



Sol-gel route for the building up of superhydrophobic nanostructured hybrid-coatings on copper surfaces



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ARTICLE INFO

Article history:

Received 12 March 2015

Revised 15 June 2015

Accepted in revised form 17 June 2015

Available online 19 June 2015

Keywords:

Thin film

Hybrid coating

Flower-like alumina

Superhydrophobicity

Copper oxides

Wettability

ABSTRACT

A wet chemical route is herein presented with the aim of building up a superhydrophobic coating on copper (Cu). A thin film of *flower-like* alumina – obtained by sol-gel – was deposited and combined with fluoroalkylsilane moieties, resulting in a hybrid coating with excellent repellence to water (static contact angle of $179 \pm 1^\circ$) and self-cleaning properties (contact angle hysteresis of $5 \pm 1^\circ$). The wetting performances were strictly related to the peculiar morphology of the coating's inorganic component and to the chemistry of the outer organic layer. The combination of the nanometric alumina lamellas with the micrometric roughness of sandblasted Cu surface proved to be essential to the formation of the hierarchical scaled structure allowing superhydrophobicity. However, the surface extension of alumina layer and its functional effectiveness were threatened by Cu oxides occasionally formed during the annealing steps necessary to stabilize the coating. Field emission-scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS) analyses of the surfaces, in fact, revealed the simultaneous presence of different chemical species and morphologies. Grains with cube-like aspect (attributable to Cu_2O) were formed on coated surfaces thermally treated at 200–300 °C, while microwires of CuO appeared at higher temperature. Once the thermal conditions are carefully tuned and the temperature kept not higher than 200 °C, it is possible to limit the presence of Cu oxides which, in turn, means preserving a high level of performances, also avoiding brittleness phenomena and keeping unchanged the surface optical properties. The coating's stability and the maintenance of superhydrophobicity were preliminarily investigated following the water contact angle evolution after immersion of samples in ethanol in an ultrasonic bath.

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1. Introduction

Copper is a very interesting, fully recyclable material showing a great variety of properties (e.g. good electrical and thermal conductivities, alloyability, malleability, corrosion resistance, etc. [1]) which makes it suitable for many different applications in energy conversion, heating and cooling processes, electronic devices, and so on [2–4]. Among the different possibilities in terms of further innovative purposes for copper, the control of wettability is receiving great attention as a powerful tool to improve the efficiency, and to limit the reactivity and the interactions with the environment of whole devices or single components. Just to mention some examples, recently it has been shown that the enhanced water repellence of Cu components in heat exchangers might lead to a significant increase of their efficiency [5,6]. On hydrophobic Cu, in fact, vapor condenses by forming droplets (dropwise condensation mechanism) not spreading on the surface but rolling off very easily. Consequently, the heat transfer between Cu surface and air is quicker

and more efficient, as it is not hindered by the presence of the liquid film. However, notwithstanding the innovative solutions that are strongly fostered, the feasibility of the industrial realization of Cu engineered surfaces and devices still needs to be deeply understood as well the material's ability to last over time [7].

Anyway, the *hydrophobization* of Cu surfaces by coating deposition is one of the key issues for many authors and in this regard the number of papers is increasing year by year. In general, scientific papers deal with organic, inorganic or hybrid coatings able to provide surfaces with low water wettability, presenting water static contact angle (WCA) higher than 150° (superhydrophobic materials) [8]. Superhydrophobic organic-based coatings can be fabricated by the self-assembled monolayer (SAM) technique [9,10], even if their durability in working conditions is not usually reported. Inorganic and hybrid superhydrophobic coatings can be considered an alternative to the previous ones and their distinctive characteristic is the need for thermal treatments as a necessary tool to their stabilization. Generally, the preparation of inorganic and hybrid copper-based coatings on Cu involves wet or dry treatments to build up microstructural features made up of single or mixed Cu oxides (CuO , Cu_2O) or hydroxide ($\text{Cu}(\text{OH})_2$), and, for hybrid coatings only, addition of an outer low surface energy layer (mostly fluoroalkylsilane, silanes, long-chain organic acids, etc.).

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An example of a fully-inorganic superhydrophobic coating on Cu was reported by Lee et al. [11], who treated copper foils by an oxidizing and a subsequent reducing atmosphere, leading to cuprous oxide (Cu_2O) whose peculiar morphology, coupled with its superhydrophobic nature [12], was responsible for WCA of about 160° . Regarding cupric oxide (CuO), the wetting behaviour is completely different. Its intrinsic hydrophilic nature, in fact, requires a proper combination with an organic compound to obtain hydrophobicity through hybridization [13]. The most common method to let Cu oxides grow on surfaces is thermal oxidation, while the control of their morphology is achieved by setting temperature, oxygen content and annealing time [14]. CuO forms above $200\text{--}250^\circ\text{C}$, Cu_2O is observed at lower temperature ($150\text{--}200^\circ\text{C}$), while they may coexist at intermediate temperatures.

Another common method for constructing hybrid superhydrophobic coatings is represented by successive ionic layer adsorption and reaction (SILAR), a type of chemical bath deposition (CBD) technique [15–19]. In this case, $\text{Cu}(\text{OH})_2$ nanoribbons are formed and then easily converted to CuO by dehydration while preserving the morphology. The subsequent hybridization with a low energy compound allows for reaching superhydrophobicity.

