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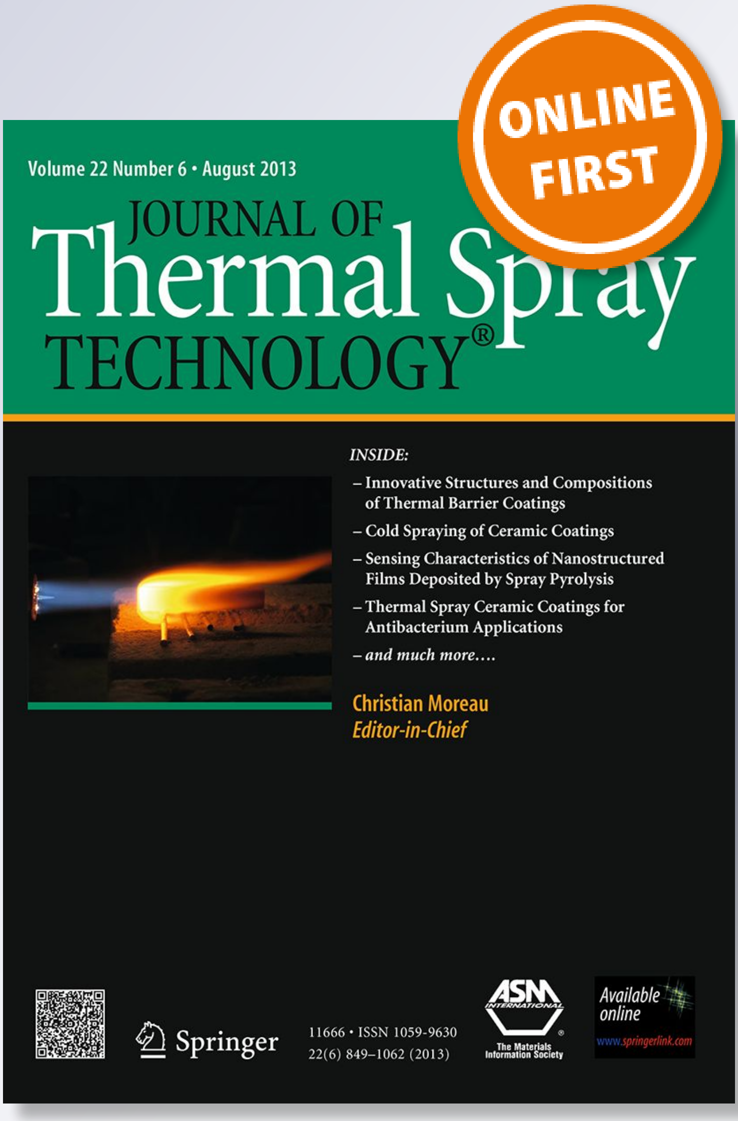

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# Suspension Flame Spray Construction of Polyimide-Copper Layers for Marine Antifouling Applications

Yi Liu[1] · Xiaomin Xu[1] · Xinkun Suo[1] · Yongfeng Gong[1] · Hua Li[1]

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**Abstract** Individual capsule-like polyimide splats have been fabricated by suspension flame spray, and the polyimide splat exhibits hollow structure with an inner pore and a tiny hole on its top surface. Enwrapping of 200-1000-nm copper particles inside the splats is accomplished during the deposition for constrained release of copper for antifouling performances. Antifouling testing of the coatings by 24-h exposure to *Escherichia coli*-containing artificial seawater shows that the Cu-doped splat already prohibits effectively attachment of the bacteria. The prohibited adhesion of bacteria obviously impedes formation and further development of bacterial biofilm. This capsulated splat with releasing and loading of copper biocides results in dual-functional structures bearing both release-killing and contact-killing mechanisms. The suspension flame spray route and the encapsulated structure of the polyimide-Cu coatings would open a new window for designing and constructing marine antifouling layers for long-term applications.

**Keywords** antifouling mechanisms · biocide release · liquid flame spray · polyimide-copper splats

## Introduction

Marine parts in specialized equipment often function under challenging environments. Any surface immersed in seawater is prone to the settlement of marine organisms, such as protein, bacteria, algae or mollusks (Ref 1-3). Marine biofouling has emerged as worldwide serious problems for artificial marine infrastructures. Among the measures taken so far to solve the abovementioned problems, construction of an antifouling layer has been proven to be effective in offering long-term antifouling performances (Ref 4-6). Thermal spray was proven successful in large-scale fabrication of protective coatings (Ref 7-10). Lots of corrosion protections of artificial marine infrastructures have been thermal sprayed over the past 100 years (Ref 7-9). Yet challenges persist as to how to solve the biofouling problem of thermal-sprayed inorganic marine coatings.

