

Facile approach of developing corrosion resistant superhydrophobic coating for copper

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ABSTRACT

A facile chemical route consisting of triethoxyoctylsilane modified SiO₂ nanoparticles (~ 25 nm) was used to develop superhydrophobic coating on copper (Cu) to inhibit corrosion. A Cu substrate of 1 × 1 cm² with a micron level pattern on its surface was produced using electrical discharge machine (EDM). The Piranha solution was used to produce micron-level uniform surface roughness on the Cu via chemical etching. A hierarchical micro and nano level roughness was created on the surface of Cu by immersing etched Cu in a solution of triethoxyoctylsilane modified SiO₂ nanoparticles. The micro-nano roughness on Cu was revealed by optical microscopy, AFM and FESEM analysis. The coated Cu displayed a water CA of 155° ± 2° with a SA of 4° ± 2° compared to uncoated Cu (CA = 97° ± 3° and SA = 47° ± 3°). EIS plots validated the corrosion inhibition performance of the coated Cu outperformed the uncoated Cu.

KEYWORDS: Corrosion resistance; Superhydrophobic coating; Cu; SiO₂ nanoparticles.

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1. Introduction

Copper (Cu) has been a well-known material to human beings since its discovery in 9000 BC. Copper is a soft, ductile, malleable metal with high thermal and electrical conductivity. Copper finds extensive use across various sectors including power transmission lines, electrodes, plumbing, spark plugs, cooking utensils, architectural applications, electrical wiring, refrigeration tubing heat exchangers and electronics industry, etc. [1]. In ordinary

conditions, copper is good against corrosion. But, under harsh environments, for instance in water pipelines and heat exchangers, corrosion of copper occurs because of impact of the environment that not only degrades the material but also ominously reduce its service life [2–4]. Currently, fabrication of superhydrophobic surfaces or coatings are preferred to protect variety of metals against corrosion [5–12]. In recent years, the outstanding water repellence of superhydrophobic

coatings were explored using different strategies and variety of materials [6,8]. The chemical etching, laser deposition, electrodeposition, chemical vapor deposition, sol-gel, self-assembling, and mussel-inspired chemistry are the popular techniques for the synthesis of superhydrophobic coatings, but these methods have merits and demerits [6,8].

Inspired by these techniques, a facile approach consisting of wire EDM, chemical etching and solution immersion was employed in this study to develop corrosion resistant superhydrophobic coating for copper metal. The promising outcomes regarding the superhydrophobic and corrosion-resistant properties of the newly created coating hold significant potential for safeguarding metals.

2. Experimental

The schematic process of producing superhydrophobic Cu is shown in **Fig. 1**. Micro-patterned Cu of $1 \times 1 \text{ cm}^2$ was produced by cutting it from bulk metal using wire EDM (Ezeewin). The micro-patterned Cu substrate was polished with sandpapers of 400–1200 Grit and ultrasonically cleaned

in acetone. Then Cu was chemically etched in a Piranha solution consisting of 7:3 ratio of conc. H_2SO_4 (98%) and H_2O_2 (30%) at 40°C for 10 min. The etched copper was rinsed multiple times with deionized water and then left to dry under ambient conditions. Triethoxyoctylsilane functionalized SiO_2 nanoparticles ($\sim 25 \text{ nm}$, Reinste Nano Ventures, Pvt. Ltd., India) [13] were dispersed in ethanol via a probe ultrasonication for 1 h. The Cu was dipped into the functionalized nanoparticle solution for 15 min and subsequently heat-treated at 400°C for 2 h to achieve a superhydrophobic coating.

The morphology of samples was characterized using Nikon Eclipse MA200 optical microscope, FESEM (Quanta 200F, FEI, USA) and AFM (NT-MDT, Ntegra). Wettability was assessed with a drop shape analyzer (DSA 100, Krüss GmbH, Germany). Polarization curves were obtained using an electrochemical workstation (CHI 660E, CH Instruments, USA), with the samples immersed in a 3.5% NaCl solution. Impedance spectroscopy frequency ranged from 200 kHz to 50 MHz, with a sinusoidal wave amplitude of $\pm 5 \text{ mV}$.

