Developing transparent copper-doped diamond-like carbon films for marine antifouling applications

Yi Liu 1, Peng Guo 1, Xiaoyan He, Lei Li, Aiying Wang, Hua Li *  

Key Laboratory of Marine Materials and Related Technologies, Key Laboratory of Marine Materials and Protective Technologies of Zhejiang Province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

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ABSTRACT

Transparent copper-doped diamond-like carbon (DLC) films were fabricated by hybrid linear ion beam technique. Antifouling performances of the films were assessed by examining attachment and colonization behaviors of E. coli and Bacillus sp. bacteria and Phaeodactylum tricornutum and Chlorella sp. The films with homogeneously dispersed Cu nanoparticles show the transmission efficiency of 40–99% at the wavelength of 400 to 900 nm. The Cu-DLC films inhibit effectively adhesion and proliferation of the algae on their surfaces. The copper added in low dosage (0.1–39.7 at.%) equips the films with the capability of resisting effectively formation of protein-associated conditioning layer and additional killing of microorganisms by sustained release of copper ions. Prohibited formation of biofilm on the surfaces of the Cu-DLC films together with their high transmission efficiencies and excellent electrochemical properties give clear insight into their potential marine applications as antifouling layers.

1. Introduction

Biofouling and corrosion are the predominating worldwide concerns for marine artificial infrastructures [1,2]. Corrosion occurs usually due to chemical or electrochemical reactions between the marine environment and metallic structures [2]. Construction of an inert layer to isolate the corrosive media and the metallic substrate is an effective approach to achieve anti-corrosion. Of particular research attentions is biofouling that any surface immersed in seawater is usually subjected to the settlement of marine organisms, such as protein, bacteria, algae, mollusks, consequently resulting in energy dissipation and device failure [2,3]. Biofouling is presumably initiated by the adsorption of organic molecules (e.g. proteins, polysaccharides) which form a conditioning layer for microbial colonization and subsequent biofilm formation. In many cases, aquatic fouling on ships and underwater structures causes deterioration of the material surfaces, giving rise to increased corrosion [4]. To achieve long-term functionality, it is therefore a prerequisite that any corrosion-resistant layers must simultaneously possess antifouling performances. Materials with antifouling properties resisting nonspecific adsorption of proteins, bacteria, or other biological species are of great interest for marine applications. Coating the materials on marine structures could effectively prevent or alleviate the abovementioned problems. Among the coatings developed nowadays, diamond-like carbon (DLC) film demonstrates the ability to reduce biofouling and improve subsequent cleaning on its surface [5,6], apart from its super mechanical and anti-corrosion properties.

Si-doped DLC films showed further improved corrosion resistance which was believed to be attributed to inhibited penetration of water and ions by their densified structure [7]. Recently attentions have been booming towards biological applications of DLC films owing to their antithrombogenicity. It has been reported that fluoride-doped DLC films [8] and silver-doped DLC films [9] inhibit protein adsorption and platelet activation. Si-modified DLC films performed better than pure DLC films in resisting bacterial adhesion in medical device-related infections [6,10]. To accomplish desirable antifouling performances, surface structure and chemistry are the two key variables that must be considered for constructing surface layers. Due to the intrinsic chemistry limit of DLC films, their antifouling performances might be enhanced by doping of certain antifouling materials. To date, however, knowledge about marine antifouling performances of DLC films is still elusive.

The antifouling technique involving the use of biocides is by far the most widespread method in modern maritime industries [11]. Extensive efforts have been made recently to develop low toxic and even non-toxic biocides. In response to prohibitions of organotin, copper has been used as an alternative biocide for more than 20 years. Cu in numerous forms is still one of the most effective and practical materials for preventing fouling on submerged aquatic structures [11]. DLC films doped with silver [12], platinum [13] or copper [14] already exhibited greatly enhanced antibacterial properties. Cu-doped DLC films offered superior antibacterial activity against Escherichia coli [14] and fungi [15]. Yet intense research efforts are required to design and fabricate Cu-doped DLC films with appropriate structure and sustainable release...
of Cu for antifouling performances. The mechanism as to whether and how the films hold antifouling properties keeps unknown.

