Hydrophobization of Metal Surfaces by Covalent Grafting of Aromatic Layer via Aryldiazonium Chemistry and Their Application in the Fabrication of Superhydrophobic Surfaces

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Superhydrophobic surfaces were prepared on iron and zinc plates by means of displacement deposition of copper and subsequent attachment of aromatic layers via diazonium chemistry.

Recently, fabrication of superhydrophobic surfaces on polymers, glasses, metals, and carbon nanotubes had been attracted intensive interest in scientific and industrial communities.[1] Generally, artificial superhydrophobic surfaces were fabricated by coating low-surface-energy materials onto solid substrates with appropriate roughness.[2] Up to now, the tailoring of the roughness of solid surfaces could be achieved by using techniques such as anodic oxidation,[3] electrodeposition,[4] chemical etching,[5] plasma etching,[6] laser treating,[7] electrospinning,[8] chemical vapor deposition,[9] sol–gel processing,[10] electroless deposition,[11] and so on.

Despite numerous studies focused on the control of solid topographies, the materials used to tune the surface-energy of rough substrates were mainly limited to fluorinated silanes and thiols. To fabricate superhydrophobic surfaces, these fluorinated compounds were deposited onto solid substrates either by spin coating[12] or by forming self-assembled monolayer (SAM). In the former cases, only weak interactions are present between the coatings and the substrates. For the later, the range of substrates on which SAM can be formed is limited, however, by the stability of the bonds between substrates and SAM. For engineering metals such as iron and zinc the bonds formed from thiols and silanes are quite weak and unstable, making this method of little practical use. Therefore, it is desirable to establish a general approach that is less dependent on the surface chemistry of substrates, and that strong bonds can be formed between the substrates and the surface coatings.

In the past decade, covalent attachment of aromatic layers to carbon,[13] metal,[14] and semiconductor[15] surfaces via reduction of aryldiazonium salt to the corresponding radicals has been extensively reported.[16] The covalent bonds between the substrates and aromatic layers were found stronger than those obtained for surface modification by self-assembly.[17] Nevertheless, the procedure has rarely been employed to the construction of superhydrophobic coatings on rough substrates.

Here, we fabricate superhydrophobic metal surfaces by spontaneous grafting of aromatic layer onto iron and zinc plates via diazonium chemistry. The rationale involves the displacement deposition of copper on iron or zinc plates for a few minuets, and subsequent dipping the plates in an acetonitrile solution of 4-tetradecylbenzene diazonium fluoroborate. The entire process is performed under ambient conditions using readily available starting materials and laboratory equipment.

The wettability of the as-prepared metal plates was evaluated by means of water contact angle (CA) measurements, as shown in Figure 1. The metal surfaces have CA values of about 160°, and their sliding angles are lower than 4°. Then, the metal plates were immersed in water for several hours to study their durability and no change in the water contact angle was observed. To evaluate the long-term stability of the superhydrophobic surfaces, the contact angles of the plates were recorded at different time intervals. After storage in air for 1 month, the water CA and sliding angle of the plates remain constant. More interesting, the metal surfaces also show superhydrophobicities in aqueous NaCl solutions. The contact angles of the metal plates remain in the scope of 156–160° when the concentration of NaCl varied from 0.01 to 2 M. These results are very important for the application of the superhydrophobic metals in marine fields where salt influence is unavoidable.

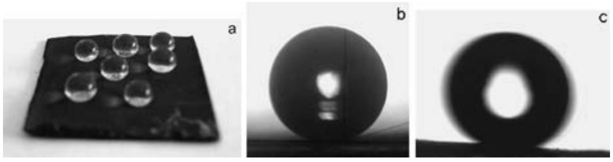

Figure 1. Water drops on the surfaces of superhydrophobic iron plates. c) is a water drop on the surface tilted at 4°. Images recorded on similarly coated zinc plates were identical.

Evidence for the presence of aromatic layers on the metal surfaces is confirmed by FT-IR spectra and XPS measurements. The survey XPS spectra of the resulting metal plates clearly show that a dramatic increase in the relative intensity of C1s and O1s peaks is observed after reaction with the aryldiazonium salt, while the intensities of the metal peaks decrease significantly. In addition, a noticeable increase in the background of XPS patterns indicates the presence of the inelastic scattering of the photoelectrons arises from organic layer. However, the characteristic peaks of diazonium salt[18] are no longer observed after rinsing treatment.

