

## Biomimetic sponge for photocatalytic water purification

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We report the design of a biomimetic sponge for photocatalytic purification of water. Our focus is on the hierarchical structural features that enable pollution remediation under natural conditions of sunlight irradiation and no stirring. The biomimetic sponge is created from the designed self-assembly of photoactive  $\text{TiO}_2$  nanoparticles with a natural organic molecule cyclodextrin. These materials assemble into a network of microscale fibers with lengths extending beyond millimeters. The highly interconnected nature of these fiber networks provides both the mechanical stability and large pore structure needed for water purification applications. We demonstrate that this biomimetic structure is capable of degrading a common organic pollutant and find that the percentage of  $\text{TiO}_2$  in the network structure controls the degree of pollutant degradation. In addition, the cyclodextrin in the network is seen to enhance photocatalysis through trapping of the pollutant molecules near the active titania surface. Finally, we discuss the next steps needed to mimic more faithfully the operation of a real biological sponge.

**Keywords:** Biomimetics, Sponge, Titania, Cyclodextrin, Photocatalysis.

### Introduction

Marine organisms have survived in a harsh environment for millions of years by evolving solutions to many problems such as energy harvesting, nutrient feeding and mechanical strength. It is valuable to examine these solutions as inspiration to address problems in human engineering. An excellent example is the marine sponge found in waters extending from the tropics to the arctic [1]. The sponge is an animal that forms a multifunctional exoskeleton with hierarchical features from the nanoscale up to the macroscale [2]. This intricate hierarchy provides an optimal combination of mechanical strength, transport and absorption of nutrients from the water [3-4].

From the human perspective the sponge's removal of nutrients from the water can be seen as a filter that removes "pollution" from the water, thus purifying it. A natural application of the sponge is therefore as a means of water purification [3]. We may therefore use the sponge's design principles as a guide to our biomimetic sponge. First among the design principles is that the hierarchical structure provides stability and flexibility in the water environment making a robust filter that can be easily separated from the purified water. Second, the open network of micrometer scale fibers provides the necessary pore structure for easy transport to the large surface area of the fibers. Third, the nanoscale structure effectively captures the pollutants and removes them from the water.

In this paper we demonstrate our preliminary design of a "living" biomimetic sponge. Here we focus on the hierarchical structural features to promote pollution remediation. The biomimetic sponge is created from the designed self-assembly of photoactive  $\text{TiO}_2$  nanoparticles with a natural organic molecule cyclodextrin [5-7]. Titania was selected as the active photocatalyst for the degradation of a pollutant molecules. Cyclodextrin is selected to both complex with the titania surface directing assembly of the network and to act as a linker to hold the pollutant molecule close to the titania. These materials assemble into microscale fibers with lengths extending beyond millimeters. The highly interconnected nature of these fiber networks provides both the mechanical stability and large pore structure needed for water purification applications. We discuss how the biomimetic structure enhances the degradation an organic pollutant under natural conditions of sunlight and without stirring.

### Experimental

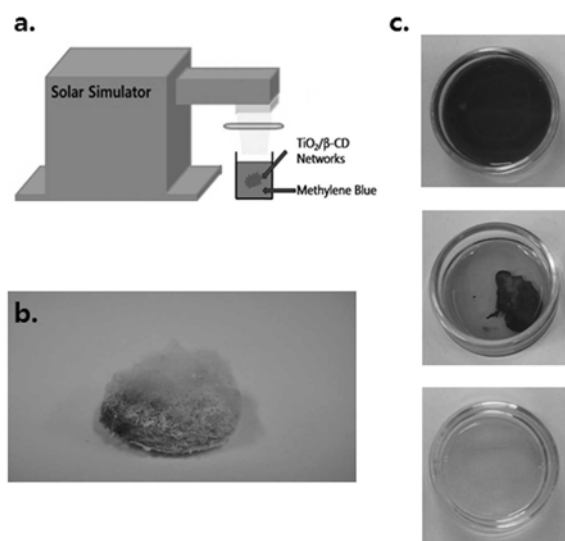
Growth of  $\text{TiO}_2$ -cyclodextrin networks were described previously [5]. Briefly, anatase titania nanoparticles with a mean size of  $\sim 15$  nm and  $\beta$ -cyclodextrin were purchased from Sigma-Aldrich and used as received. For synthesis, 1.0 g/L of  $\text{TiO}_2$  nanoparticles and 8.8 mM of  $\beta$ -cyclodextrin were mixed in ultra-pure water and uniformly dispersed in an ultrasonic bath. The mixture is then irradiated with simulated AM1.5 sunlight (Oriel Solar Simulator) at  $1000 \text{ W/m}^2$  for 24 hrs. After exposure, the mixture is transferred to a closed vial and stored in a cool, dark cabinet for 30 days to allow the components to assemble into centimeter

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scale networks. It has been found that local variations in the relative concentrations of the  $\text{TiO}_2$  nanoparticles and cyclodextrin result in networks with  $\text{TiO}_2$  concentrations ranging from 0% to at least 85% [6]. This feature is utilized here to select networks with various percentages of  $\text{TiO}_2$  to evaluate the network performance.