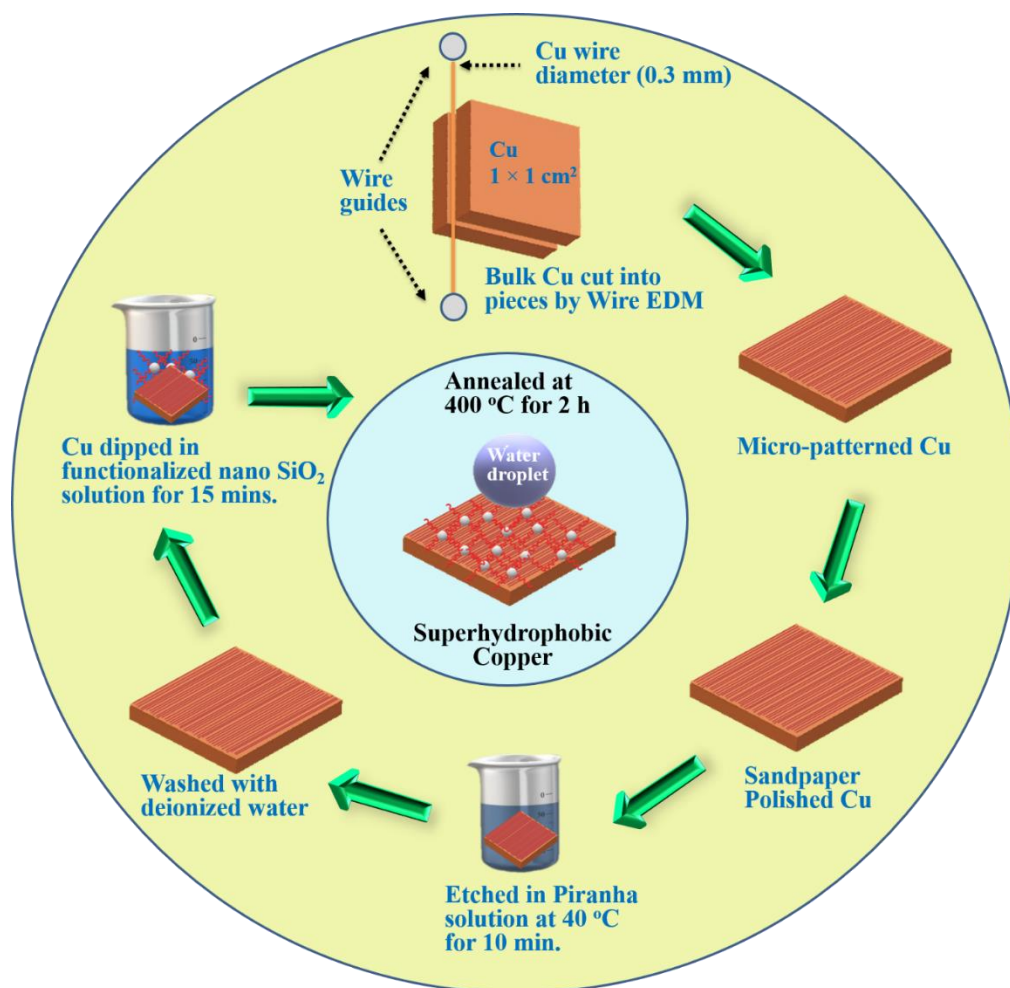


Fig.1. Graphical process of producing superhydrophobic Cu.

3. Results and Discussion

Fig. 2 displays optical images of polished, etched, and coated Cu substrates at various magnifications. Insets within **Fig. 2** illustrate water contact angles (CAs) on polished, etched, and coated Cu substrates. The polished Cu substrate exhibits a uniform surface but with some large size scratches and voids. However, the polishing of the Cu substrate using sandpaper completely cleaned wire EDM created micro pattern and results in generation of some scratches and voids on the surface (**Fig. 2(a, b)**). The hydrophobic nature of the polished Cu substrate was evidenced by a water contact angle of 97° (as shown in the inset of **Fig. 2a**). Chemical etching of Cu, observed at low magnification, displayed a distinct surface with uniform roughness (**Fig. 2c**). The presence of unetched Cu is revealed by bright spots on the surface. However, the

higher magnification image of Cu shows the clear etching of the surface (**Fig. 2d**). The surface shows large size uniform grains of etched Cu. The unique morphology and uniform surface roughness lead to a noteworthy improvement in the water CA from 97° to 140° (inset of **Fig. 2c**). The coating on etched Cu surface notably changed the morphology and exhibits smooth and shiny surface (**Fig. 2(e, f)**). The water CA of coated Cu significantly improved to 155° (inset of **Fig. 2e**) compared to the CA of polished and etched Cu surface. This phenomenon likely occurred because of the silanized SiO_2 nanoparticle coating, which decreased the surface energy of the Cu surface and generated a hybrid micro-nano roughness. Thus, the wetting behavior of Cu can be easily regulated with the help of developed technique [14–17].