Antifouling based on the use of biocides is the most important method in modern maritime industries (Ref 11, 12). After organotin compounds were banned, copper has been widely used as an important alternative for antifouling applications. Various copper agents including copper metal, copper alloy, copper oxide and copper compounds have been used as biocides for decades (Ref 13-16). However, to utilize the biofouling functions of copper, it is essential to design and fabricate a smart coating that has appropriate structure for sustainable release of copper for long-term application. Antifouling is usually achieved by controlled release of biocides from matrix. There have been certain efforts in past years for constructing copper-containing layers, and some technical routes were attempted for instance embedding (Ref 17, 18) and encapsulating (Ref 19, 20).

Many methods have been tried to fabricate polymer capsules that could control the release of encapsulated

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contents. Generally, there are two approaches for making polymer capsules, template-free and template-assisted techniques. Self-assembly, layer-by-layer assembly, single-step polymer adsorption, bioinspolyimidered assembly, surface polymerization and ultrasound assembly have been applied to prepare polymer capsules with diverse functionality and physicochemical properties (Ref 21). Triggering mechanisms responsible for covalent bond cleavage that results in the release of capsule contents involve chemical, biological, light, thermal, magnetic and electrical stimuli (Ref 22). Moreover, a two-level antibacterial coating with both release-killing and contact-killing capabilities has been fabricated using a combination of an aqueous layer-by-layer deposition technique, nanoparticle surface modification chemistry and nanoreactor chemistry (Ref 23).

In recent years, thermal spray route has been developed to endow polymer capsules with novel and interesting properties. Polyimide-copper antifouling coatings with capsule structures that were synthesized by reaction between dianhydride and diamine dissolved in copper nanoparticle-containing dimethylformamide solvent have been described previously (Ref 24). The polyimide splat exhibited hollow structure with an inner pore of 10-15 μm and a tiny hole of 1-5 μm on its top surface. Transversal cut by focused ion beam milling of the individual splats and scanning electron microscopy characterization further revealed unique dispersion of the copper nanoparticles inside the polyimide shell. However, release mechanism and behaviors of individual splats in corrosive media are not established. In this paper, the suspension flame-sprayed copper-containing polymer coatings were further investigated and a new starting suspension feedstock was used for the coating fabrication. Microstructural features, releasing mechanism and antifouling properties of individual polyimide-copper splats were characterized. The antifouling performances of individual splats were assessed by examining colonization behaviors of typical marine bacteria.

## Materials and Methods

### Synthesis of Polyimide-Cu Suspension and Fabrication of Coatings

For the polyimide-Cu suspension preparation, polyimide composite solution was prepared by dissolving polyimide powder in DMF solvent. Cu particles with the size of 200-1000 nm were dispersed in polyimide solutions for 5 h in a tip sonicator with the ultrasound power of 600 W. After ultrasonic treatment, the precursor suspensions were atomized by a homemade spray atomizer. The precursor feedstock injector with the diameter of 1.5 mm was positioned just next to the flame torch, and the angle between the injector and flame was 30 degrees. Pressure of the atomizing air was 0.7 MPa. Prior to coating deposition, the polished stainless steel substrates were rinsed in distilled water and ultrasonically cleaned in acetone. The spraying was carried out using the Castodyn DS 8000 system (Castolin Eutectic, Germany). For the liquid flame spraying, acetylene was used as the fuel gas with flow rate of 1.5 Nm$^3$/h and working pressure of 0.1 MPa. Pressure and flow rate of oxygen were 0.5 MPa and 2.5 Nm$^3$/h, respectively. The precursor feed rate was 40 mL/min, and the spray distance was 200 mm. The preparation procedure is schematically shown in Fig. 1.

### Microstructure Characterization and Antifouling Testing

Microstructure of the splats and the coatings was characterized by field emission scanning electron microscopy (S4800, Hitachi, Japan). Antifouling performances of the coatings were assessed by examining formation of bacterial biofilm and colonization of algae on their surfaces. *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 10$^6$ CFU/mL at 30 °C under aerobic conditions. Bacterial number was determined based on the standard calibration with the assumption that an OD value of 1.0 was equivalent to 10$^9$ cells/mL. For FESEM observation of the bacteria attaching on the surfaces of the samples, the cells after 24-h incubation were fixed by 2.5% glutaraldehyde for 12 h, dehydrated gradually and coated with gold.

