Electronic Supplementary Information (ESI)

Patterned tailored hydrophobic films designed by synergy effect of electrochemical deposition and chemical deposition

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Content

SI1. Experimental details

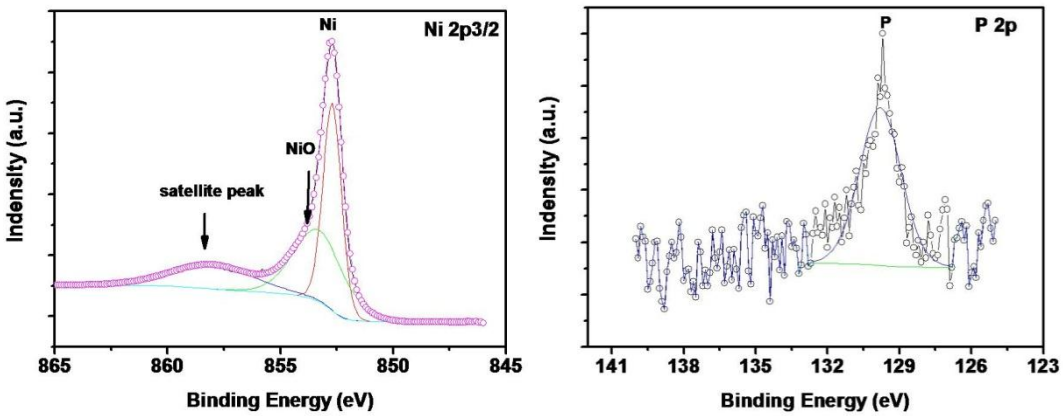
Experiments

The deposition of superhydrophobic coatings was carried out at the current density of 150 mA/cm^2 on low alloy steel substrates from electrolytic bath containing 0.125 mol/L $NiSO_4$•$6H_2O$, 0.05 mol/L NaH_2PO_2, 0.05 mol/L citric acid, 1.2 g/L sodium dodecyl sulfate (SDS), and 0.075g/L 2-Butyne-1,4-diol. And the concentration of Na_2SO_4 was adjusted to 0.3 mol/L to enhance the electrolyte's ion strength. The pH value of electrolyte was adjusted by the aqueous ammonia to 5.5. All of electrolytes were prepared using analytical grade reagents and deionized water. Prior to electrochemical deposition, substrates were activated in a diluted hydrochloric acid and subsequently cleaned by water. Deposition processes were performed at different temperature (60, 65, 70, 75, 80℃) in a two-electrode electrochemical cell with a Ni plate as the anode and a steel substrate as the cathode. During deposition, the electrolyte was kept stirring with a magnetic stirrer. Pure Ni films were also deposited at the five different temperatures from solution without NaH_2PO_2 for comparison.

Surface morphologies of coatings were examined by a scanning electron microscope (SEM, FEI Quanta 250 FEG, US). The micro-structures of films were performed by an X-ray diffraction (XRD, Bruker-AXS: D8 Advance, Germany). The valence state of element Ni

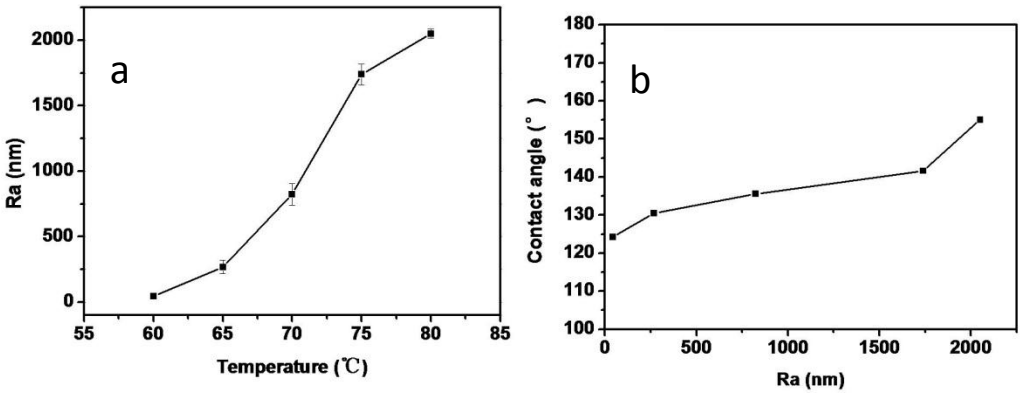
and P in the film deposited at 80℃ were performed by an X-ray photoelectron spectroscopy (AXIS ULTRA^{DLD}, England). The surface roughness was measured by a surface profilometer (Alpha-Step IQ, US). Surface contact angle (CA) and contact angle hysteresis (CAH) with water were detected by a contact angle meter (OCA20, Germany). Water droplets with a volume of 2.0 μL were dropped carefully onto surfaces. Before the contact angle performance, all coatings were ultrasonic cleaned in ethanol solution for 10 seconds to eliminate the unexpected contamination. All the tests were performed at room temperature.