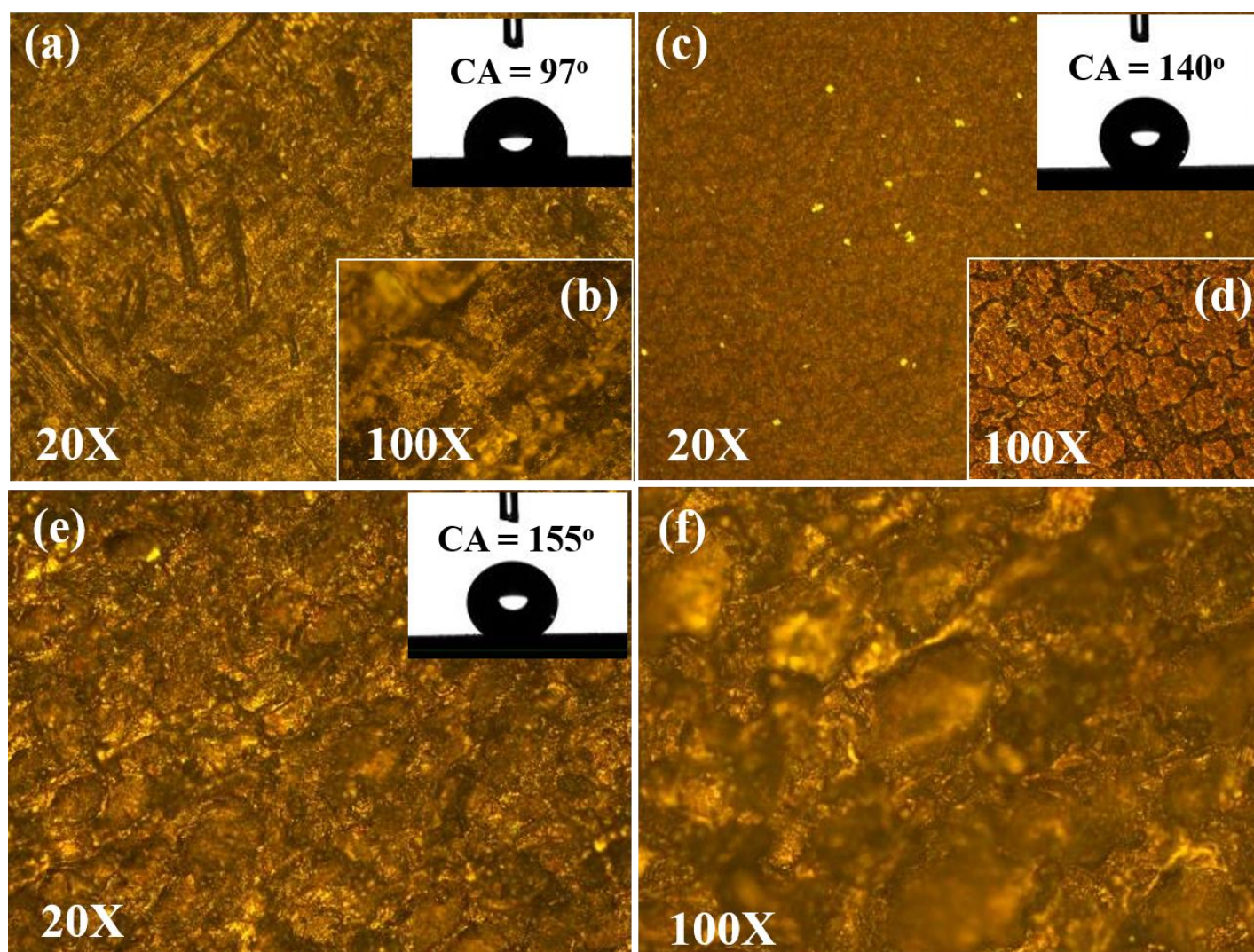


Fig. 2. Optical images of (a, b) polished Cu, (c, d) etched Cu and (e, f) coated Cu at different magnifications with respective water CAs (insets (a), (c) and (e)).