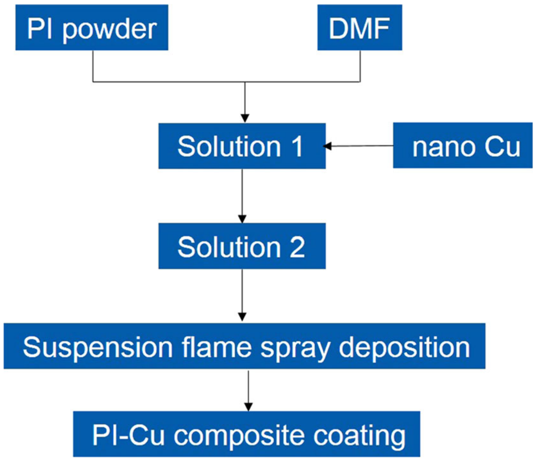


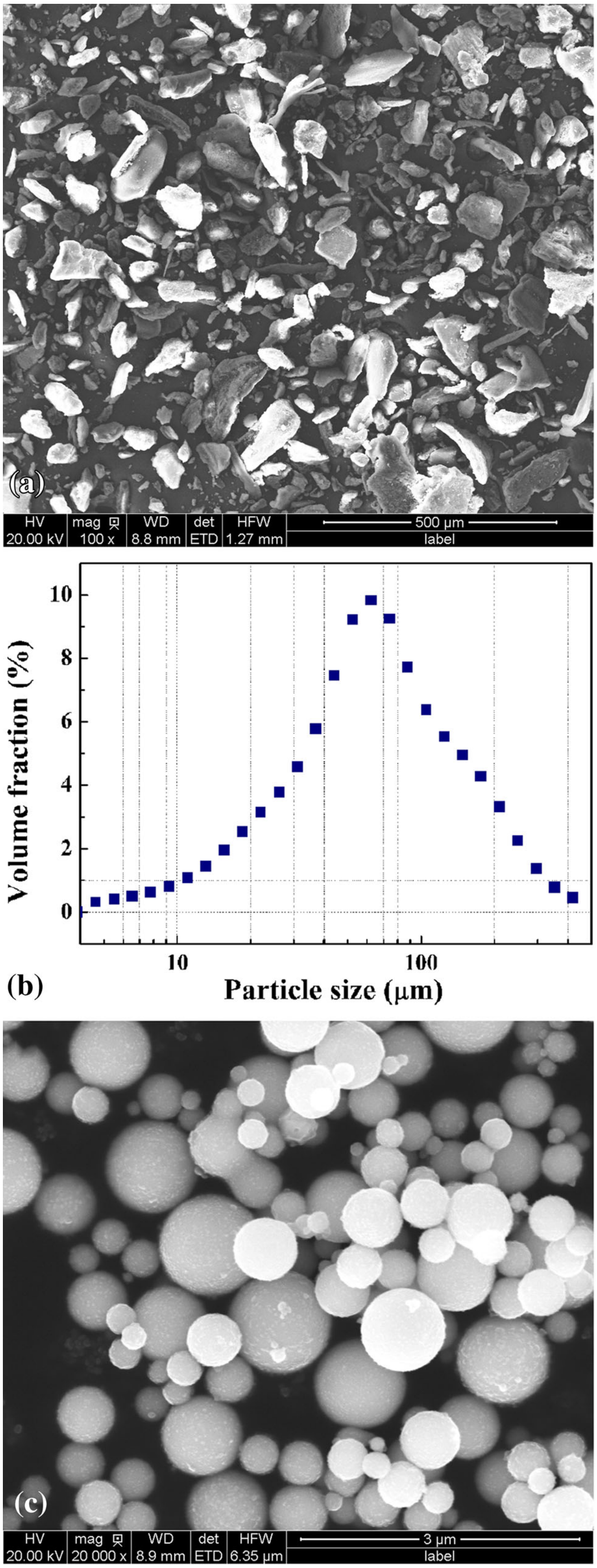
**Fig. 1** Processing flowchart for the coating fabrication

## Results and Discussion

The commercially available polyimide particles exhibit irregular contours (Fig. 2a). The starting powder particles present a wide granularity distribution, and their average diameter (d50 of the particle size distribution) is 58.5 µm (Fig. 2b). The nano-copper particles have the size of 200-1000 nm (Fig. 2c).

Prior to the coating fabrication, polyimide-10%Cu and polyimide-30%Cu splats were collected by suspension flame spraying onto polished stainless steel substrates. During the suspension flame spraying of the PI-Cu precursor, surface maximum temperature of in-flight particles is 945 °C, which was acquired by DPV-2000 measurement. Since the coating deposition was made at high temperature, it is not surprising that oxidation of Cu is seen in the as-deposited splats (Fig. 3). It is noted that CuO whiskers are formed. As reported by other researchers (Ref 25), near spherical CuO nanoparticles were made by flame spray pyrolysis method. Several parameters such as flame temperature, residence time and precursor concentration can change the features of CuO (Ref 26). CuO nanoparticles are effective in killing a wide range of bacterial pathogens that are involved in hospital-acquired infections. However, in comparison with nano-Cu, antibacterial performance of Cu is better than that of CuO, higher concentration of nano-CuO is required to achieve pronounced bactericidal effect (Ref 27). A novel method is therefore needed to protect nano-Cu against oxidation during the coating deposition. This consequently raises the concerns of selecting appropriate techniques for capsule fabrication with retained Cu particles.

