



# Developing polyimide-copper antifouling coatings with capsule structures for sustainable release of copper



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## ABSTRACT

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 nanoparticles-containing dimethylformamide solvent. The polyimide splat exhibited hollow structure with an inner pore of 10–15  $\mu\text{m}$  and a tiny hole of 1–5  $\mu\text{m}$  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. After 1000 h exposure to the testing synthetic seawater, continuous release of copper from the coatings containing up to 30 wt%Cu kept remarkable. Antifouling performances of the constructed layers were assessed by examining colonization behaviors of typical bacteria *Bacillus* sp. and marine algae *Phaeodactylum tricornutum* and *Chlorella* on their surfaces. Distribution of the inorganic nanoparticles endows the polyimide coatings with special capsule structure and exciting hydrophobicity and antifouling performances. The liquid flame spray route and the encapsulated structure of the polyimide-Cu coatings would open a new window for designing and constructing environment-friendly marine antifouling layers for long-term applications.

## 1. Introduction

Any surface immersed in seawater is prone to the settlement of marine organisms, such as protein, bacteria, algae, or mollusks [1]. As a consequence, artificial marine infrastructures usually suffer from biofouling attacks throughout their services in the marine environment [2,3]. 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. However, due to complexity of the marine environment and diversity of the fouling species, universality and sustainability still remain as the two main challenges for man-made antifouling coatings. The antifouling technique based on the use of biocides has been the most widespread approach in modern maritime industries [4]. During the last decades, however, growing awareness of environmental issues pertaining to the use of biocides have triggered booming research efforts in searching green alternatives [5]. There is also a growing demand for surface protection techniques that meet the requirements of material durability and environmental sustainability.

Exciting research progresses have been made in recent years towards developing novel environment-friendly antifouling materials

and coatings, some of which have shown promising performances, for example nontoxic or green biocides [6–8], new organic matrixes [9,10], new embedding [11,12] and encapsulating technologies [13,14], photo-induced nanocomposites [15], and the antifouling structures mimicking natural hydrophobic surfaces [16]. Copper has been the most important alternative biocide since organotin compounds were banned. Various copper agents including copper metal, copper alloys, copper oxides, and copper compounds have been used as principal biocides for decades [17–20]. Regardless of the role copper plays as the essential element for marine organisms, it is still a big concern about its tolerable concentration, above which unexpected deterioration usually happens to marine species. Design and fabrication of smart coatings with appropriate structure for sustainable release of copper ions for long-term antifouling performances are therefore essentially required.

It is established that for biocides-involved antifouling techniques, effective prevention of fouling is usually achieved by controlled release of the biocides from matrix materials. Copper nanowire films and their incorporation into elastomeric polydimethylsiloxane exhibited the low levels of copper ions released after 50 days [19]. In addition, it was reported that chemically bound acrylated copper nanoparticles showed significantly reduced amount of copper ions leaching from functiona-

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lized Cu nanoparticles compared to nonfunctionalized biocides [20]. The major hurdle for widespread use of copper ions for antifouling applications is yet how to effectively control their release. Long-term sustainable release of the biocides is crucially influenced by matrix materials and physicochemical interaction of biocides with the matrix. For application in the marine environment, it is essential that matrix materials are stable in terms of anti-corrosion/wear in seawater, apart from the ease of making the biocides-containing structure.

To achieve constrained release of copper ions without deteriorating antifouling efficiency, the measures taken to incorporate copper into polymeric matrices are to be further explored. Due to their inert nature, polymers as surface coatings on metal surface could act as barrier resisting invasion of corrosive species and fouling organisms [21]. Among the polymeric materials developed for marine applications, aromatic polyimide attracted extensive attention owing to its excellent mechanical properties, superior thermal stability, good chemical resistance and processability [22,23]. To date, cross-linking is the most commonly used approach for fabrication of polyimide coatings [22]. As an alternative processing route, thermal spray in particular flame spray was proven successful in fabricating polymer coatings for its advantages of easy operation, cost efficiency, and capability of large-scale manufacturing [24,25]. However, fabrication by thermal spray of polymer-based composite coatings keeps challenging for spraying the polymers in the form of powder, due mainly to the difficulties in incorporating the additives like copper particles into polymeric matrix. Liquid flame spray that employs liquid as the starting feedstock for coating deposition has the potential for one-step fabrication of polymer-encapsulated composite coatings. Desired additives can be easily added into the liquid for subsequent deposition of the coatings with unique dispersion of the second phases. It is anticipated that liquid thermal spray approach provides controllable heat input for synthesis of polyimide during the spraying. To date, however, there are few reports available pertaining to thermal sprayed polyimide-based coatings, deposition mechanism of hollow capsules and related knowledge of polyimide coatings for marine antifouling applications is still lacking.