To unveil the hybrid micro-nano roughness, the coated Cu surface underwent additional characterization through FESEM and AFM. **Fig. 3(a, b)** presents FESEM images of the coated Cu at various magnifications. The coated surface exhibits high roughness including the existence of SiO₂ nanoparticles and their clusters as micro particles.

The 2D and 3D AFM images in **Fig. 3(c, d)** showcase the topography and surface roughness profile of the coated Cu. These images unveil uniformly distributed nanoparticles with few agglomerates of silica particles on the coated Cu, affirming the existence of hybrid micro-nano roughness

responsible for its superhydrophobicity. **Table 1** outlines the correlation between the average surface roughness (R_{avg}), water contact angle (CA), and sliding angle (SA) of polished, etched, and coated Cu samples.

The coated Cu surface exhibits maximum R_{avg} (140 nm), but polished Cu shows minimum R_{avg} (70 nm), while etched Cu shows the R_{avg} (100 nm) in-between [18]. The water CA monotonically increases with the increase of R_{avg} [19–21], while SA decreases with increase of roughness and is in close agreement with the literature [22,23].

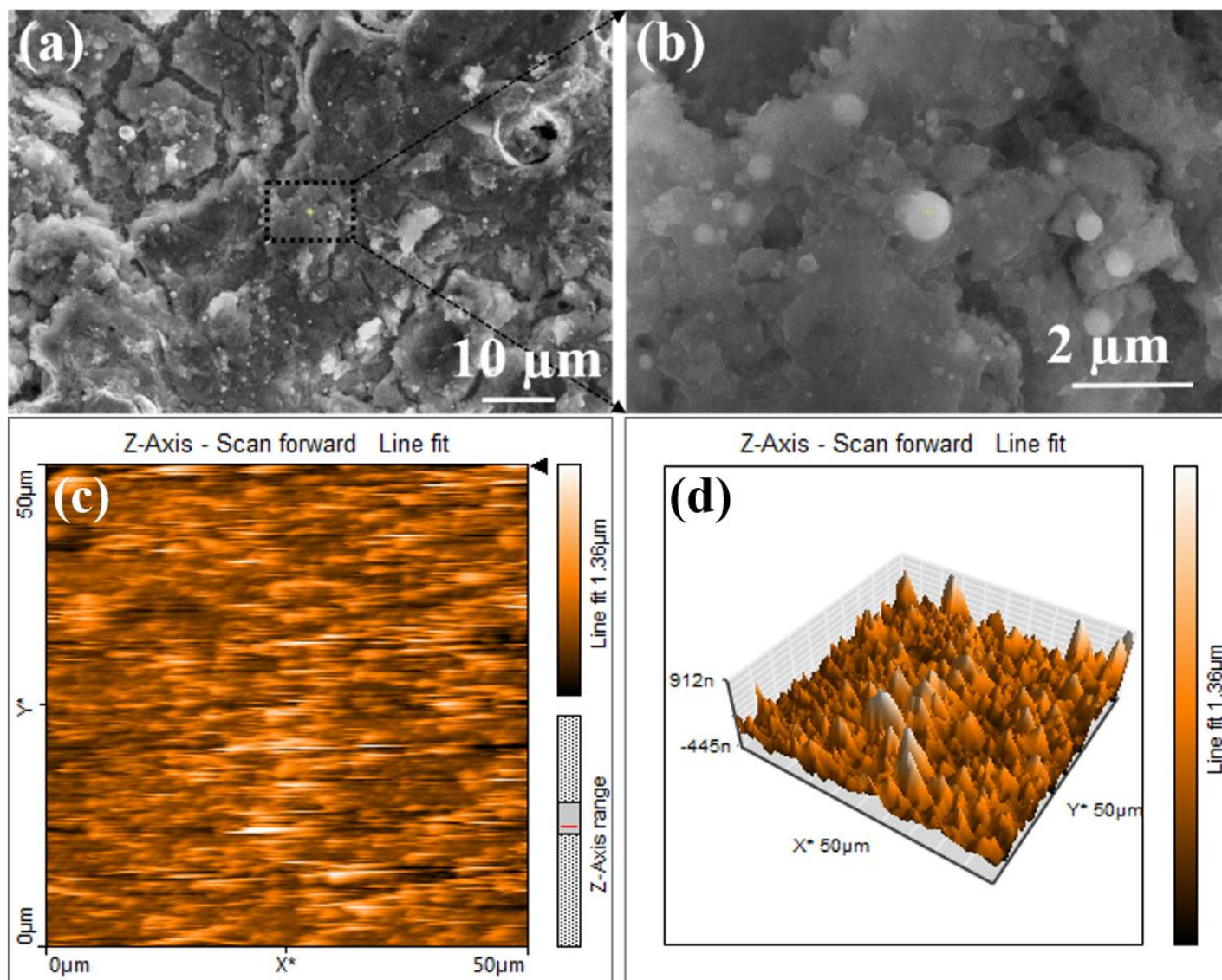


Fig. 3 (a, b). FESEM images of coated Cu and (c) 2D and 3D (d) AFM images of coated Cu.

Table 1. The relation between R_{avg} , CA and SA of the polished, etched, and coated Cu.