SI 2. XPS data of element Ni and P in the film deposited at 80℃



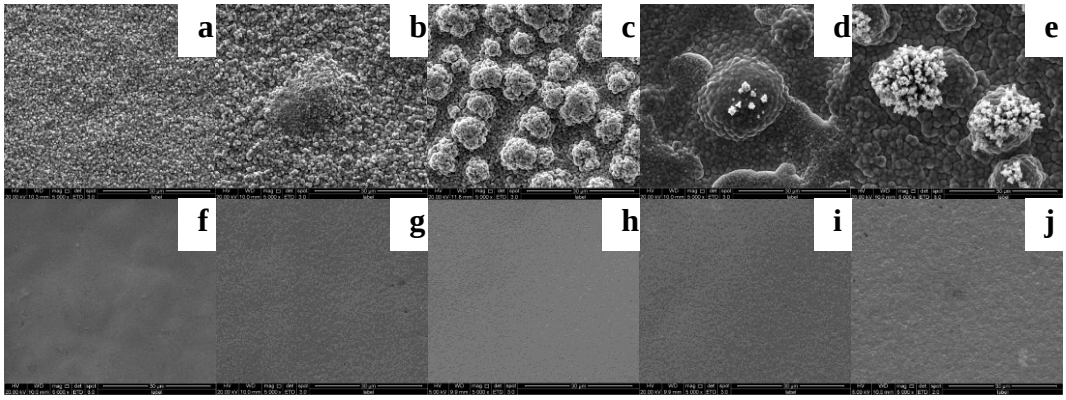
SI2. XPS analysis of element Ni and P in the film deposited at 80℃. The line-ring curves in the two spectra are the original data obtained by the XPS instrument and the solid curves are fitted curves for different valence states of elements. The data show that element Ni in this film is almost elemental form with a little of oxidation state. The oxidation state of Ni may be formed by the oxidation of oxygen in the air. Element P here is also elemental form comparable to that of phosphorous in its elemental form in red phosphorous.[1-3]

SI 3. Roughness variation of films with the solution temperatures



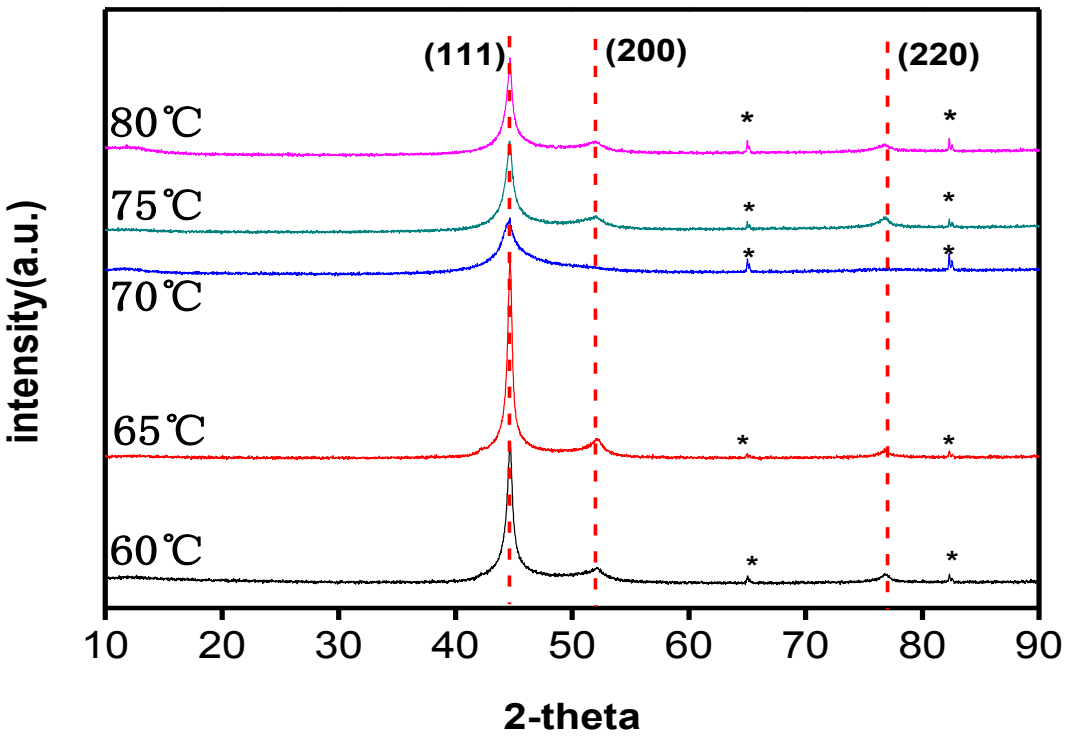
SI 3. a) Roughness variation of films vs. solution temperature. This curve pattern shows that the surface roughness gradually increases along with the solution temperature raising. This regulation has a good correspondence with the variation of film contact angles with water (figure b).

SI 4. SEM images of Ni-P and Ni films deposited at different temperatures



SI 4. The morphology comparison of Ni-P films (a-e) with pure Ni films (f-j) deposited at different temperatures: a, f) 60℃; b, g) 65℃; c, h) 70℃; d, i) 75℃; e, j) 80℃. These images clearly show the differences between the Ni-P films and pure Ni films. And the reason caused this phenomena may be the addition of reducing agent NaH_2PO_2, the only variable between the two experiment series.

SI 5. XRD patterns of Ni-P films



SI 5. XRD patterns of films deposited at different temperatures. Peaks have been index in the figure and correspond to Ni crystal structure. These peaks marked by "*" are index to Fe substrates. There is no significant difference between these five spectra.

References:

1. J. Balaraju, C. Anandan and K. Rajam, *Appl. Surf. Sci.*, 2005, **250**, 88-97.
2. A. S. M. A. Haseeb, P. Chakraborty, I. Ahmed, F. Caccavale and R. Bertoncello, *Thin Solid Films*, 1996, **283**, 140-144.
3. M. C. Oliveira and A. M. B. do Rego, *J. Alloys Compd.*, 2006, **425**, 64-68.