In addition, DLC films also have the features of transparency and colorlessness [16], which could further extend their existing applications, for instance, for certain devices operated in the marine environment. For underwater transparent webcam that has been used to monitor daily life of critically endangered species in deep sea [17], the grand challenge is marine biofouling triggered by build-up of microorganisms on the glass dome that protects the camera. To achieve long-term underwater services of transparent devices, traditional antifouling paints hardly meet the needs [17–19]. In this work, transparent DLC films with doping of low dose Cu were fabricated and sustained release of Cu was achieved. Systematic antifouling testing of the films was carried out by characterizing adsorption of typical proteins, attachment and colonization of bacteria, and adhesion of algae on their surfaces. Microstructure, anticorrosion and antifouling performances of the films were examined and the antifouling mechanisms of the films were further elucidated, shedding light on their potential marine applications.

2. Materials and methods

2.1. Deposition of DLC and copper-doped DLC films

DLC films were fabricated using an ion beam deposition system (P600, J&L Tech Co., Korea) powered with anode layer linear ion source (ALIS). Prior to the deposition, silicon wafer substrates were sputter-cleaned for 20 min using Ar ions with a pulsed bias voltage of −100 V. The base pressure was evacuated to ~2.7 × 10⁻³ Pa. During the film deposition, 35 sccm hydrocarbon gas (C₂H₂) was introduced into the ion source to obtain hydrocarbon ions, and the working pressure was kept at ~0.2 Pa. ALIS voltage and current were set at 1200 V and 0.2 A, respectively. A negative pulsed bias voltage of −100 V (350 kHz, 1.1 μs) was applied to the substrate. The deposition time was 40 min. (0.1–39.7 at.%) Cu-DLC films were fabricated using a hybrid linear ion beam system consisting of a rectangular DC magnetron sputtering with a Cu target (99.99%) and a linear anode-layer ion source. Prior to the deposition, the base pressure was adjusted to 2.7 × 10⁻³ Pa. During the deposition, C₂H₂ of 15 sccm was introduced into the ion source. The values of the ion source voltage and current were 1200 V and 0.2 A, respectively. The sputtering gas Ar of 65 sccm was supplied for sputtering Cu. DC sputtering current was set at 1.2, 1.5 and 2 A, respectively, to control the concentration of doped Cu. The work pressure was 0.53 Pa. A negative pulsed bias voltage of −100 V (350 kHz, 1.1 μs) was applied to the substrate and the deposition time was 15 min. For comparison purposes, pure DLC film was also prepared using the ion source without magnetron sputtering.

2.2. Microstructure characterization

Chemical composition of the films was analyzed by Raman spectrometer (Renishaw inVia Reflex, Renishaw, UK) and X-ray diffraction (XRD, D8 Advance, Bruker AXS, Germany) using CuKα radiation (λ = 1.5418 Å) operated at 40 kV and 40 mA. The goniometer was set at a scan rate of 0.02°/s over a 2θ range of 35–75°. Microstructure of the samples was characterized by field emission scanning electron microscopy (FESEM, FEI Quanta FEG250, the Netherlands), confocal laser scanning microscopy (CLSM, TCS SP5, Leica, Germany), and transmission electron microscopy (TEM, FEI Tecnai F20, the Netherlands). For the TEM observation, bright field images and selected area electron diffraction (SAED) patterns were acquired. Topographical morphology of the films was also examined by atomic force microscopy (AFM, Dimension FastScan, Bruker, USA). Water contact angle measurements were carried out using a video-based optical system (Dataphysics OCA20, Germany) operated at ambient temperature. Three samples were measured for each type of the films and five points were tested for each sample.
2.3. Antifouling testing

