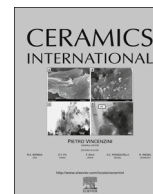Contents lists available at ScienceDirect

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Short communication

Electrodeposited ultraviolet-durable biomimetic super-hydrophobic surface

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A B S T R A C T

An ultraviolet (UV)-durable super-hydrophobic ZnO/Ni lotus-like nanostructure was fabricated via a simple two-step electrodeposition method at low temperature. The as-prepared ZnO/Ni nanostructure showed excellent UV-durable super-hydrophobicity and water ultra repellency. The Ni nanoclusters with different density could be successfully fabricated on the surface of ZnO NR by modulating the electro-deposition time of Ni nanoclusters, which affected surface roughness and wettability. The triple-level roughness resulted from high density Ni nanoclusters played a important role in the super-hydro-phobicity of ZnO/Ni nanostructure. This super-hydrophobic surface showed high stability in water for long term. Furthermore, the layer of Ni nanoclusters avoided the photoinduced wettability conversion of ZnO and hence greatly improved the UV-durability of this super-hydrophobic surface, which were es-sential elements for practical applications. This simple method could be applied to various substrates, such as metal surfaces and other electric conductive substrates.

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1. Introduction

During the past decades, super-hydrophobic surfaces have drawn great attention due to their self-cleaning, water repellent and anti-sticking properties [1–5]. Generally, super-hydrophobic surfaces are prepared by surface roughening followed by the hy-drophobization with organic materials which possess low surface energy [6,7]. However, these fabrication processes are complicated and the modified organic materials are expensive and harmful. Furthermore, the modified organic materials are not stable under UV irradiation for a long term, which will reduce the hydro-phobicity and limit their applications. To solve this problem, a new strategy without modification of low surface energy material should be found. Semiconductor nanomaterials have attracted much attentions because of their excellent physical and chemical properties [8–12]. Zinc oxide (ZnO) is one of the most important oxide semiconductor materials due to its optoelectronic, electronic and photocatalytic properties [13–20]. In particular, one-dimen-sional ZnO nanorod (NR) arrays can offer a highly composite air-solid surface in contact to water, which is beneficial for obtaining super-hydrophobic surface [7,21,22]. Recently, several approaches have been reported to prepare super-hydrophobic ZnO surfaces without any modification [23,24], but the photoinduced wett-ability conversion of ZnO material under UV light or sunlight is disadvantageous to outdoor applications.

In the present work, a simple two-step electrodeposition method was proposed to fabricate a UV-durable super-hydro-phobic surface without modification of organic material. Inspired by the typical morphology of lotus leaves, the strategy of depos-iting Ni nanoclusters onto the surface of ZnO NR arrays in order to create lotus-like surface with roughness. The results showed that Ni nanoclusters of well-controlled density were successfully fab-ricated on the surface of ZnO NR, and ZnO/Ni NR arrays with Ni nanoclusters of high density exhibited UV-durable super-hydrophobicity.

2. Experimental section

2.1. Materials

Zinc nitrate (A.R.), hexamethylenetetramine (A.R.), ammonium acetate (A.R.), and nickel acetate (A.R.) were purchased from Beijing Chemical Co. (Beijing, China). 99.999% pure Ni target was purchased from GRIKIN Advanced Materials Co. (Beijing, China). All of these chemicals and materials were used as received. The

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water used throughout this work was ultrapure water (18.2 MΩ cm) produced by a Milli-Q system. All of the glassware used for this experiment was washed with distilled water before use.

2.2. Preparation of ZnO/Ni NR arrays

The ZnO/Ni NR arrays were prepared by two steps. First, ZnO NR arrays were prepared by an electrodeposition method, using indium tin oxide glasses (ITO) as substrates. Applied potential was −0.9 V and deposition time was 30 min. After deposition, the samples were rinsed with deionized water. Then, Ni nanoclusters were electrodeposited onto the surface of ZnO NR at room temperature. The growth time was intentionally changed in order to investigate the influence of different growing conditions on the morphologies of ZnO/Ni NR arrays. Finally, the as-prepared samples were rinsed with deionized water and dried at 90 °C. The ZnO NR arrays and ZnO/Ni NR arrays with Ni deposition time of 10 s and 60 s were denoted as sample A, B and C, respectively. It is important to point out that the present NR arrays are not

substrate-limited and it can be fabricated on different electric conductive material surface.

2.3. Characterization

The morphology and composition of the samples were investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800) equipped with an attached EDX system. The crystal structure of the samples was studied by a Bruker X-ray diffraction (XRD) using Cu Kα radiation with an area detector.

