Functional coating preparation based on zinc oxide using low temperature plasma

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Abstract. The work describes the synthesis of superhydrophobic coating based on zinc oxide with a UV-driven reversible switching between hydrophilic and hydrophobic properties. A coating of vertically oriented acicular crystals of zinc oxide with dimensions of 1-2 μm in length and 50-200 nm in width on a metal substrate was obtained. According to the phase composition and morphology, the crystals correspond to zinc oxide - zincite. The contact angle for the coating after its exposure in a box isolated from daylight for 14 days is 150 °, while for the control metal substrate, the contact angle is 40 °. It is shown that the use of low temperature Ar plasma of low pressure allows changing the surface topography of acicular nanocrystals due to etching of their vertices and edges.

1. Introduction
Hydrophobic coatings are those for which the contact angle with water and aqueous solutions exceeds 90 °. Highly hydrophobic materials with water contact angle > 120 ° are of greatest practical interest. Materials/coatings with contact angles of more than 150 ° are allocated in a separate class – superhydrophobic materials/coatings. A distinctive feature of hydrophobic materials is the instability of thin wetting water layers on their surface what is determined not so much by the material characteristics as a whole, as by the properties and structure of the near-surface layer a few nanometers thick [1].

2. Objects and Methods
The coating of zinc oxide acicular nanocrystals on a metal substrate was obtained using the sol-gel method. A ZnO nanoparticle sol was obtained by hydrolysis of a 0.1 M solution of zinc acetate in absolute ethanol with the addition of LiOH in an ultrasonic bath [2]. The ZnO nanoparticle sol was concentrated on a rotary evaporator, deposited onto metal substrate by deep-coating method, dried and calcined at 420 °C. Then, the substrate with a film of nanoparticles was placed in a solution of zinc nitrate and methenamine and kept at 85 °C for 15 hours. After the crystals were grown, the samples were washed with deionized water and dried at 80 °C for 2 hours with following exposure under UV/dark conditions [3].

For zinc oxide coatings treatment, a capacitively coupled RF vacuum chamber of low pressure with flat electrodes, the general view of which is shown in Figure 1. Plasma treatment conditions are: gas –
Ar, chamber pressure – 26 Pa, frequency – 13.56 MHz, RF signal power supplied to the electrodes in the chamber – 800 W, treatment time – 60 minutes.

ZnO particle size in the sol was determined using a NanoBrook 90Plus Zeta Particle Size Analyzer (Brookhaven). Polystyrene sample cells with an optical path length of 10 mm were used.

Wide-angle X-ray diffraction patterns were obtained with a D2 Phaser X-ray diffractometer (Bruker Axs GmbH) in the Bragg-Brentano geometry (θ-θ) using CuKα radiation (30 kV, 10 mA). The software package DIFFRAC.SUITE (EVA, TOPAS) and the PDF-2 database were used.

Scanning electron microscopy (SEM) micrographs were obtained on a Merlin high-resolution scanning electron microscope (Carl Zeiss). The surface morphology was recorded at an accelerating voltage of 5 kV and a probe current of 300 pA for minimal exposure on the object in the detection mode of secondary electrons (SE InLens).

The contact angle for the coating of ZnO crystals was determined geometrically by applying a drop of deionized water.

3. Results and Discussion
The histogram of particle size distribution in the ZnO sol shown in Figure 2 indicates that size of the seed crystals for deposition on the substrate is in the range of 19-30 nm.
The X-ray diffraction pattern of a metal substrate coated with a film of zinc oxide nanoparticles (Figure 3a) shows reflections of zincite (P63mc) and substrate material. Structural parameters of zincite particles are: \(a = 0.3246(3)\) nm, \(c = 0.5192(5)\) nm; crystallite size in the directions: [002] – 13 nm, [010] – 12 nm, [011] – 12 nm. According to X-ray diffraction data, the acicular crystals grown on the substrate have significantly increased reflections from the zincite phase, compared to the substrate reflections, which indicates an increase in the content of zinc oxide. In addition, the 002 reflection has a much higher intensity compared to reflections from other planes, which suggest the predominant orientation of the crystals along the 00l direction perpendicular to the substrate. Structural parameters of zincite crystals are: \(a = 0.32475(3)\) nm, \(c = 0.51999(4)\) nm; crystallite size in the directions: [002] – 294 nm, [010] – 58 nm, [011] – 48 nm.

![Figure 3](image3.png)

**Figure 3.** X-ray diffraction patterns of a film of zinc oxide nanoparticles (a) and coating of zinc oxide crystals on a metal substrate (b).

Figure 4 shows SEM micrographs of the grown zinc oxide crystals, the linear dimensions of which vary within 1-2 microns in length and 50-200 nm in width.

![Figure 4](image4.png)

**Figure 4.** SEM images of zinc oxide crystals on a metal substrate.

The contact angle for a substrate with grown zinc oxide crystals after its exposure for 14 days in the dark was 150 °, and after 2 hours of exposure under UV – 18 °. For the case of a substrate without coating, the contact angle remained the same – at 40 °.

For the changing the coating relief at the nanoscale and creating a surface with an even smaller contact area at the surface-drop interface, it seems appropriate to use the plasma etching technology at low temperatures and pressures. According to the accumulated literary experience, it should lead to etching of surface sites with the highest electric field intensity. Vertices and edges of acicular crystals...
act as such sites, the gradual etching of which will lead to the “spheroidization” of the end sections of the crystals (crystal faces with indices 001).

SEM micrographs shown in Figure 5 confirm the validity of the hypothesis for the predominant etching of the vertices and edges of the acicular nanocrystals in RF plasma.

**Figure 5.** SEM images of zinc oxide crystals on a metal substrate before (left) and after (right) treatment in low pressure capacitively coupled RF argon plasma

4. Conclusion
Coatings of zinc oxide acicular nanocrystals possess unique properties of switching between superhydrophobicity and superhydrophilicity. In addition to all possible technological methods for increasing the contact angle values (thickness, density, direction of acicular nanocrystals), the coating properties can be changed by selective etching of the surface in low temperature RF plasma of low pressure.

References
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