In the literature many examples of superhydrophobic Cu-based hybrid coatings have been reported. Zhang et al. [20] prepared CuO nanowires by thermal oxidation of thin porous copper foils, then they reached superhydrophobicity by adding a fluoroalkylsilane layer (WCA = 162°). Nam and Ju [21] synthesized superhydrophobic Cu surfaces (WCA = 170°) by treating thin copper foils in hot alkali solutions, or by subjecting them to thermal oxidation process, followed by spin-coating a 2 wt.% teflon solution. Huang and Leu [22] prepared superhydrophobic Cu (WCA = 150°) by dipping metal foils in a 30 wt.% hydrogen peroxide solution, followed by rinsing in deionized water, drying, heating at 60°C and spin-coating of teflon. Zhang et al. [23] prepared Cu foils with WCA = 161° by immersion in a hot basic solution (0.06 M $\text{K}_2\text{S}_2\text{O}_8$, 3.0 M NaOH) followed by subsequent dipping in an organic solution (5 wt.% lauric acid in ethanol).

Generally, all these methods are more complex and time-consuming than direct wet or dry substrate oxidation and further they imply the use of materials other than copper [24–26].

With this outcome, we present hereafter a route to superhydrophobic Cu surfaces bearing a hybrid coating obtained by sol–gel synthesis, with the optimization of the corresponding deposition process. Sandblasted Cu foils were dip coated into an alumina sol and thermally treated in order to generate a porous nanostructured inorganic layer. Then, the hybridization was achieved by treatment with a commercial fluoroalkylsilane solution, which chemically links to the inorganic underlying Al_2O_3 film. The best performing samples were obtained when thermal annealing was carried out at temperatures not higher than 200°C , since these conditions limit the degree of Cu oxidation and preserve the adhesion of the Al_2O_3 thin film to the substrate. The whole technology, which has already been described in a previous work dealing with the functionalization of aluminum [27], was revealed to be suitable to be applied to Cu under controlled conditions, overcoming the limitations relative to substrate reactivity. Outstanding values of WCA approaching the limit of 180° and CAH lower than 4° (to this extent not yet reported in the literature) were obtained, also involving a good stability of performances.

2. Experimental

2.1. Preparation of the alumina sol

Alcoholic alumina sol was prepared according to the literature [27, 28]: aluminum-tri-sec-butoxide (97%, Sigma-Aldrich) was stirred in isopropyl alcohol (99%, Sigma-Aldrich) for 1 h at room temperature. Then, ethyl acetoacetate (>99%, Sigma-Aldrich) as the chelating agent was added and the solution was stirred for 3 h. Finally, water was gradually added to the solution to promote the hydrolysis of the alkoxide.

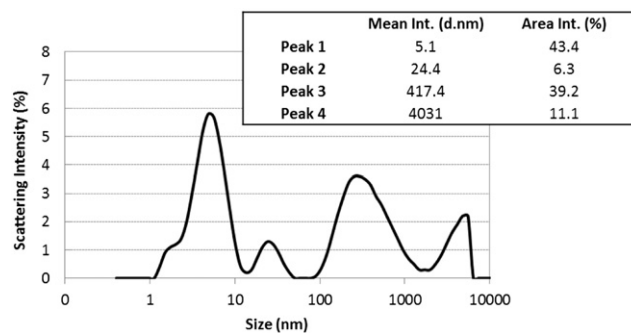


Fig. 1. DLS spectrum of alumina sol showing a multimodal size distribution. Mean size values for each peak and corresponding scattering intensity percentages are reported in the in-set table.

The molar ratios of isopropyl alcohol, chelating agent and water with respect to Al were set, respectively, to 20, 1 and 4. Particle size distribution of the alumina suspension, in terms of hydrodynamic diameter, was evaluated by dynamic light scattering (DLS) analyzer (Zetasizer Nano S, Malvern Instrument) working in the backscattering modus (2θ equal to 173°) at 25°C . The alcoholic-based sol showed a multimodal particle size distribution (Fig. 1). The peak with the highest scattering intensity is centered at 5 nm with smaller amounts of aggregated particles.

2.2. Deposition of the hybrid coating on copper

Before deposition, Cu (99%) foils ($100 \times 50 \times 1.5$ mm of dimensions) were sandblasted to improve their roughness and to promote the coating's adhesion. In order to degrease the surface and to remove possible scraped residues, foils were then cleaned by sonication in soapy water and afterwards in ethanol. Samples were dip-coated with the alumina sol with a dipping–withdrawing speed of 2 mm/s and a permanence time of 5 s. After drying at room temperature, they were thermally treated at 200°C , 300°C and 400°C for 60 min to get an amorphous Al_2O_3 thin film, then immersed in boiling water for 30 min to form flaky bohemite, and thermally treated again (10 min) to stabilize the inorganic film. As a final step, a commercial fluoroalkylsilane (FAS) solution (Dynasylan® SIVO CLEAR EC, Evonik) was dip-coated on the underlying Al_2O_3 layer (dipping–withdrawing speed: 2 mm/s, permanence time of 120 s), followed by consolidation at 150°C for 30 min [28]. The resulting samples have been labeled, respectively, as C200, C300 and C400 (Table 1).

In order to analyze the contribution of substrate roughness and to allow the calculation of solid–liquid and air–liquid interface fractions

Table 1
Cu sampling according to the different process conditions.

Sample	Sandblasting	Al_2O_3 coating	Annealing T ($^\circ\text{C}$)	FAS coating
U200	*	–	200	*
U300	*	–	300	*
U400	*	–	400	*
C200	*	*	200	*
C250	*	*	250	*
C300	*	*	300	*
C400	*	*	400	*
S200	–	–	200	*
S300	–	–	300	*
S400	–	–	400	*
SC200	–	*	200	*
SC300	–	*	300	*
SC400	–	*	400	*

* = performed; – = not performed. FAS = fluoroalkylsilane commercial solution.

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