The measurement of the contact angle (CA) of the samples were measured with the "sitting drop" method and the water CA values were acquired on a SL-2800 contact angle system (Solon Tech. Inc. Ltd. Shanghai) at room temperature in ambient atmosphere. For each measurement, a 2 μL water droplet was dispensed onto the sample under investigation. Super-hydrophobicity was identified in cases where the water droplet did not adhere to the surface. Therefore, the wettability of the samples were measured by the contact/compression/release technique
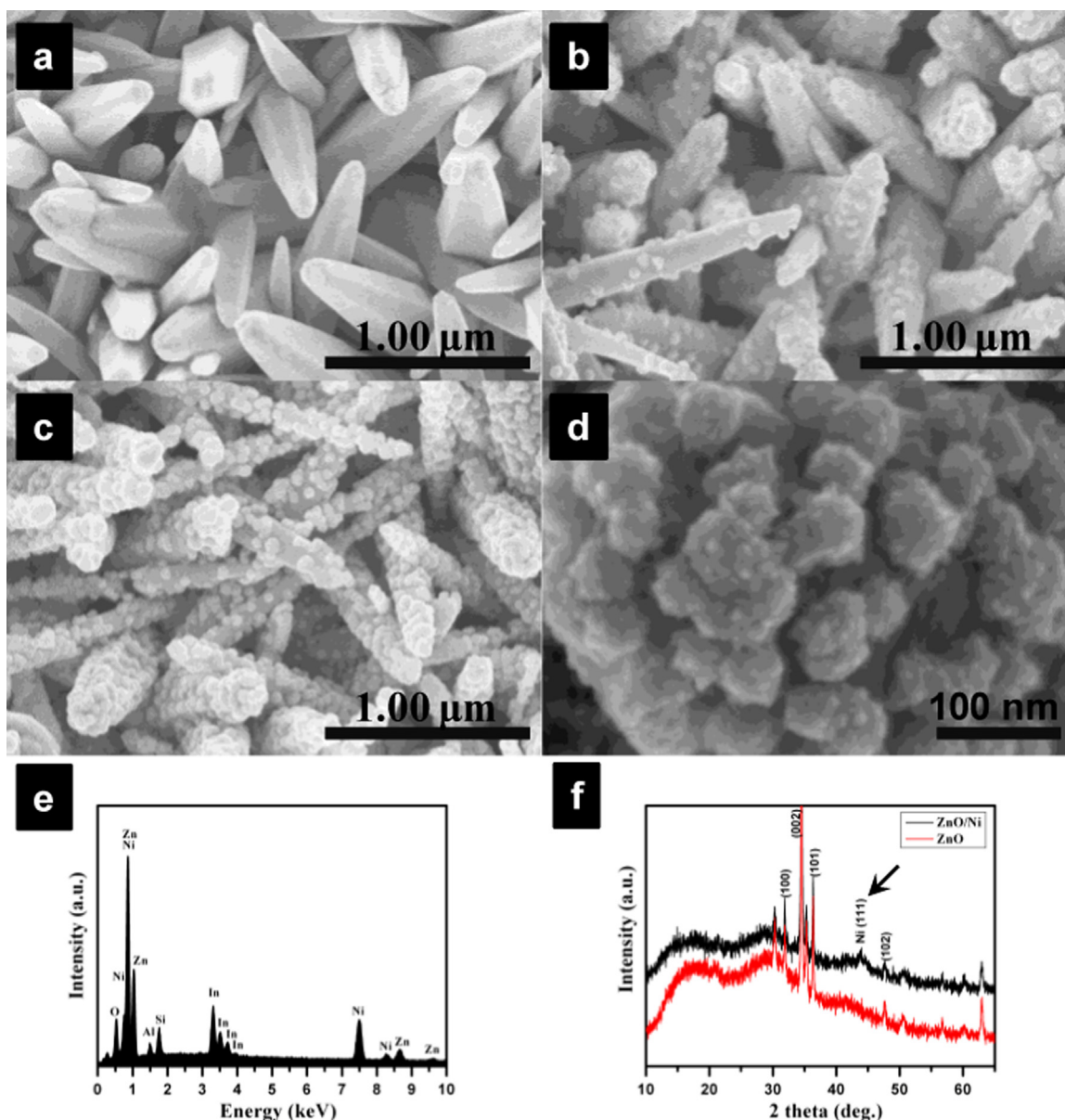

Fig. 1. (a, b) SEM images of ZnO NRs (sample A) and ZnO/Ni NRs (sample B). (c, d) SEM images of ZnO/Ni NRs (sample C) taken at different magnifications. (e) The EDS spectrum of ZnO/Ni NRs (sample C). (f) The XRD patterns of ZnO NRs (sample A) and ZnO/Ni NRs (sample C).

developed by Gao and McCathy [1]. Videos with recording speed of 24 frames per second were taken during the measuring course.

