

Supporting Information

A Bio-inspired Versatile Free-Standing Membrane for Oral Cavity Microenvironmental Monitoring and Remineralization to Prevent Dental Caries

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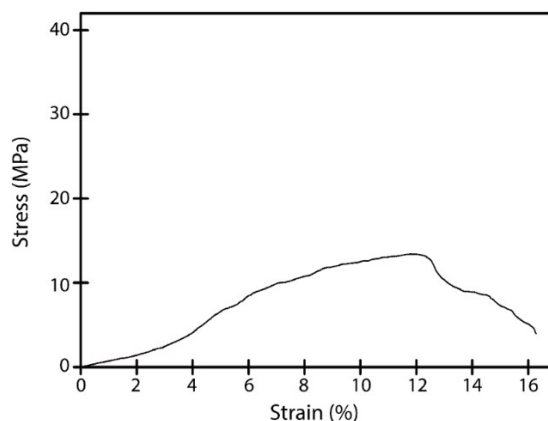


Figure S1. (a-c) The stress-strain curve of SF membrane.

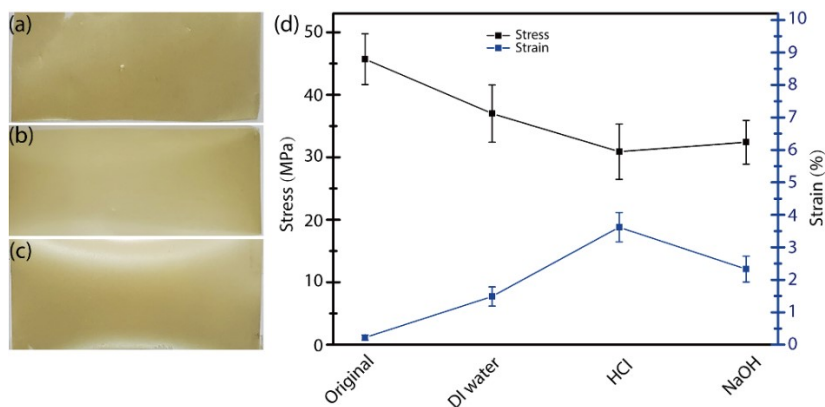


Figure S2. (a-c) The photograph of SF/TiO₂ NTBs membrane immersed in different solution for 30 min at room temperature, DI water (a), HCl (b), NaOH (c). The maximum elastic strain and maximum stress of SF/TiO₂ NTBs under different conditions (d).

Fig. S2 (a-c) shows the photograph of SF/TiO₂ NTBs membrane immersed in DI water, HCl (pH=1) and NaOH (pH=14) for 30 min at room temperature, all samples still maintains excellent integrity. Moreover, the maximum elastic strain increases but the maximum stress decreased obviously under the wet condition, include in acid or alkaline solution as we can see from Fig. S1 d. These results suggested that the SF/TiO₂ NTBs membrane has the advantage of corrosion-resistant property.

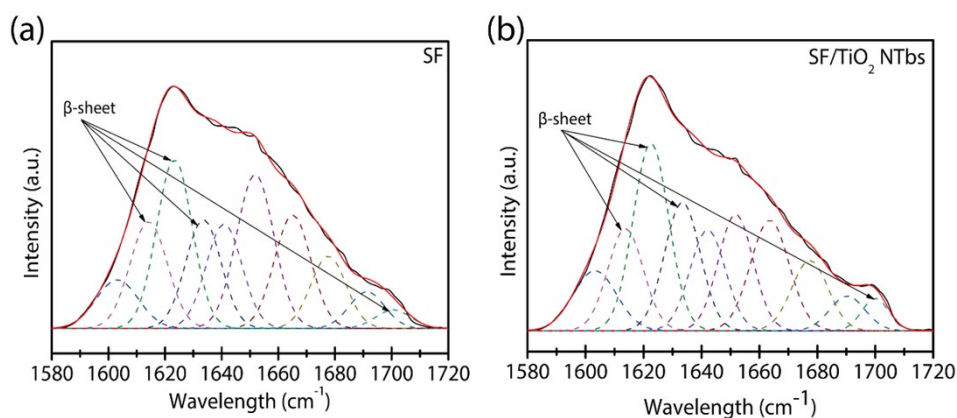


Figure S3. The FT-IR peak splitting spectra of SF membrane (a) and SF/TiO₂ NTBs membrane

(b).

Figure S3 shows the FT-IR peak splitting spectra of SF membrane (a) and SF/TiO₂ NTbs membrane (b), the content of β -sheets of SF membrane and SF/TiO₂ NTbs membrane was 42.58 % and 46.24 %, respectively. We can see the contents of β -sheets had increasing trends but shows no obvious variation.