In order to determine if any part of the XPS signals originates from the carbon–metal bond, the C1s spectrum of the iron plate is fitted with three components at 285.0, 284.5, and 283.2 eV (Figure 2). The first two components are attributed to the carbon of aromatic rings.[19] The component at 283.2 eV can be assigned to the carbon–metal bonds according the result of Pinson et al. performed on several metals modified by the same

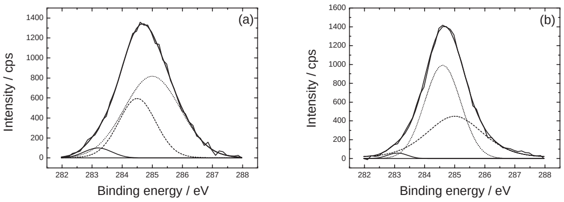

Figure 2. C1s spectra of the iron (a) and zinc (b) plates covered with aromatic layers.

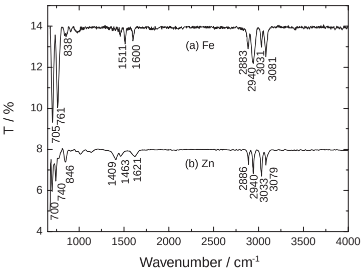

Figure 3. FT-IR spectra of the iron (a) and zinc (b) plates covered with aromatic layers.

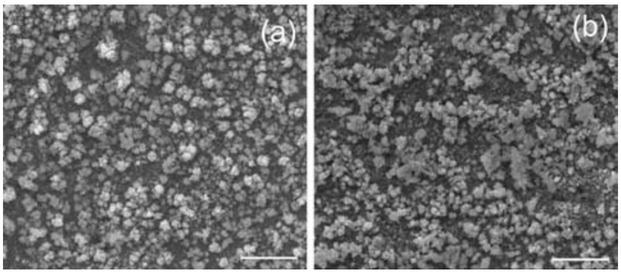

Figure 4. Scanning electron microscopy images of copper deposited on the surfaces of (a) iron and (b) zinc. The scale bar is 5 µm.

approach.[20] The reason for the assignment of such a component lies in the fact that the low binding energy side of the C1s signal exhibits indeed a slight shoulder around a position corresponding to a carbide species.[21] In the case of zinc plate, the C1s peak is also fitted with a carbon–metal component at a low binding energy of 283.1 eV, together with two components at 284.6 and 285.0 eV.

FT-IR spectra in Figure 3 show the C=C stretching modes of aromatic ring between 1500 and 1600 cm^{-1}, and the aromatic C–H bending modes at 740–760 and 830–850 cm^{-1}. The vibration bands associated with methylene C–H and aromatic C–H are observed at 2880–2940 and 3030–3080 cm^{-1}, respectively. The absence of a diazonium band at 2269 cm^{-1} and the aromatic C–N band between 1174 and 1349 cm^{-1} confirms the complete removal of the diazonium group upon rinsing.

The superhydrophobicities of the metal plates are considered to originate from the binary roughness of the copper deposited, as shown in Figure 4. The copper deposited on zinc and iron surfaces are clusters with diameters of about 1 µm, and each cluster is composed of 60 to 200 nm particles, indicating the presence of binary structures at both micro- and nanometer scales. As a result, the rough surfaces together with low-surface-energy aromatic layers are responsible for the superhydrophobicities of the metal plates.

In conclusion, we have fabricated superhydrophobic metal surfaces with high water contact angles, low sliding angles, and long-term stability by displacement deposition and diazonium chemistry. Owing to the diversity and reactivity of aryldiazonium salts, the method offers an alternative and efficient strategy for the hydrophobization of various solid surfaces by forming strongly bonded aromatic layers, especially in the case where thiols and silanes should be avoided. In addition, spontaneous grafting of aryl groups by simple dipping substrates in a solution of diazonium salt also enable us to tune the surface energy of the object of any size or shape.

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