, the first thermal degradation process occurred in the temperature range of 225-300 $^{\circ}\text{C}$. The weight loss in the first stage was attributed to the degradation of the carboxyl group, as CO_2 was released. The second stage occurred when the temperature was higher than 650 $^{\circ}\text{C}$, which was due to the depolymerisation of polymer and formation of a carbonaceous residue. The weight loss of T/CA in the first stage decreased, indicating the thermo stability was improved after the addition of TiO_2 .

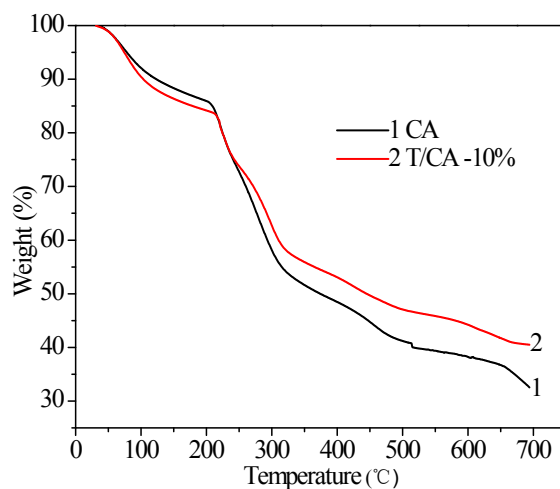


Fig. S3. TGA of CA film and T/CA composite films with various TiO_2 .

3.6. Mechanical properties of T/CA film.

Fig. S4 can illustrate the reason of the favorable mechanical performance of T/CA. Firstly, the abundant hydroxyl groups on the surface of TiO_2 can form hydrogen bonds with hydroxyl groups in SA to improve the mechanical properties of the composite film. Secondly, each alginate chain contains a large number of G blocks, many of which form ionic crosslinks with G blocks on other chains when Ca^{2+} ions are present. Calcium alginate hydrogel is similar to a "zipper" structure and the ionic bond is like the zipper connector [32]. A part of the alginate chain may crack and lose certain mechanical strength under ultraviolet irradiation. But the damage can be repaired by re-zipping because the ionic crosslinking between the G blocks and the other G blocks can form again. In addition, the photocatalytic

degradation mainly occurs on the surface of T/CA composite film and the internal materials can remain the same, so the mechanical properties of the T/CA films remained constant after ultraviolet irradiation.

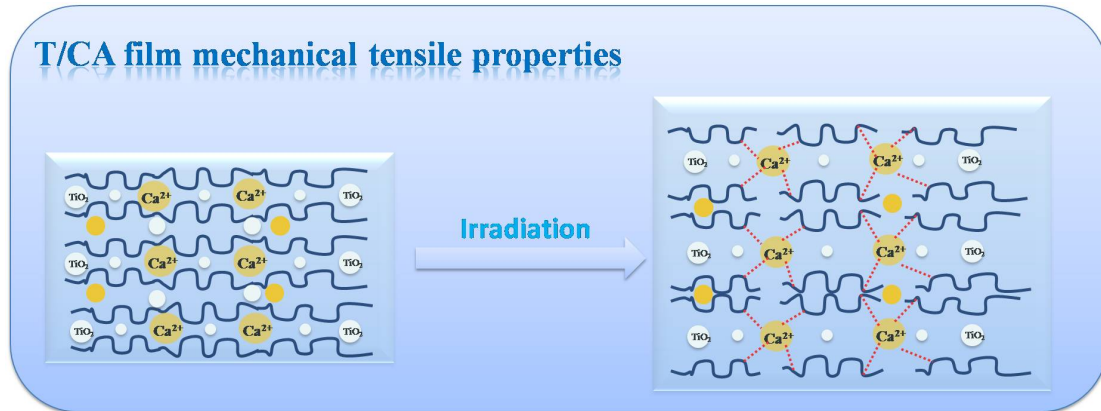


Fig. S4. Schematic diagram of mechanical tensile properties of T/CA film.

3.9. Test of HPCL

Fig. S5 shows the UV scanning spectrum of MO solutions before and after degradation by T/CA-10%. It can be seen that the absorption peak of MO almost disappeared after being degraded for 120 min.

Fig. S6 shows the HPLC peak height and peak area of MO solutions before and after degradation. According to the residence time of standard material, it can be judged that the adsorption peak at about 1.8 min was attributing to formic acid, and the peak basically remained constant. The peak height and peak area of MO after degradation were much smaller than those of MO before degradation, revealing that the photocatalytic degradation efficiency was favorable.

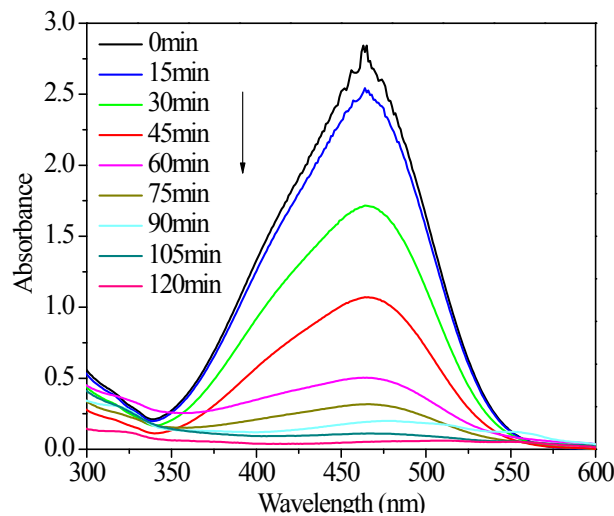


Fig. S5. UV scanning spectrum of MO solutions before and after photocatalytic degradation.

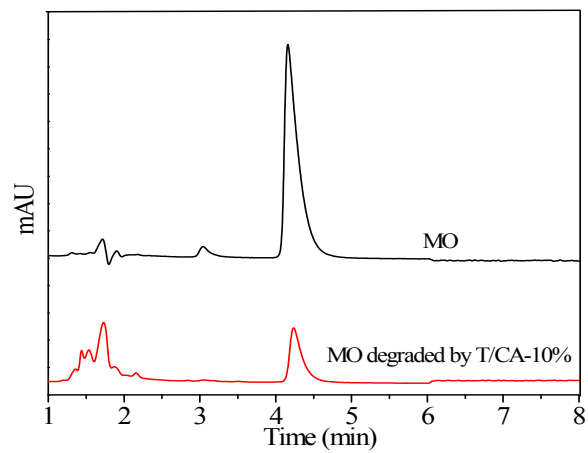


Fig. S6. HPLC of MO solutions before and after photocatalytic degradation.