Recent exciting findings of hollow or capsulated polyimide have shed light on potential processing routes. Ultrathin and defect-free polyimide hollow fiber membranes were fabricated using a dry-jet, wet quench process with spin dopes (Ref 28). In our previous research, polyimide-copper layers consisting of individual capsule-like splats were one-step fabricated by solution precursor flame spray through controlling the reaction between dianhydride and diamine dissolved in copper nanoparticle-containing dimethylformamide solvent. During the spraying, combustion products of DMF solvent are carbon oxides (CO, $CO_2$), nitrogen oxides (NO, $NO_2$), etc. The high-temperature heating results in solvent evaporation, in turn leading to generation of gases in particle core. This presumably accounts mainly for the microsized hollow polyimide spheres formed in the coatings (Ref 24). In this study, polyimide composite solution was prepared by dissolving polyimide powder in DMF solvent. Nano-Cu particles are further dispersed in polyimide solutions. This preparation procedure is schematically shown in Fig. 1. In consistent



◀**Fig. 2** Characteristics of the starting powder: (a) FESEM image of the starting polyimide powder, (b) particle size distribution of the starting polyimide feedstock and (c) FESEM image of the starting nano-copper powder

with our previous work, current results show that the polyimide splats exhibit hollow structure with a tiny hole on their top surface (Fig. 4), which implies that DMF solvent likely gives rise to the capsule structure.

Structure of the polyimide-based splats was further examined by SEM through removing upper half of polyimide shell. The inner view of the splat clearly shows that dispersed Cu particles are encapsulated by polyimide shell. During the deposition, polyimide solution could protect effectively the nano-copper particles from possible oxidation. Copper particles retain their contours and other physical features after the spraying, and they are coated with a thin layer of polyimide (Fig. 5b). It is therefore clear that the nanosized biocides can be readily loaded directly into the polyimide spheres.

Release-killing capacity is offered to the capsule usually by incorporating Cu particles. Additionally, the surface can also be equipped with contact bacteria-killing capability through the enwrapped Cu particles, which are able to kill bacteria upon their direct contact. The capsulated splats with releasing and loading of the biocides exhibit dual-functional structures, which bear both release-killing and contact-killing capabilities. A previously reported dual-functional coating showed very high initial bacteria-killing efficiency due to the release of Ag ions and retained significant antibacterial activity after the depletion of embedded Ag because of the immobilized quaternary ammonium salts (Ref 23). In this research, the polyimide-copper layers accumulated by individual capsule-like splats can be one-step deposited by thermal spray processing.

It is known that the antifouling performances differ depending on the concentration (release rate) of biocides (Ref 27). Therefore, controlling the release of biocides from the capsules is of top importance (Ref 29). Morphologies of the polyimide splats already showed exciting hollow structures and copper nanoparticles are dispersed in polyimide shell. The tiny top hole of the polyimide splat would facilitate sustained release of copper ions (Fig. 4). Further assessment of the releasing of copper ions shows that the polyimide-Cu splats immersed in bacteria-containing artificial seawater for 24 h give rise to sustained release of copper. FESEM characterization together with EDX analyses reveals homogeneous dispersion of Cu element on the surfaces (Fig. 6), suggesting that top hole of the capsule offers the probability of release of the encapsulated antifoulants in a controllable manner.

In addition, antifouling properties of individual polyimide-Cu splats against *E. coli* bacteria were examined. After 24-h exposure, the Cu-doped polyimide capsule already prohibits effectively attachment of the bacteria, as compared to polished stainless steel substrate. Much less