Sample Name	Avg. Roughness, R_{avg} (nm)	CA (°)	SA (°)
Polished Cu	70	$97^{\circ} \pm 3^{\circ}$	$47^{\circ} \pm 3^{\circ}$
Etched Cu	100	$140^{\circ} \pm 4^{\circ}$	$12^{\circ} \pm 4^{\circ}$
Coated Cu	140	$155^{\circ} \pm 2^{\circ}$	$4^{\circ} \pm 2^{\circ}$

The corrosion resistance of both uncoated and coated Cu samples was assessed by dipping them in a corrosive salt solution (3.5% NaCl) for a minimum of one month. **Fig. 4** illustrates optical images of uncoated and coated Cu after dipping in the corrosive salt solution. The surface of uncoated Cu is completely corroded (**Fig. 4a**), but coated Cu seems almost corrosion free (**Fig. 4b**). However, some spots on the coating can be seen which indicates some sort of damage to the coating. **Fig. 4(c)** displays a nearly spherical water droplet resting on the coated Cu after undergoing a one-

month corrosion test, demonstrating the efficacy of the coating. The water CA of the coated Cu was almost 20° declined after the corrosion test and exhibit CA of $\sim 135^{\circ} \pm 3^{\circ}$, which is in close agreement with the literature. It infers that the prepared coating for Cu is quite effective to control the corrosion. In **Fig. 4(d)**, the coating's resilience to a water jet test is depicted. The rebounding of water droplets from the surface provides a distinct indication of the coating's enduring hydrophobicity, even following the corrosion test.