Once fully self-assembled, the networks are removed and washed in copious amounts of water to remove excess, unbound cyclodextrin. The networks are then freeze-dried in order to prevent collapse of the structure during ambient drying. In this process, the wet network is first frozen then loaded into a freeze dryer (Eyela FD1000) overnight under vacuum at a temperature of  $-50^\circ\text{C}$ . The dried networks are analyzed with scanning electron microscopy (SEM, JEOL JCM 5700) and transmission electron microscopy (TEM, JEOL 2010). To prepare a SEM specimen, dried samples are cut with a razor blade and a sub-monolayer of gold is sputtered onto the specimen in order to reduce charge-up effects during imaging. For TEM analysis, it was necessary to fragment the nano-bers via a brief sonication in water due to the thickness of the individual nanobers. A drop of the resulting solution was then applied to a carbon-coated grid and dried for TEM analysis.

The objective of our study is to evaluate the effectiveness of the biomimetic sponge structure to degrade environmental pollution. Therefore, our photocatalytic tests are designed to test the networks in “natural conditions” of sun-light irradiation without external stirring. The experimental set up is shown schematically in Fig. 1. The  $\text{TiO}_2$ -CD network (Fig. 1(b)) is placed in a non-stirred vial of polluted water. Here we use methylene blue as a test contaminant due to its easily visible color and its frequent appearance as a real contaminant in effluent from textile manufacturing.



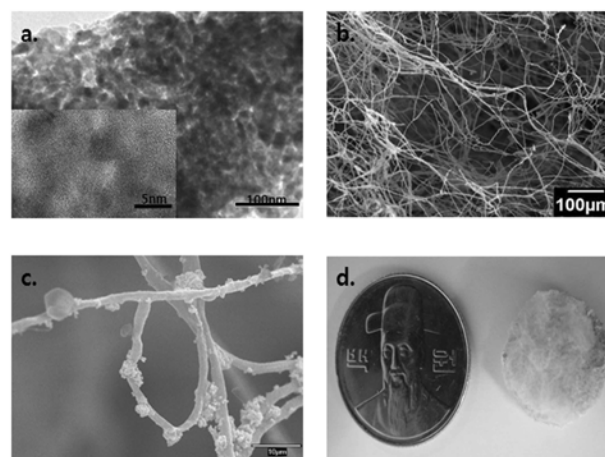
**Fig. 1.** (a) Experimental setup for photocatalyst measurements; (b) photographs of the network and subsequent dye degradation.

Networks with  $\text{TiO}_2$  percentages of 85%, 59% and 48% were tested to evaluate the effect of network composition. The networks were exposed to simulated sunlight ( $1000 \text{ W/cm}^2$  AM 1.5 radiation) for a total duration of 5 hours. To determine the decomposition kinetics, 0.1 mL aliquots of solution were removed every 15 minutes and measured with an UV-Vis spectrometer.