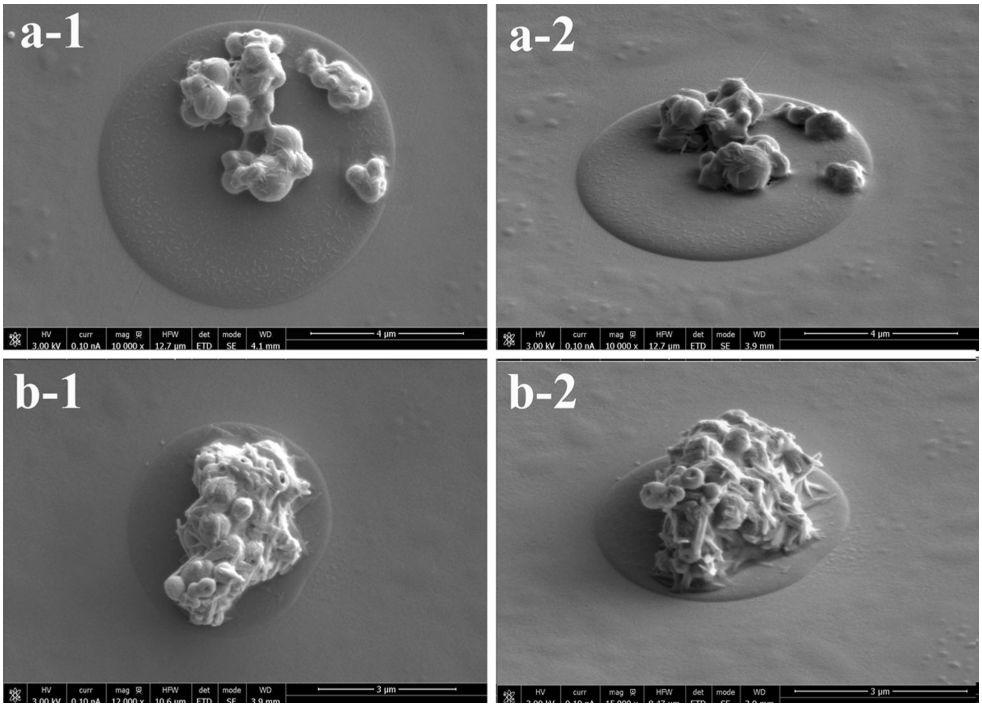


**Fig. 3** Morphology of the as-sprayed splats using polyimide-copper composite powder as the starting feedstock showing copper oxides being enwrapped by molten polyimide layer. (a) polyimide-10% Cu, (b) polyimide-30% Cu, -1: surface view, -2: 52° view

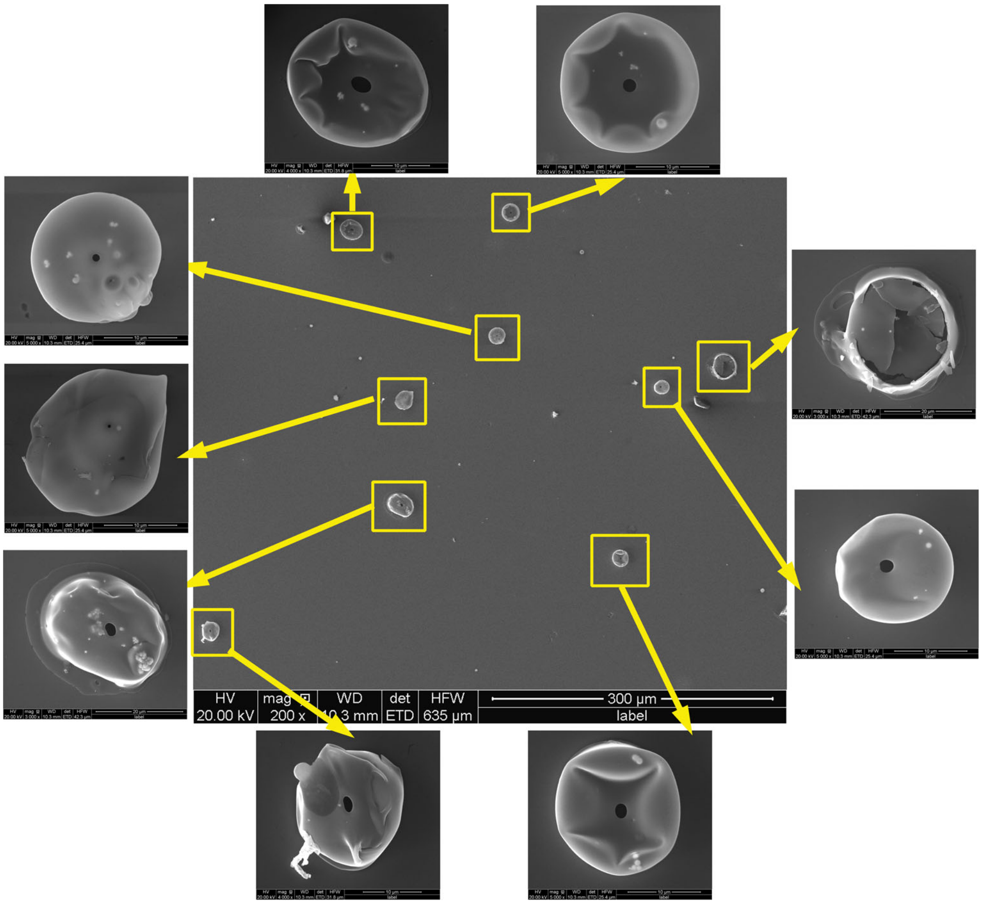


**Fig. 4** Morphologies of the as-deposited polyimide-Cu splats deposited by suspension flame spray. The enlarged views of individual splats show special capsule structure with top micron-sized hole