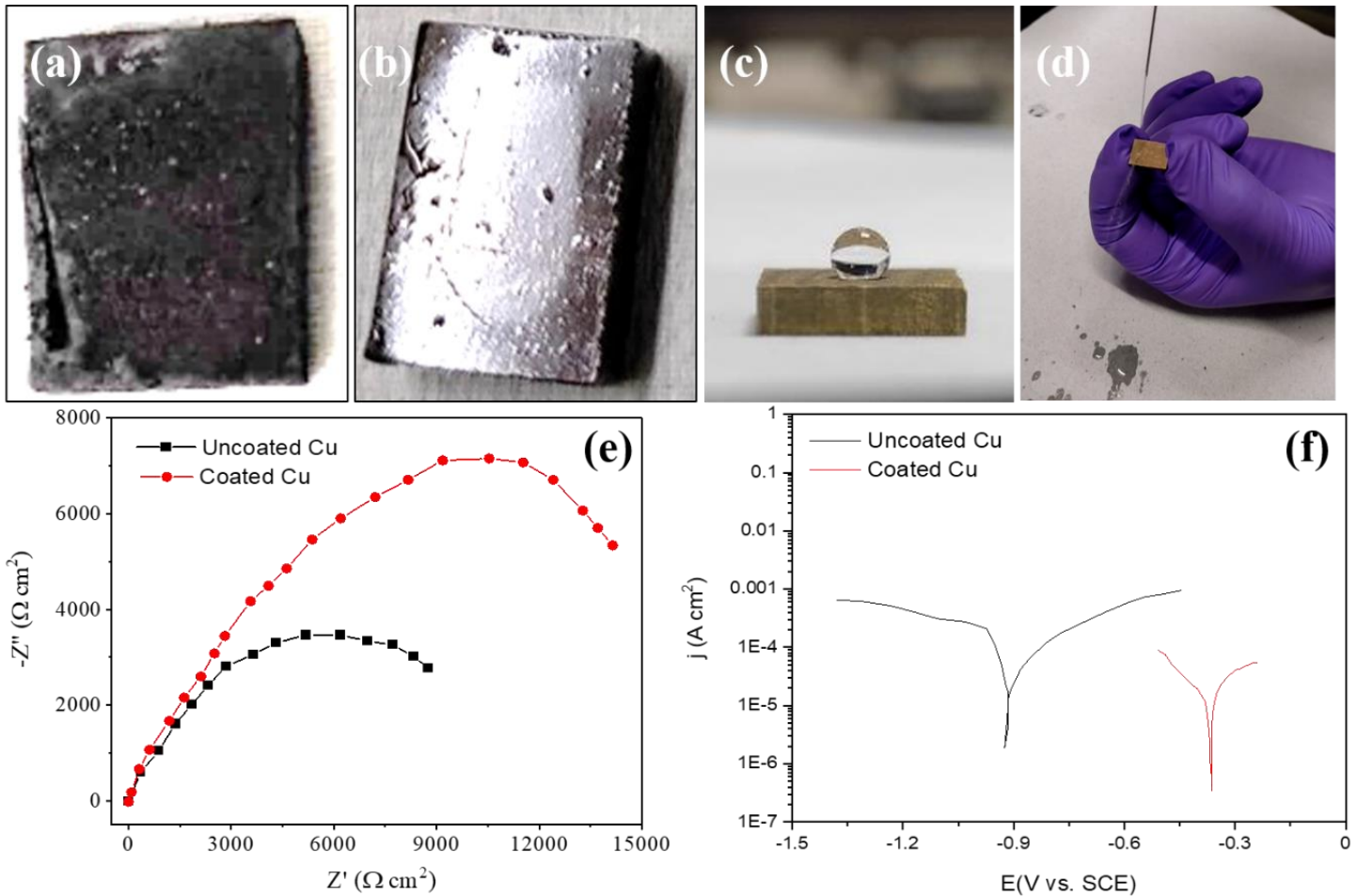


Fig. 4. Optical images of (a) uncoated Cu and (b) coated Cu after immersion in 3.5% NaCl solution after undergoing a one-month corrosion test. Image of (c) water droplet and (d) water jet test on Cu substrate after corrosion test. (e) Nyquist and (f) potentiodynamic polarization curves of uncoated and coated Cu.

The Nyquist plots illustrate that the impedance of the coated Cu is significantly greater than that of the uncoated Cu, as depicted in **Fig. 4e**. The higher impedance is a clear indication of enhanced corrosion resistance of the coated metal [24,25]. Comparatively high E_{corr} and low current density (I_{corr}) observed in the polarization curves of coated Cu indicate enhanced corrosion resistance compared to uncoated Cu, attributable to the superhydrophobic coating (**Fig. 4f**). The presence of this coating prevents moisture from encountering the metal substrate [26,27].

In general, for coated metals, low corrosion rate is indicated by low value of I_{corr} . The layer of silica particles acts as a coupling element to shield metals against corrosion. The silica particle-based layer possesses the capability to form Si-O metal bonds on the metal surface, thereby decreasing the corrosion rate by regulating the corrosion reaction [28]. Furthermore, the superhydrophobic layer is accountable for decreasing both cathodic and anodic currents while elevating the corrosion potential (E_{corr}) [29,30]. Therefore, the silica particle-based hybrid micro-nano superhydrophobic coating can avoid the corrosion of metals in a corrosive environment.

4. Conclusions

A superhydrophobic corrosion resistant coating, based on silanized SiO₂ nanoparticles, was synthesized through a solution immersion method. FESEM and AFM analysis validated the existence of micro-nano hierarchical roughness, essential for attaining superhydrophobic properties. The initially hydrophobic Cu (with a CA of $102^\circ \pm 4^\circ$) was effectively transformed into a superhydrophobic Cu (with a CA of $152^\circ \pm 2^\circ$). Electrochemical impedance spectroscopy illustrated that the coated metal exhibited superior corrosion resistance compared to uncoated metal. Consequently, following thermal and mechanical performance testing, this corrosion-resistant superhydrophobic coating holds promise for applications within the metal industry.

Disclosure statement

The authors declare no relevant financial or non-financial interests.

Data availability

Raw data of the research article is available with the authors and will be provided as per a request from the journal.

Ethical approval

Not applicable.

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