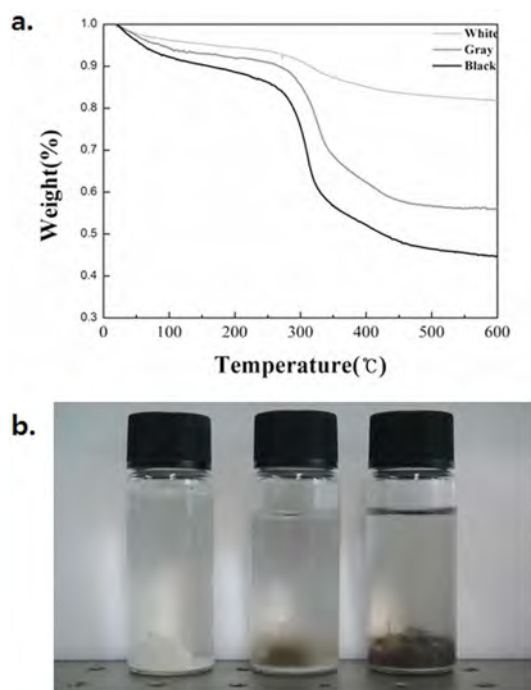
## Results and Discussion

The growth of the biomimetic networks was discussed previously [5-6]. It was shown that a balance between hydrophobic forces at the molecular scale and surface tension at the microscale drive the self-assembly of the networks. The materials chosen have several important advantages for applications in photocatalytic degradation. Anatase  $\text{TiO}_2$  nanoparticles show excellent photocatalytic performance due to their large surface activity and large surface to volume ratio [8-9]. Moreover, holding together  $\text{TiO}_2$  nanoparticles as a continuous network enables the photocatalyst to be inserted and removed from polluted water without costly and difficult separation that is necessary for dispersed nanoparticles. Cyclodextrin also presents several advantages. First, it forms a stable complex with  $\text{TiO}_2$  that maintains its structure even under extended solar irradiation [10]. Second, its cone-like molecular structure may hold pollutant molecules near  $\text{TiO}_2$  surface for longer duration acting as an artificial enzyme improving the probability of degradation [11].

Fig. 2 shows the hierarchical features of the biomimetic  $\text{TiO}_2$ -CD sponge. At the nanoscale (Fig. 2(a)) the anatase  $\text{TiO}_2$  nanoparticles maintain their crystalline structure and are dispersed in a porous matrix of cyclodextrin molecules. At this scale the pollution molecules interact with the large surface area of the photoactive titania and are broken down. Fig.



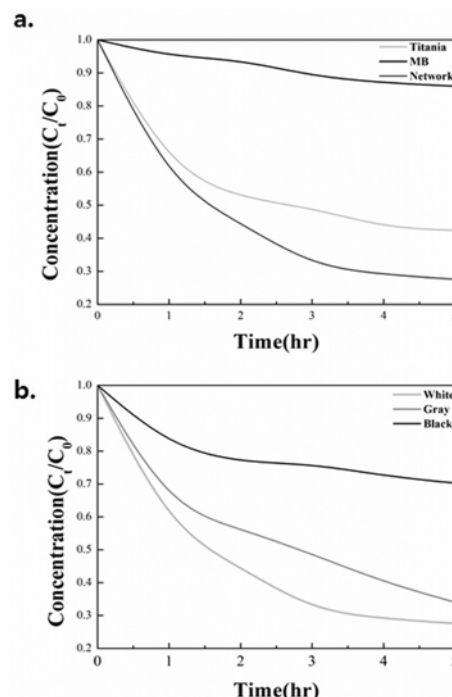
**Fig. 2.** Hierarchical structure of the biomimetic sponge. (a) TEM image at the nanoscale; (b) SEM image at the microscale; (c) SEM image at the mesoscale; (d) Photograph at the centimeter scale.



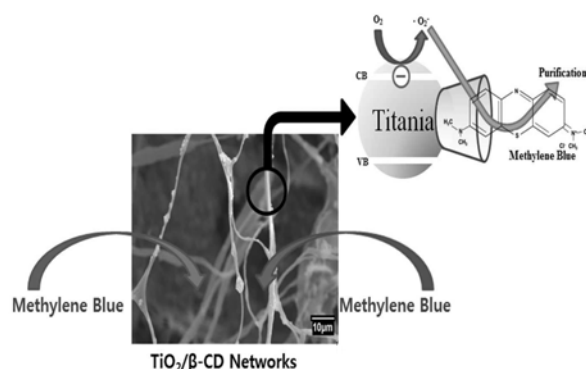
**Fig. 3.** (a) TGA analysis of the TiO<sub>2</sub>-CD networks with different titania composition; (b) corresponding photographs showing the color variations of the grown biomimetic sponges.

2(b) and 2(c) show the TiO<sub>2</sub>-CD fibers are approximately 1 micrometer in diameter and more than 1 mm in length. This microscale structure provides a large surface to volume ratio of the active titania. The porosity inherent in the open structure of the network is also important to promote the transport of pollutant molecules to the surface and by-products out of the sponge. Fig. 2(d). shows the mesoscale structure of the networks. At this level, the highly interconnected nature of the fiber network provides both mechanical stability and flexibility necessary for use as a photocatalytic filter which can be added to contaminated water and pulled out after decontamination.