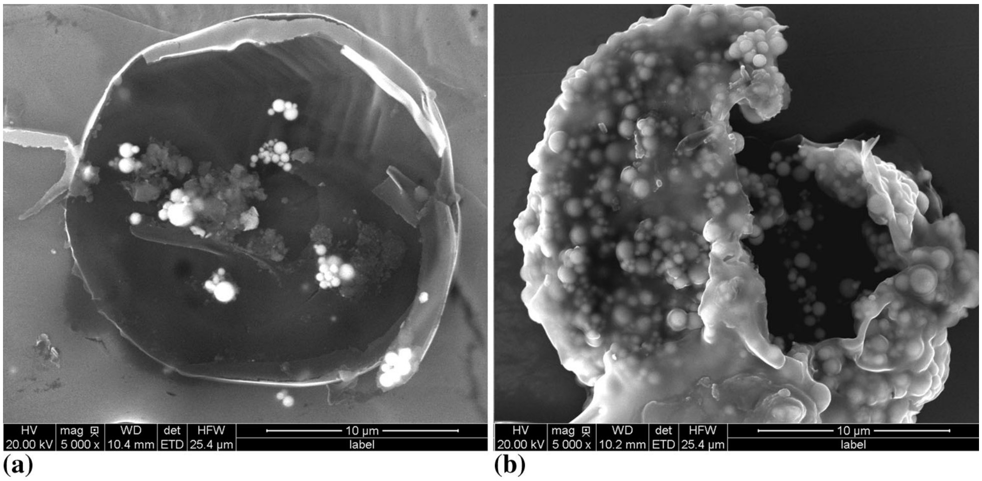


**Fig. 5** Characteristics of the as-sprayed polyimide-Cu splats showing distribution of copper particles in polyimide capsule after removing upper half of polyimide shell (a) and enwrapped state of the copper particles by polyimide shell (b)

bacteria are seen on the splats than on the stainless steel (Fig. 6). The prohibited adhesion of the bacteria obviously impedes formation and development of bacterial biofilm. It is therefore anticipated that the newly constructed copper-containing polyimide coatings possess promising antifouling performances.

Further examination of bacterial adhesion on twin splats shows that after being immersed in the bacteria-containing