3. Results and discussion

The typical scanning electron microscopy (SEM) image of the as-prepared ZnO NR array (sample A) is shown in Fig. 1a, which indicates that the diameter of ZnO NR is 100–300 nm. Fig. 1b, c show that a layer of nanoclusters is on the surface of ZnO NRs after the electrodeposition of Ni (sample B and C). Fig. 1d shows a magnified top-view image of sample C, which indicates that Ni nanocluster is made up of many nanoparticles with diameter in the range of 5–10 nm. Thus the rod-cluster-particle triple-level roughness surface of hierarchical ZnO/Ni NR arrays was obtained. Such roughness can bring a sufficient proportion of trapped air and efficiently improve the hydrophobicity. The composition of sample C was confirmed by EDS technique, as shown in Fig. 1e. In the EDS spectrum, only peaks of Zn, O and Ni are observed, besides Al, In and Si peaks which originated from the aluminum tray and the ITO glass substrate. The XRD pattern is displayed in Fig. 1f. Besides the diffraction peaks of ZnO and ITO (not marked in the Figure), the Ni (111) diffraction peak can be observed after electrodeposition of Ni (as shown by the arrow), which also confirms the existence of Ni. All of these measurements indicate that a layer of Ni clusters has been successfully fabricated on the surface of ZnO NR arrays by electrodeposition method.

The ZnO/Ni NR arrays exhibit lotus-like structure and the growth mechanism was described as following. The applied electric field could disperse on the surface of ZnO NRs in a short time, which resulted in the whole surface of ZnO NRs releasing the electrons and reducing the Ni^{2+} ions in the solution. Therefore, Ni nanoclusters were formed on the surface of ZnO NRs. At the beginning of electrodeposition, a few Ni nanoclusters were formed on the surface of ZnO NRs (Fig. 1b). By increasing the deposition time to 60 s, the density of Ni nanoclusters increased with a slight augmentation of cluster size (Fig. 1c).

The wettability of the samples was evaluated by water contact angle (CA) measurements. For sample A, a water droplet (2 µL) stuck to the sample surface when the water droplet contacted the sample surface, and the water droplet could not separate from the sample surface (Fig. 2A), the CA of sample A is 137°, which indicated that the surface is hydrophobic, but the adhesive force between water and the sample surface was very strong. The surfaces of sample B and C showed water repellency. The static contact angle of water on these surfaces could not be measured by the same method since the adhesive force between the water droplet and sample surface was negligible and the water droplet could not be put onto the surface. Thus, the wettability of sample B and C were examined by the contact/compression/release technique developed by Gao and McCathy [1]. Fig. 2B and C showed sequential photographs which were taken from a water droplet as it
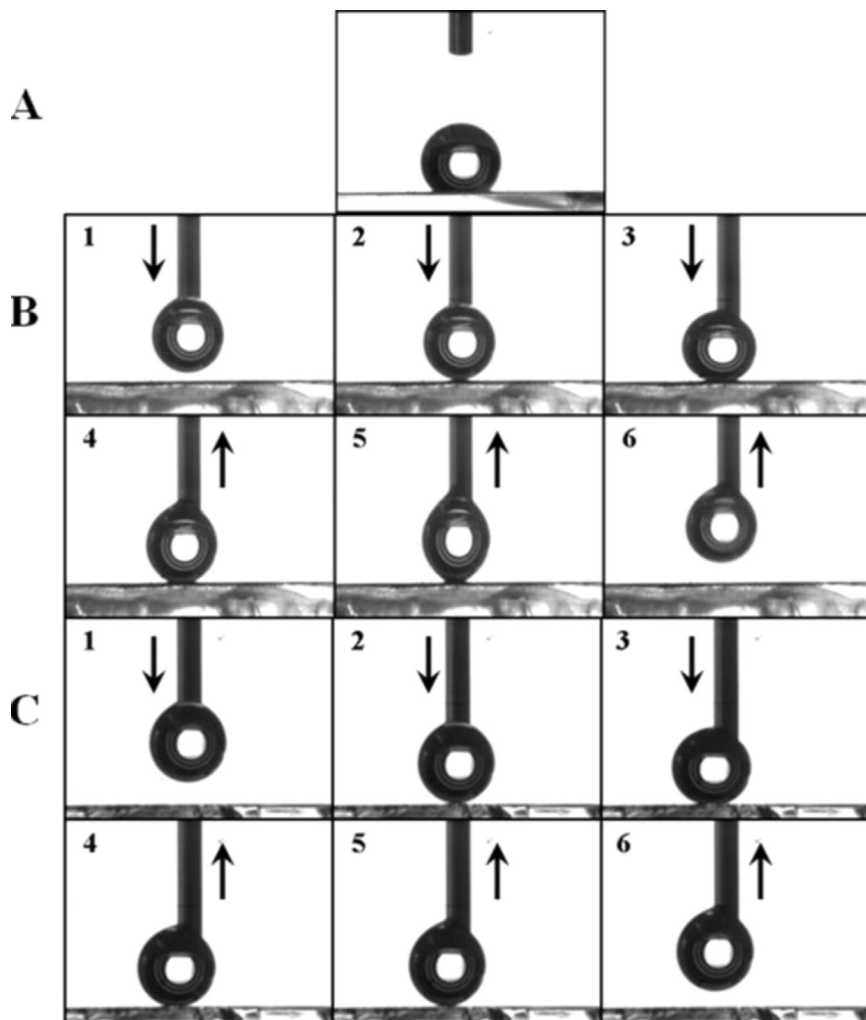