Attachment behaviors of typical proteins, bacteria, and marine algae on the DLC and the copper-doped DLC films were examined. Bovine serum albumin (ref. A1933, Sigma) was selected for the protein adsorption testing, which is directly related to formation of simplified conditioning layer. The albumin solution was prepared in sodium chloride solution at the concentration of 2 mg/ml (pH = 8.2) at 25 °C. The samples had the dimension of 15 × 15 × 0.5 mm. Three specimens for each type of the samples were used for each testing condition. After 1 h incubation, the proteins were desorbed by 2% SDS for 1 h. Adsorbed albumin was quantitatively analyzed using the bicinchoninic acid (BCA) protein assay [20]. Reagent A was prepared by dissolving 1 mg sodium bicinchoninate, 2 mg sodium carbonate, 0.16 mg sodium tartrate, 0.4 mg NaOH, and 0.95 mg sodium bicarbonate in 100 ml distilled water. The solution was adjusted to pH 11.25 with 10 M NaOH. Reagent B contained 0.4 mg cupric sulfate (5 times hydrated) in 10 ml distilled water. Standard working solution (SWR) was mixed by 100 volumes reagent A with 2 volumes reagent B. 1 ml SWR was added to each 20 μL desorbed protein solution sample and was then incubated for 30 min at 37 °C. The BCA testing was carried out as per the standard protocol provided by the supplier and data reading was made using 562 nm wavelength on a microplate reader machine (Spectra Max 190, MD, USA).

Gram-positive *Bacillus* sp. (MCCC No. 1A00791), Gram-negative *Escherichia coli* (*E. coli*, ATCC No. 25922) bacteria, *Phaeodactylum tricornutum* (provided by Ningbo University, China) and *Chlorella* sp. (provided by Ningbo University, China) were typically used in this study. *Bacillus* sp. bacteria were cultured in 2216E (CM 0471) media prepared by dissolving 1 g yeast extract, 5 g peptone, 1 g beef extract, and 0.01 g FePO4 in 1000 ml artificial seawater (ASW) prepared according to the ASTM D1141-98 (2003). The media containing the bacterial strains were shaken for 24 h at 25 °C. The inoculated medium was prepared by adding *Bacillus* sp. for an initial concentration of 10⁶ CFU/ml at 25 °C under aerobic conditions. *E. coli* bacteria were grown in LB media prepared by dissolving 10 g NaCl, 5 g yeast extract and 10 g peptone in 1000 ml deionized water. The media containing the bacterial strains were shaken for 24 h at 37 °C. The inoculated medium was prepared by adding *E. coli* for an initial concentration of 10⁶ CFU/ml at 30 °C under aerobic conditions. Bacterial number was determined based on the standard calibration with an assumption that an OD value of 1.0 was equivalent to 10⁹ cells/ml. For FESEM observation of the bacteria attaching on the surfaces of the samples, the bacteria after 48 h incubation were fixed in 2.5% glutaraldehyde for 24 h, dehydrated gradually and coated with gold. Extinguishing efficiency of the bacteria

![Fig. 2.](image)

**Fig. 2.** Quantitative analyses of the adsorbed albumin on the films.

![Fig. 3.](image)

**Fig. 3.** Examination of the adhesion of the bacteria *E. coli* (A) and *Bacillus* sp. (B) on the surfaces of the films, (C) and (D): sterilization results of the samples against *E. coli* (C) and *Bacillus* sp. (D), −1: pure DLC film, −2: 7.0 at.%Cu-DLC film, −3: 24.4 at.%Cu-DLC film, −4: 39.7 at.%Cu-DLC film (the bacterial colonies are highlighted by the red circles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
was determined by the standard plate counting approach through triplicate experiments. Pure DLC film was used as blank group. Colony-forming units (CFUs) of the bacteria were examined and the bacterial extinguishing efficiency was calculated according to:

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\text{Bacterial extinguishing efficiency} = \frac{\text{CFUs of blank group} - \text{CFUs of experimental group}}{\text{CFUs of blank group}} \times 100\%.
\]

The diatoms *Phaeodactylum tricornutum* and *Chlorella sp.* were cultured in synthetic seawater-based culture media under sterile conditions at 20 °C. Adhesion of the algae on the different surfaces for 7 days was examined. After the fixation by 2.5% glutaraldehyde for 6h, the samples were characterized by CLSM.

