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Supporting information

Photocatalytic antifouling coating based on carbon nitride with dynamic acrylate boron fluorinated polymers

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Thickness of CNP films

The prepared the CNPs and control sample were placed into an aquarium with 3 L of artificial seawater (prepared according to ASTM D1141-98). All the films were gently taken out from the artificial seawater every two days and diluted with deionized water water for 3 min to remove the impurities and seawater. The clean samples were dried at 75 °C for 6 h, and then a micrometer (Mitutoyu, 293-240-30, Japan) was used to measure the thickness of the dry films.Every sample was measured five times at different spots, and the reported values represent the average results of the five parallel tests.

Diatom antisettling test

The antifouling performance of the CNPs was evaluated using a model organism in the biofilm-*Nitzschia closterium minutissima*. The algae cells were cultured in F/2 culture medium at 20.5± 1 °C. All the prepared samples and a piece of a glass slide used as blank were placed into a diatom solution with a concentration of 5.5×10^5 algal cells per mL. Then the aquarium with the samples and the diatom solution was put into an illumination incubator with a 500 W Xeon-lamp (420 nm) every 12 hours. After incubation for 15 days, all the CNPs, control samples and blank were removed from the algae solution and eluted by ultrapure water for 5 minutes to detach the unsettled diatoms. The morphology of the algae cells attached on the surfaces of the prepared samples was recorded and observed using a fluorescence microscope (Nikon DS-Ri2, Japan) with a confidence value of $p < 0.05$.

Photocatalytic antibacterial experiments

The photocatalytic antifouling experiments were carried out as follows: Typically, the as-prepared the CNPs and control samples were added into different individual conical flasks containing 50 mL of sterilized artificial seawater. Then 120

μL bacterial suspensions of *Escherichia coli* (*E. coli*) and *Staphylococcus aureus cells* (*S. aureus*), with concentrations of 3.5×10^7 cells per milliliter, were added into the above-mentioned conical flasks. All the flasks were gently shaken on an oscillating table (Eppendorf, Innova 42R, German) with a rotating speed of 60 rpm at 37 ± 0.25 °C in the dark for 45 min. After that, A 500 W Xeon lamp with a 420 nm cut-off filter was used as the visible-light source to illuminate the shaking flask to initiate the photocatalytic activity. During the illumination process, 2 mL of bacterial suspension in each flask was withdrawn and diluted with sterilized artificial seawater on a super clean bench every 45 mins. After that, 120 μL diluted solution with a concentration of 1×10^6 cells per milliliter was dropped in a petri dish which contained 10 mL Luria–Bertani (LB) liquid culture medium. After incubation for 24 hours at 37 °C, the number of *E. coli* and *S. aureus* colonies growing on the solid culture medium was recorded. For each sample, five parallel measurements were performed. Therefore, the reported antibacterial rates were the average values of the five test values. The antibacterial rates (A) of the CNPs and control sample were calculated according to the equation: $A = 100 - (N_t/N_0) \times 100$, where N_0 and N_t are the numbers of two kinds of bacteria without illumination and under illumination for t min, respectively.

The band gaps (E_g) for the C_3N_4 nanoparticles were calculated to be 2.05 eV, which was based on the following equation (S1):

$$ahv = A\left(hv - E_g\right)^{n/2} \qquad \text{(S1)}$$

Where a*, h, n, A* and E_g are the absorption coefficient, Planck's constant, light frequency, proportionality constant and band gap, respectively. In the equation, n depends on the characteristics of the transition in a semiconductor, for instance, n=1 for a direct transition semiconductor, whereas n=4 for an indirect transition semiconductor. From the linear relationship between $(ahv)^{1/2}$ and photon energy, the

band energy (E_g) could be obtained by the intercept of the tangent to the linear region of the plot with the abscissa.

Mussel settlement assay

The mussels used were *Mytilus galloprovincialis,* which are model macrofouling organisms and invade different sea areas by extremely aggressive fouling on ship hulls.[1] The antifouling properties of the CNPs were further investigated by mussel attachment. As a blank, two pieces of glass slides were placed between two coated substrates. Two ABFP polymer substrates were used as a control. All the samples (20 samples: CNP-1–5, 2 control samples and 13 blank samples) were fixed on a sterilized phenolic resin plate (15 cm × 28 cm) using medical adhesive tape. Then, the phenolic resin plate with different samples was placed into a sterilized aquarium (40 cm × 70 cm × 60 cm), which was filled with artificial seawater. The settlement process was recorded by a video camera and photographed at regular intervals.

Active species trapping tests

To detect the specific photo-generated oxidative species of active radicals on CNP films during the photocatalytic activities, active species trapping tests were carried out. Before the active species trapping experiments, the concentrations of different scavengers were adjusted to show the best trapping effects as well as to ensure the cell viability. Therefore, 1 mL of sterilized artificial seawater (control), a certain amount of TEMPOL (a scavenger of O_2^-), sodium oxalate (a scavenger of h^+) and isopropanol (IPA, a scavenger of ·OH) were added separately into the *E. coli* solution (1×10^6 cells per milliliter) in the presence of CNPs to make sure the concentrations of TEMPOL, sodium oxalate and isopropanol were 2.0 mM, 10.0 mM and 10.0 mM, respectively. Then, a 500 W Xeon lamp with a 420-nm cut-off filter was used to generate the reactive oxygen species (ROS). After incubation for 24 hours

at 37 °C, the amount of *E. coli* dyed with crystal violet was recorded by a laser scanning confocal microscope (TCS SP8 X, Leica, German).

Toxicity test

The growth rate of *Nitzschia closterium minutissima* in diatom solutions containing different films was determined to analyze the environmental properties of the CNPs. The test procedures were as follows: 60 mL of diatom solution with a concentration of 2.5×10^5 cells/mL was added into 100-mL individual Erlenmeyer flasks containing different CNPs and an ABFP polymer matrix film. The diatom solution with the ABFP polymer matrix film in it was named as the control solution, and the diatom solution alone in the Erlenmeyer flasks was named as the blank solution. The growth rates of the diatoms in the control solution and blank solution were used for comparison with those of the CNPs. The cell number at an incubation time of 0 day and *t* days in an illumination incubator with a temperature of 20.5 ± 1 °C were counted on a blood counting chamber with a microscope (Leica DML 300B, Germany). The growth rate of algae was obtained by the following equation (S2):

$$\mu = t^{-1} \cdot \ln(N_t/N_0) \qquad \text{(S2)}$$

Where, *t,* N_0 and N_t are the number of test days, the initial microalgae cell number and microalgae cell number incubated for time *t* respectively. The reported values represented the average results of five parallel tests, and the standard deviations were presented as error bars for quantitative comparison.[2]

To verify whether the organic pollutant released from the self-polishing process was degraded by the CNPs or not, the COD values of ultrapure water containing the CNPs and ABFP film were tested. The COD values were tested and calculated according to the standard ISO6060 at regular intervals.

References

[1] J. W. Chapman, T. W. Miller, E. V. Coan, *Conserv. Biol.* 2003, 17: 1386-1395.

[2] A. Dauta, J. Devaux, F. Piquemal, *Hydrobiologia.* 1990, 207: 221-226.