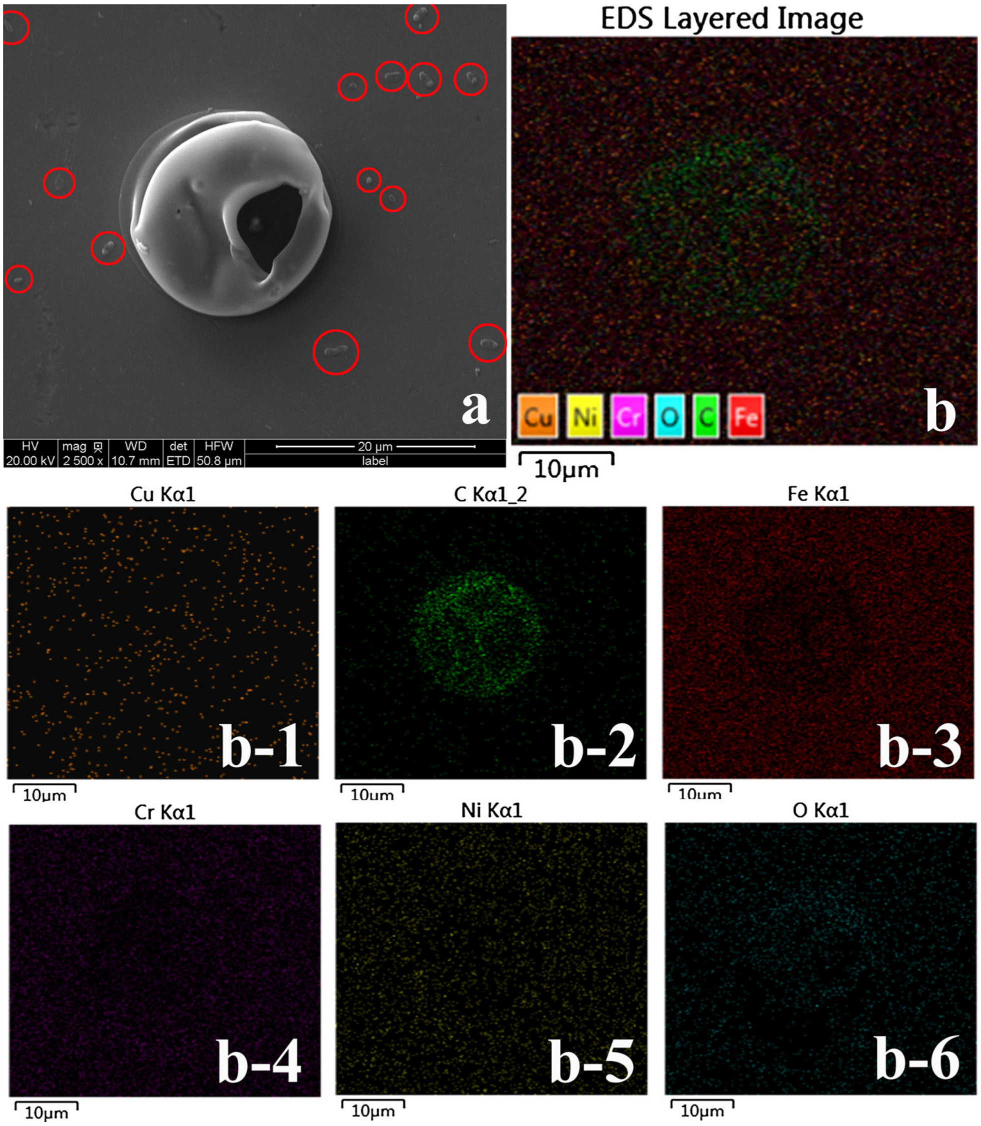


**Fig. 6** Antifouling mechanism and releasing features of Cu nanoparticles from the polyimide-Cu splats, (a) topographical view of the polyimide-Cu splat deposited on polished stainless steel after being incubated in bacterial seawater for 24 h, and (b) further EDS detection results revealing released copper from the polyimide capsule for antibacterial performances. The red circles highlight the typical bacteria attaching on the surface

seawater for 24 h, the percentage of bacterial removal strongly correlates with the concentration of Cu released from the capsules. Comparing to the *E. coli* attached on the polished stainless steel (Fig. 7b), the bacteria adhered on capsule structure exhibit abnormal shape and distinctive damage regime is suggested as a result of Cu-induced extinguishment (Fig. 7c and d). This further indicates that release of copper ions into the local environment is required for optimal antimicrobial activity. The results show that the polyimide-Cu splats can repel and kill bacteria at the same time.

It is realized that the polyimide and polyimide-Cu splats have 50-95% extinguishing efficiency against bacteria. Preliminary research on the antibacterial capabilities of nanomaterials has shown that nano-Cu particles release $Cu^{2+}$, in turn causing changes in local pH and conductivity. This liberation of metal ions into solution will then have the capability to inactivate or kill bacteria. $Cu^{2+}$ is also small enough to disrupt bacterial cell membrane and gains entry to disrupt enzyme function. Indirect effects through changes in the surrounding charge environment may also impact on the effectiveness of nanoparticulate metals against microorganisms (Ref 27, 30).

It is interesting to note that polyimide acts as binder entrapping copper particles, which is promising since this structural feature would facilitate constrained release of copper into physiological media for long-term functional services (Fig. 5b and 8). Excellent sterilization performances were further revealed for the enwrapped Cu in splats. Studies to assess the potential of nano-Cu embedded within a range of polymer materials have shown lower contact-killing ability in comparison with release-killing ability against MRSA strains (Allaker, Vargas-Reus and Ren, unpublished observations) (Ref 27). However, it seems clear that contact of the bacteria with the Cu-containing surface ruptures the membrane of the bacteria by contact-killing (Fig. 8). This enwrapped structure might