### 2.4. Corrosion testing of the films

To assess the anti-corrosion performances of the films, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) spectra were acquired using a Modulab system (Model 2100A, Solartron Analytical, UK) in ASW. A traditional three-electrode cell was used, with 1 cm² platinum as the counter electrode, a saturated calomel electrode as the reference electrode and the specimen with an exposed area of 1 cm² as the working electrode. EIS measurement was performed with an applied ac signal of 10 mV and the frequency ranging from 100 kHz to 0.01 Hz. After the measurement, the acquired data were fitted and analyzed using a ZSimpWin software based on equivalent circuit models. The equivalent circuits were chosen based on the number of time constants and quality of the fits. Potentiodynamic polarization curves were acquired with the potential range of −1300 mV to 700 mV versus *E*<sub>ocp</sub> at a scan rate of 5 mV s<sup>−1</sup>. In addition, the release rate of copper ions from the films as a function of immersion time was also examined, and the concentration of copper ions was measured using inductively coupled plasma mass spectrometer (ICP-MS, NexION 300, USA). For the ICP measurement, the tested liquid was refreshed every day.

### 3. Results and discussion

The films have been fabricated by the sputtering and Cu concentration (0, 7.0, 24.4, and 39.7 at.%) in the Cu-DLC films was tailored by varying the sputtering current. Based on high resolution TEM characterization and corresponding SAED analyses (Fig. 1A and B), no crystalline phase is found in the plan-view of the Cu-free DLC film, and the diffused SAED ring indicates amorphous structure. As noticed from the image of the Cu-containing DLC films (Fig. 1B), Cu nanoparticles are homogeneously dispersed in DLC matrix. Clear crystalline diffraction rings are observed in the film comprising 7.0 at.% Cu, suggesting the presence
of polycrystalline phases, which are identified to be the (111), (200), (220), (311) and (420) reflections of FCC Cu crystals. Compared with the XRD patterns shown in Fig. 1C, the two peaks at 43.3° and 50.4° refer to Cu (111) and Cu (200), respectively. According to the TEM and XRD results, it is clear that crystalline Cu becomes detectable in the films as Cu concentration reaches 7.0 at.%.

In addition, doping of Cu already changed the atomic bond structure of the DLC matrix. Raman spectra of the films show that all the samples exhibit a broad asymmetric scattering band in the wavenumber range of 1000–1700 cm\(^{-1}\) (Fig. 1D). For further elucidation, the spectra are fitted using two Gaussian peaks after background correction to get the G-peak position and the peak area ratio of D-peak to G-peak (ID/IG). Clearly, as Cu concentration increases, G-peak position shifts upwards from 1540 cm\(^{-1}\) for the pure carbon film to 1557 cm\(^{-1}\) for the Cu-doped film, and ID/IG ratio also increases from 0.8 to 2.4. These imply increased sp\(^2\)/sp\(^3\) ratio and C-sp\(^2\) cluster size [21]. These structural features might affect biofouling behaviors of microorganisms on the surfaces of the films, since it was reported that sp\(^2\)/sp\(^3\) ratio is a key factor for regulating bacterial adhesion [6].