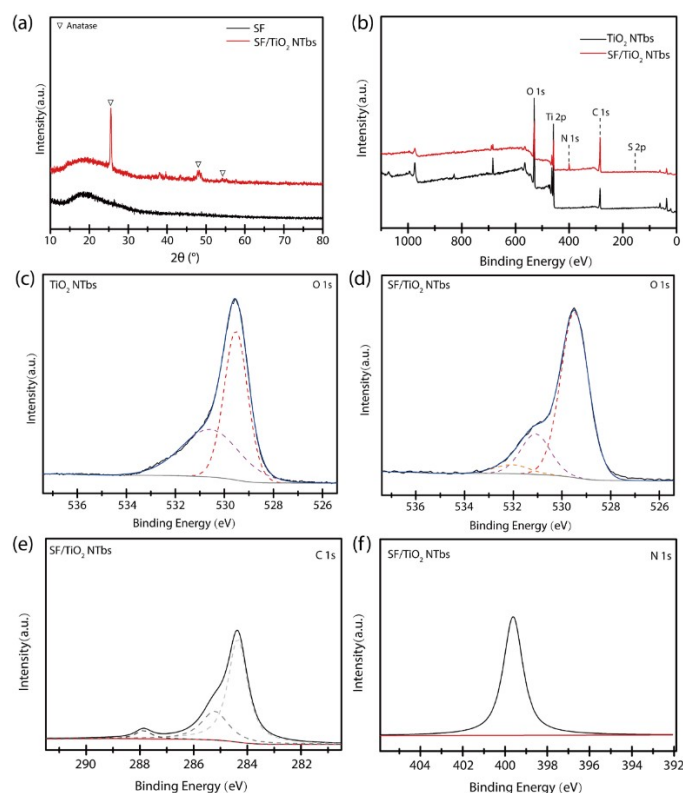


Figure S4. XRD pattern of TiO₂ NTbs and SF/TiO₂ NTbs (a), The XPS survey scan spectra of TiO₂ NTbs and SF/TiO₂ NTbs (b), O 1s spectra of TiO₂ NTbs (c) and SF/TiO₂ NTbs (d), C 1s spectra of SF/TiO₂ NTbs (e) and N 1s spectra of SF/TiO₂ NTbs (f).

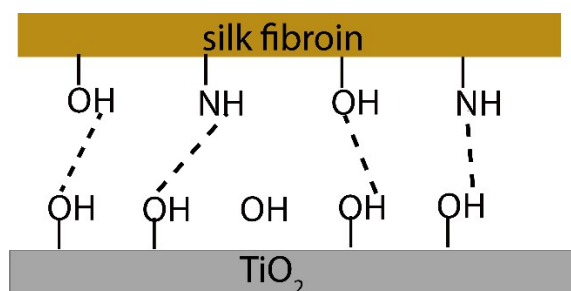


Figure S5. Hydrogen bonds between silk fibroin membrane and TiO₂ surface.

Figure S5 shows the schematic of hydrogen bonds between silk fibroin membrane and TiO_2 surface. As we all know, the TiO_2 NTbs showed efficient adsorption property because of its small size, big specific surface area and a lot of hydroxyl group, which probably forming hydrogen bonds with $-\text{OH}$ or $-\text{NH}$ in silk fibroin membrane.

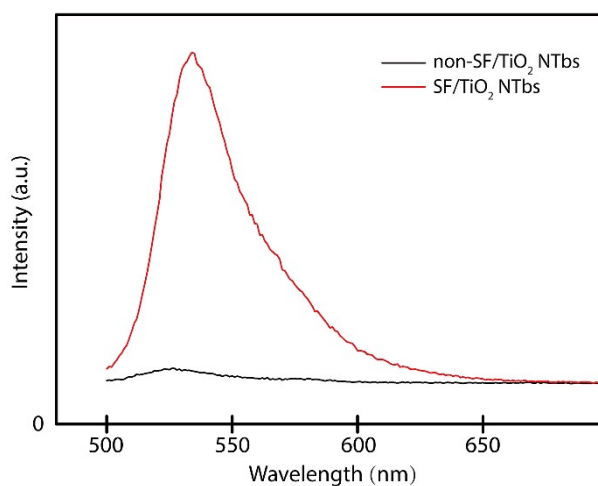


Figure S6. The fluorescence spectrum of singlet oxygen sensor green (SOSG) with and without SF/ TiO_2 NTbs after UV irradiation.

Singlet oxygen sensor green (SOSG) was used to evaluate the production of singlet oxygen. SOSG has a weak fluorescence at excitation/emission of 488 nm/527 nm and react quickly with singlet oxygen to form a high green fluorescent endoperoxide. Therefore, the increased intensity at the 527 nm emission peak proved the generation of singlet oxygen species.

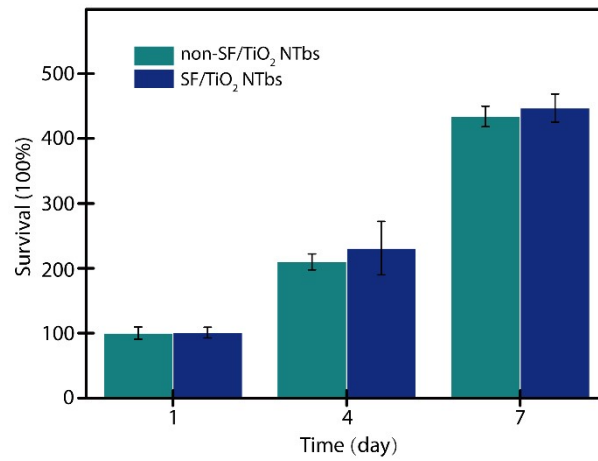


Figure S7. Cytotoxic effect of SF/TiO₂ NTbs against L929.

The biosafety of the membrane was tested by evaluating the cell viability of mouse fibroblast cell, L929 in the presence of SF/TiO₂ NTbs, as shown in Figure S7. It has been found that the SF/TiO₂ NTbs did not express obvious cytotoxicity, but the proliferation of cell.