The TiO<sub>2</sub>-CD sponge networks can be grown with various titania concentrations. Three different networks were chosen with varying concentrations of incorporated TiO<sub>2</sub> nanoparticles in order to test their effectiveness for photocatalytic water decomposition. Figure 3 shows photographs of the three sponge networks along with thermo-gravimetric measurements (TGA) to determine the TiO<sub>2</sub> concentration. The TGA data is characterized by three regions: water desorption around 100 °C; cyclodextrin decomposition around 300 °C [12]. Since TiO<sub>2</sub> is stable to very high temperature the remaining mass gives the total titania content. It can be seen that the total concentration of networks with “black”, “gray” and “white” colors are 48%; 59% and 85% titania respectively. The color variation has been explained previously as due to ring breaking of the cyclodextrin molecules and their subsequent tight assembly in the network [6].



**Fig. 4.** (a) Kinetics of the photocatalytic degradation of methylene blue under simulated sunlight for networks of different TiO<sub>2</sub> content; (b) network effect on the photocatalytic degradation comparing TiO<sub>2</sub> nanoparticle powder and TiO<sub>2</sub>-CD network.



**Fig. 5.** Schematic suggesting the ways that the biomimetic sponge structure enhances the photocatalytic decomposition of pollutants.

Fig. 4(a) shows the photocatalytic decomposition kinetics as a function of the TiO<sub>2</sub> content. Clearly the efficiency increases with the percentage of TiO<sub>2</sub> nanoparticles in the structure. This result is expected since TiO<sub>2</sub> is the photo-active component in the network [13]. At high concentrations of TiO<sub>2</sub> in the network results in more surface exposed due to less blocking by the cyclodextrin molecules. Therefore, it can be expected that there will be an optimal content that maximizes the surface exposure while still maintaining a stable network structure. The importance of the network structure can be seen in Fig. 4(b) where the TiO<sub>2</sub>-CD network shows significantly better decomposition than the same mass of free TiO<sub>2</sub> nanoparticles. Therefore, the structure building features of cyclodextrin are important for the overall photocatalytic

efficiency of the biomimetic sponge.

In order to effectively degrade pollutants, two steps must occur: 1) the pollutant molecule must diffuse to the photocatalytic surface; 2) the pollutant molecule must reside on the surface long enough for electron transfer to occur. The network structure of the biomimetic sponge likely improves both of these steps as shown schematically in Fig. 5. First, the highly porous sponge structure has a surface area around  $40 \text{ m}^2/\text{g}$  providing a significant active surface area for photocatalysis. Unless it is vigorously stirred, nanoparticle powder will aggregate and settle presenting a much lower active surface area compared to the networks as seen in Fig. 4(b). Second, the pollutant molecule can be held in the cavity of the cyclodextrin at the surface of the  $\text{TiO}_2$ . This would increase the residence time of the pollutant at the surface and thus increase the probability of degradation. In this way the cyclodextrin- $\text{TiO}_2$  complex can be thought of as an artificial enzyme in that it both holds the target molecule and catalyzes its chemical transformation [14-15]. Due to the hydrophobic character of the CD interior, hydrophobic molecules would be expected to be removed most effectively.

These results show that the hierarchical structure of the biomimetic sponge is effective for pollution remediation. Like the natural marine sponge, our biomimetic sponge will need to evolve in order to achieve optimal functionality. In particular, Fig. 4(a) suggests that more  $\text{TiO}_2$  surface area is better. This will require larger nano-porosity within the fibers. An added advantage of more porosity is that light will be scattered by the larger number of interfaces increasing the path length of the light through the sponge structure increasing the photocatalytic conversion. Finally, an even more significant improvement would be to enhance pollutant flow through the structure. In the natural marine sponge, cilia pull water in through the sides of the sponge structure where the nutrients are absorbed on the network surface [3]. Then the filtered water is expelled out through the top of the structure. Our next step is to mimic this macro-flow through our artificial sponge structure.

## Conclusions

In this paper we demonstrated our preliminary work on the design of a “living” biomimetic sponge. In particular we focused on mimicking the hierarchical

structural features of natural marine sponges. The biomimetic sponge was created from the designed self-assembly of photoactive  $\text{TiO}_2$  nanoparticles with a natural organic molecule cyclodextrin. These materials assemble into microscale fibers with lengths extending beyond millimeters. It was shown that the highly interconnected nature of the fiber networks provided both the mechanical stability and large pore structure needed for water purification applications. We demonstrate that this biomimetic structure is capable of degrading an organic pollutant. Finally, we suggested that the next steps should be to optimize the porosity of the network structure and to mimic more faithfully the flow of water through the marine sponge.

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