Prevention of protein adsorption onto material surface is presumably one of the potential technical routes to achieve antifouling performances of the material. Quantitative analyses of the protein adsorption on the surfaces of the films show that the amount of adsorbed albumin on the Cu-DLC film is much less than that adsorbed on the pure DLC film (Fig. 2). In addition, few proteins are seen adhering on the 7.0 at.%Cu-DLC and the 24.4 at.%Cu-DLC films, likely due to remarkably reduced surface energy of the Cu-containing films [22]. However, of special attention is the slightly increased amount of the adsorbed proteins on the film comprising 39.7 at.% Cu. To explain this phenomenon, root-mean-square roughness (Rq) of the films was measured by tapping mode 2D-AFM imaging. It is realized that the incorporation of Cu in DLC matrix results in significantly increased surface roughness from 0.518 nm to a maximal value of 4.13 nm, as the Cu concentration varies from 0.1 at.% to 38.9 at.% The rougher surface of the 39.7 at.%Cu-DLC film likely accounts for the more pronounced adsorption of the protein on its surface.

To gain clear insight into effect of the addition of Cu on biofilm formation on the DLC-based films, bacterial adhesion was further examined. During the formation of biofilm, the pure DLC and the (7.0 at.%, 24.4 at.%Cu-DLC films perform better than the 39.7 at.%Cu-DLC film in resisting E. coli adhesion (Fig. 3). It is noted that incorporation of copper caused significant changes in water contact angle of the films. For the pure DLC film, the contact angle is ~66.8°, while as the Cu concentration is increased from 0.1 to 7.0 at.%, the contact angle increases from 76.6° to 82.7°. When the Cu concentration is 24.4 at.%, the contact angle reaches 104.4°. It was found that hydrophilic materials are usually

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**Fig. 6.** SEM images showing significantly prohibited attachment of Bacillus sp. bacteria on the DLC film (B) as compared with that on silicon wafer (A). (C): damage of cell wall of the bacteria is the major regime of the Cu-induced bacteria-killing (from the left image to the right one: obvious cell damage, ruptured cell membrane, further enhanced damage).

**Fig. 7.** SLCM images showing adhesion of Chlorella sp. (A) and Phaeodactylum tricornutum (B) on DLC and Cu doped DLC films after 7 days incubation, (C): transparency of the copper-doped DLC film versus testing wavelength.
more resistant to bacterial adhesion than hydrophobic materials [23]. The effect of Cu on the wettability of the Cu-doped films might be reflected by changes in surface energy components, which has been shown to determine bacterial adhesion [24]. Interestingly, after 48 h exposure, ~100% E. coli were already killed by the 24.4 at.%Cu-DLC and the 39.7 at.%Cu-DLC films (Fig. 3A and C). In contrast, Bacillus sp. bacterial adhesion shows minimum value on the pure DLC and the 39.7 at.%Cu-DLC films (Fig. 3B). For the Cu-doped DLC films, the higher the Cu dosage is, the lower the number of Bacillus sp. colonies attaching to the films is realized. Moreover, it is observed that the Cu-DLC films have 40–80% extinguishing efficiency against Bacillus sp. (Fig. 3B).

Surface roughness of the films and concentration of copper ions in the incubation solution are predominately the two key factors responsible for the varied bacterial adhesion. It is noted that, during the biofilm formation stage, E. coli adhesion is mainly influenced by topography of the films, whereas the major effect applied on Bacillus sp. adhesion is the concentration of Cu (Fig. 3B). The films with 24.4 at.% Cu perform the best among the samples in bacterial removal and bactericidal coefficient. Compared with the DLC matrix, copper nanoparticles are highly active, and copper ion is believed to be determinant on the remarkable antibacterial properties of Cu-DLC films [25–27]. For the Cu-DLC film, biocides are released from the film surface and then enter in the solution in the form of free copper ions Cu^{2+} or Cu^{+}. Cu^{2+} is the main biocidal form, which is more stable than Cu^{+}. The antibacterial action of copper ions is usually attained through corrosion, diffusion, and sustained-release. The release rate of copper from the films is probably controlled by enwrapping of the chemically stable DLC matrix. Further assessment suggests clearly continuous release of copper from the films (Fig. 4). The release rate of Cu^{2+} is dependent on the dosage and exposure level of Cu in the films. However, it is noted that there is a rapid release of Cu after 10 days incubation, probably indicating crushing of the enwrapping structure that triggers rapid release of Cu from the film.