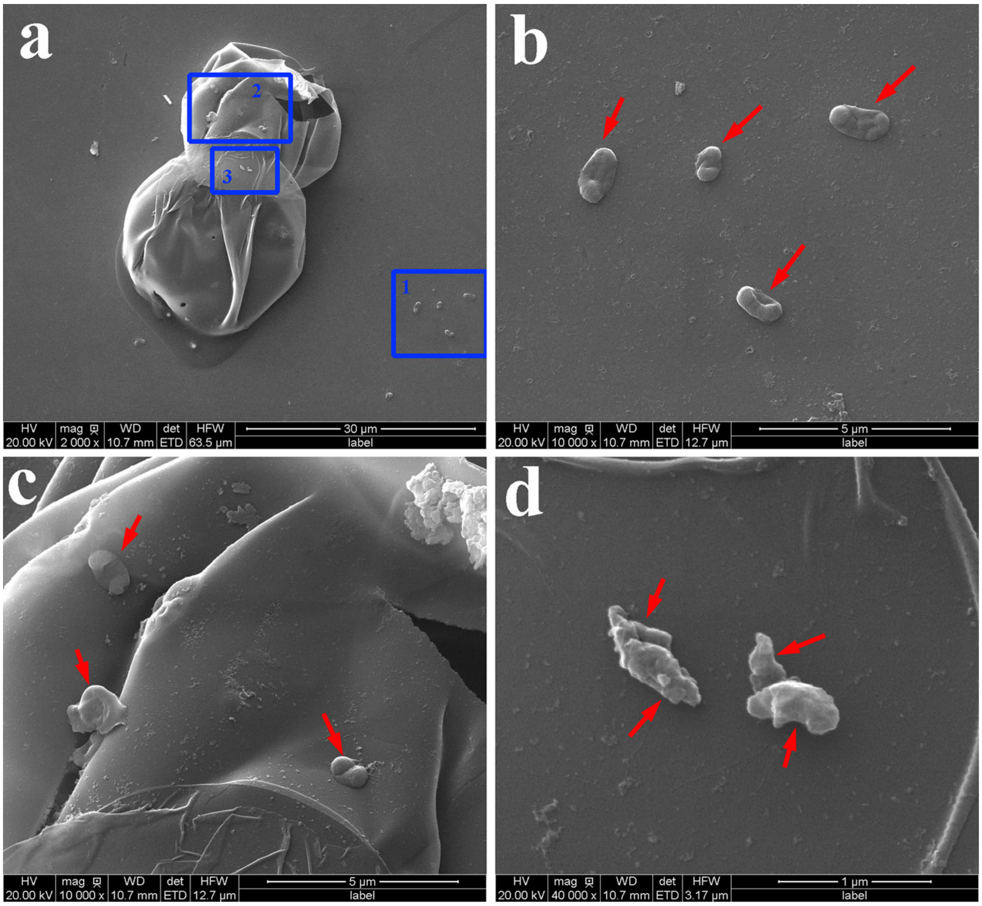


**Fig. 7** Characteristics of the adhered bacteria on the twin polyimide splats (a) showing release-killing mechanism, (b) enlarged view of the selected area 1 in (a), (c) enlarged view of the selected area 2 in (a) and (d) enlarged view of the selected area 3 in (a). The red arrows point to the bacteria seen on the top surfaces

offer a great opportunity to obtain effective and long-lasting antibacterial coatings.

Taking into account the releasing regime of copper from the splats and the antibacterial phenomena (Fig. 6, 7, and 8), two main mechanisms, namely biocide-releasing bacteria-killing and contact bacteria-killing, are suggested for the antifouling polyimide-Cu coatings. The dual-functional coatings showed high initial bacteria-killing efficiency due to the release of Cu ions and retained significant antibacterial activity with the depletion of embedded Cu particles. The cost-effective large-scale fabrication route for making the polymer-based antifouling layers sheds light on constructing marine antifouling coatings for long-term applications.

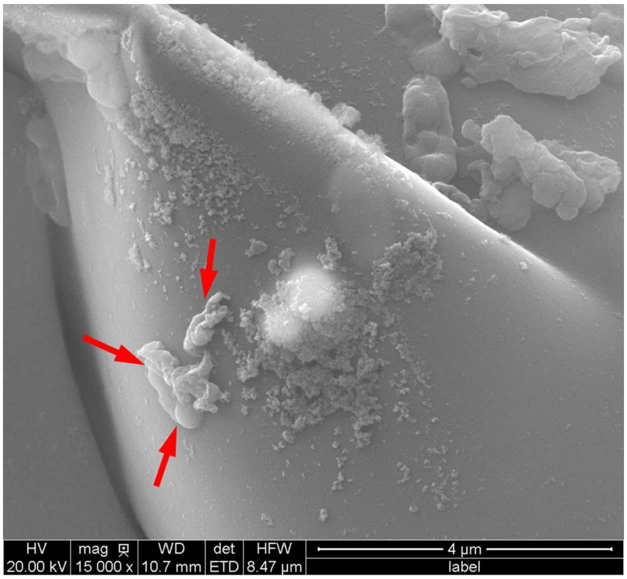


**Fig. 8** Antifouling properties of the enwrapped copper particles showing contact-killing mechanism. The red arrows point to typical dead bacteria seen on the splat surface

## Conclusions

Polyimide-copper splats have typical capsule structure with nano-copper biocides being enwrapped by polyimide shell have been fabricated by suspension flame spray. The polyimide splat exhibits hollow structure with a tiny hole on its top surface, offering splat the capability to release copper in a controllable manner. The capsule surface provides the coatings with contact bacteria-killing capacity through constrained release of enwrapped Cu particles, which are able to kill bacteria upon their contact. These structural characteristics would facilitate long-term antifouling functions. The results would give insight into thermal spray coating construction of organic–inorganic composites for desired functional applications.

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