In this paper, liquid flame spray route was proposed for constructing copper-containing polymer coatings. Nano copper particles were added in polyimide precursor for subsequent synthesis of polyimide and coating fabrication. Microstructural features of individual polyimide-copper splats and coatings were characterized by focused ion beam technique and antifouling performances of the coatings were assessed by examining colonization behaviors of *Bacillus* sp. and *Phaeodactylum tricornutum* and *Chlorella*. This research provides a new processing route for large-scale fabrication of capsules with polymer as shell and inorganic particles as filler.

## 2. Materials and methods

### 2.1. Synthesis of polyimide and polyimide-Cu precursors

Kapton-type aromatic polyimide precursor solution was prepared by mixing monomer pyromellitic dianhydride (PMDA, 80,112,127 CP, Sinopharm Chemical Reagent Co. Ltd., China) and 4,4'-oxydianiline (ODA, 30049926CP, Sinopharm Chemical Reagent Co. Ltd., China) in dimethylformamide (DMF) solvent. For the polyimide-Cu suspension preparation, Cu particles with the size of ~300 nm were dispersed in DMF-ODA at room temperature with the stirring speed of 200 r/min for 5 h. Then PMDA was added into the above solution with an equivalent molar ratio to ODA. The polycondensation occurred at room temperature for 12 h and Poly (amic acid) (PAA) -Cu precursor solution was obtained. PAA-Cu solutions with different contents of Cu (0, 10 wt%, 20 wt%, and 30 wt%) were prepared. The synthesis of polyimide during flame spray was based on the chemical reaction shown in Fig. 1a.

### 2.2. Fabrication of coatings

The liquid precursor solution was atomized and injected into the oxygen-acetylene flame where the liquid phase was evaporated and thermochemical reactions were completed to produce coatings. The coating fabrication by the liquid flame spray is schematically depicted (Fig. 1b). During the spraying, the precursor suspensions were atomized by a home-made spray atomizer. The precursor feedstock injector with a diameter of 1.5 mm was positioned just next to the flame torch, and the angle between the injector and flame was 30°. Pressure of the atomizing air was 0.7 MPa. Prior to coating deposition, the grit-blasted carbon steel Q235 plates and 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 the flow rate of 1.5 Nm<sup>3</sup>/h and working pressure of 0.1 MPa. Pressure and flow rate of oxygen were 0.5 MPa and 2.5 Nm<sup>3</sup>/h respectively. The precursor feed rate was 40 ml/min and the spray distance was 200 mm.

### 2.3. Characterization of microstructure

Microstructure of the splats and the coatings was characterized by field emission scanning electron microscopy (FESEM, S4800, Hitachi, Japan). For further examination, focused ion beam (FIB) milling of the samples was performed in a FIB/scanning electron microscope dual beam system (Helios Nanolab 660, FEI, USA). Transversal cut of the samples was carried out at a stage tilt of 52°. A focused beam of Ga<sup>+</sup> ions was rastered across the specimen surface. Larger beam currents quickly milled away sections of material from the sample surface, while lower currents were used for polishing the milled surface. The samples were also analyzed by fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Fisher Scientific, USA) with the resolution of 4 cm<sup>-1</sup> and a scan range of 4000–400 cm<sup>-1</sup>. Release rate of copper ions from the coatings as a function of immersion time was also examined through measuring the concentration of copper ions in testing solution using inductively coupled plasma mass spectrometer (ICP-MS, NexION 300, USA). For the measurement, the coating samples were exposed with an area of 2 × 2 cm in artificial seawater (ASW) prepared according to the ASTM D1141–98 (2003). Wettability of the coating samples was assessed by measuring the contact angle of deionized distilled water droplets spreading on their surfaces using a contact angle measurement instrument (Dataphysics OCA20, Germany).

### 2.4. Antifouling testing

Antifouling performances of the coatings were assessed by examining formation of bacterial biofilm and colonization of algae on their surfaces. Marine *Bacillus* sp. (MCCC No. 1A00791) was 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 FePO<sub>4</sub> in 1000 ml deionized water. 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 10<sup>6</sup> CFU/ml at 25 °C under aerobic conditions. 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. Diatoms *Phaeodactylum tricornutum* (provided by Ningbo University, China) and green algae *Chlorella* sp. (provided by Ningbo University, China) were used in this study to further clarify the antifouling performances of the coatings. The microorganisms were cultured in artificial seawater-based culture media under sterile conditions at 20 °C. Adhesion of the algae on the surfaces of the samples for 1 week was inspected. After the fixation by 2.5% glutaraldehyde for 1 h, the samples were

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