Further microstructure characterization of the surfaces after 2 days incubation of the samples in bacteria-containing ASW suggests clearly the release of Cu to out-layer of the films (Fig. 5). In general, a smoother surface is presumably more capable of inhibiting bacterial adhesion [10]. We found that adherence of E. coli to smooth DLC surface induces the formation of fimbriae around the bacteria (Fig. 5A), generating more adhesion sites for facilitated attachment. In addition, the shape of the bacterium adhered on the Cu-free DLC film is irregular. The shape turns to be rod-like as the adherence occurs on the Cu-doped DLC films (Fig. 5B). Surprisingly, after the 2 days incubation, surface view of the 39.7 at.%Cu-DLC film shows copper compound clusters being embedded in DLC matrix and damage of bacteria is clearly seen (Fig. 5C). The Cu-dominant clusters are proven by the EDS analyses (Fig. 5D). In addition, widespread even distribution of Cu is revealed on the top surface of the film (Fig. 5D). The copper clusters with the size of 2 μm anchor/embed the bacteria in them and cause their disintegration (Fig. 5C). This phenomenon is likely a result of localized corrosion and consequent collapse of the clusters in response to resisted colonization of the bacteria. Colonization of microorganisms on copper particle would change the electrochemical reaction at bacterial/metal interface, in turn accelerating the corrosion or reaction between copper, incubation solution and secreted extracellular polymeric substances [2,4]. Corrosion products and EPS might benefit E. coli adhesion on copper-rich areas by providing a barrier against copper toxicity. This could be the partial reason why the number of the bacteria adhered on the Cu-DLC film with high Cu content, 39.7 at.% in this case, is high. The promoted recruitment by the clusters for attachment of the bacteria would simultaneously bring about subsequent extinguishment of the bacteria by copper ions.

Comparing to E. coli, Bacillus sp. bacteria exhibit distinctive damage regime as a result of the Cu-induced extinguishment (Fig. 6). After two days exposure, the Cu-doped DLC film already prohibits effectively attachment of the bacteria, as compared to silicon wafer (Fig. 6B versus A). Damaging cell membrane is presumably the major regime operated by the copper ions released from the films (Fig. 6C). This further indicates remarkable differences in bacteria-killing mechanisms in response to copper sensitivity and damage mode. There have been extensive reports on copper-associated bacteria-killing [28,29]. In this case, it seems clear that contact of Bacillus sp. with the Cu-containing surface ruptures the membrane of the bacteria by contact killing. This is not surprising since membrane is the first target of copper toxicity. Large amount of copper ions released from the films usually react with oxygen, thereby forming reactive oxygen species which can react with
cell biomolecules and cause further damage [30]. This gives rise to the loss of cell cytoplasmic content with a shell being left over (Fig. 6C). The Cu-doped DLC films attained contact killing of the bacteria through damaging cell envelope and depleting cytoplasmic content of Bacillus sp.

Further testing against attachment of the algae shows excellent antifouling performances of the Cu-doped DLC films. SLM observation of the algae attached on the surfaces of the films after one week incubation shows remarkably constrained adhesion and proliferation of both Phaeodactylum tricornutum and Chlorella sp. on the Cu-DLC films (Fig. 7A and B). The Cu-doped DLC films show the biofilm-free feature, indicating their remarkable antifouling performances. Higher Cu dosage in the films gives rise to more pronounced constrained adhesion. This is not surprising since continuous release of copper ions from the Cu-doped DLC films has been realized (Fig. 4). It was reported that incorporation of copper ions depresses cell division and photosynthesis of typical algae and toxicity of ionic copper may result from an intracellular reaction between copper and reduced glutathione, leading to suppression of mitosis [11,31,32]. For the Cu-DLC films, optical assessment by measuring their transmittance by spectrophotometer already suggests their transmission efficiency of 40–99% at wavelengths ranging from 400 to 900 nm (Fig. 7C). The antifouling Cu-DLC films with favorable transparency might open doors for developing new transparent marine antifouling devices for underwater applications.

Apart from the antifouling performances, corrosion resistance is another essential requirement for the films for potential marine applications. The electrochemical testing shows that corrosion current density of the pure DLC film in ASW is lower than that of the Cu-DLC films (Fig. 8), indicating relatively better anti-corrosion performances of the pure DLC film. Ecorr of the Cu-DLC film is more negative because ASW accelerates anodic dissolution of copper (Fig. 8A). EIS is a powerful non-destructive approach for characterizing electrochemical reactions at film/ASW interfaces. The Nyquist diagrams and Bode plots of the films in ASW media reveal that diameters of the impedance loops decrease with increase in Cu content in the films (Fig. 8B and C), implying accelerated corrosion of the Cu-doped DLC films. Additionally, for the 24.4 at.%Cu-DLC film, the measured impedances exhibit a tail corresponding to Warburg impedance in low-frequency regions. This suggests that the corrosion is presumably controlled by a diffusion process. Doping of Cu slightly reduces the corrosion resistance of the films. It has been clear that there is continuous release of Cu from the Cu-doped films, accounting for the above electrochemical behaviors. The Cu-DLC films already demonstrate excellent antibacterial effect and inhibitory attachment of algae with Cu2+ concentration of 0.006–0.054 mg/L. Further efforts are yet needed to elucidate long-term stability of the Cu-doped DLC films in turbulent physiological media, since release of Cu is an important concern. Nevertheless, our results already give clear insight into design and construction of antifouling films by doping Cu in transparent DLC films.

For the Cu-doped DLC films, biocides are the active ingredients that bring about the capability to resist adhesion, settlement, and growth of marine organisms. The effectiveness of biocides differs depending on their concentration and exposure duration. Therefore, controlling the release of copper ions from the films is of top importance. The release usually involves dissolution and diffusion of copper ions from the film, whereas seawater must get into the film to dissolve the biocides and the dissolved active components must get back to the film surface. A highly efficient getting-in and getting-out path is thus critical for biocide-associated antifouling. Based on the characterization results of the films, as the dosage of copper in the films is higher than 7.0 at.% copper nanoparticles with the size of ~6 nm appear in DLC matrix. Upon contact with the solution, copper nanoparticles would react with the solution since the electrolyte solution could permeate through submicron-sized cracks existing within films [33]. Subsequently, copper would be ionized to copper ions [25], which can destroy the bacteria being in contact with them. While in the Cu-DLC films, copper nanoparticles are well separated by the carbon matrix and pores and cracks are seen from the top view of the films (Fig. 9A), which may in turn result in a sustained release of copper ions. This process is schematically depicted in Fig. 9B. This regime has already been proven in other nanocomposite systems [27,34].

Conclusions

(0.1–39.7) at.%Cu-DLC films with the transmission efficiency of 40–99% at wavelengths of 400 to 900 nm have been fabricated by hybrid linear ion beam deposition technique. Homogeneous dispersion of ~6 nm copper nanoparticles in the films is achieved and diffusion of the copper particles through microsized flaws of the DLC films to their surfaces in contact with incubation solution is revealed. Further ionized copper gives rise to significantly inhibited adsorption of albumin and constrained adhesion of E. coli and Bacillus sp. bacteria, and Phaeodactylum tricornutum and Chlorella sp. on the surfaces of the Cu-doped films. The excellent antibacterial and antifouling performances against formation of algae-/bacteria-associated biofilm provide exciting possibilities of extending the applications of the DLC-based films.

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