Fig. 2. (A) Photograph of water droplet shape on the surface of sample A before UV irradiation with CA value about 137°. (B, C) Photographs of water droplet shape as it contacted and separated from the surfaces of sample B and C, respectively (before UV irradiation). The arrows represent the moving direction of the water droplet.

was pushed onto and removed from the surfaces of sample B and C. These photographs demonstrated the wettability and adhesion property of sample B and C. Photographs from 1 to 6 showed different states of the water droplet as it just contacted, tightly compressed, gradually removed and completely separated from the sample surface. For sample B, the shape of the water droplet was deformed from sphere to oval before the droplet separated from the sample surface (shown in Fig. 2B-5), indicating that strong adhesion existed between the water droplet and sample surface. However, the shape of the droplet was nearly unchanged before the droplet separated from the surface of sample C (shown in Fig. 2C-5), indicating very slight adhesion existed between the water droplet and sample surface. There was no water residue on the surfaces of sample B and C when the water droplet separated from the sample surfaces. In addition, the droplets of water flow dropped on the surface of sample C kept their spherical shape and rolled off very quickly even at small inclinations (see the Video in Supporting information), which also demonstrated that the adhesion between water and sample surface was negligible.

The reason that leads to different wettability was proposed as below: when the density of Ni nanoclusters was low, water droplet could impregnate between ZnO NRs, but it was still not completely wetted into nanoclusters, resulting in increasing adhesion. Thus, the deformation of the water droplet occurred when the droplet was removed from the surface of sample B. However, nanoclusters with high density prevented the transition from Cassie-Baxter to Wenzel regime, and led to an increased propensity of air pocket formation between ZnO NRs and Ni nanoclusters, which could

effectively reduce adhesive force [25]. In addition, when sample C was immersed in water and viewed at certain angle, it appeared as a silver mirror (shown in Fig. 3), which indicated that an air layer was formed at ZnO NRs-water interface. The air layer prevented the penetration of water into the cavities in the sample. This phenomenon suggested that sample C possess a Cassie-Baxter surface.

For a given material, the CA is usually associated with the surface roughness. It is believed that triple-level roughness, besides high density nanoclusters, is responsible for the super-hydrophobicity of sample C. To validate this hypothesis, a thin layer of Ni nanoparticles was fabricated on the surface of ZnO NRs via magnetron sputtering method. Ar gas was used to generate the plasma. This ZnO/Ni NRs array was denoted as sample D which possessed a dual-level roughness structure.

As shown in Fig. 4, uniform Ni film made up of dense nanoparticles was coated on the surface of the ZnO NRs after magnetron sputtering. The wettability of sample D was investigated via the same procedure mentioned above. As shown in Fig. 5, there was strong adhesive force between the water droplet and the sample surface. Thus, the shape of the water droplet was deformed when the water droplet removed from the sample surface. These results indicated that existence of high density nanoclusters and triple-level roughness was both essential for achieving a super-hydrophobic surface [26].

Sun et al. [23] and Jiang et al. [2] have demonstrated the photoinduced wettability conversion phenomena on ZnO film and ZnO NRs array. As ZnO is a photosensitive material, when ZnO is
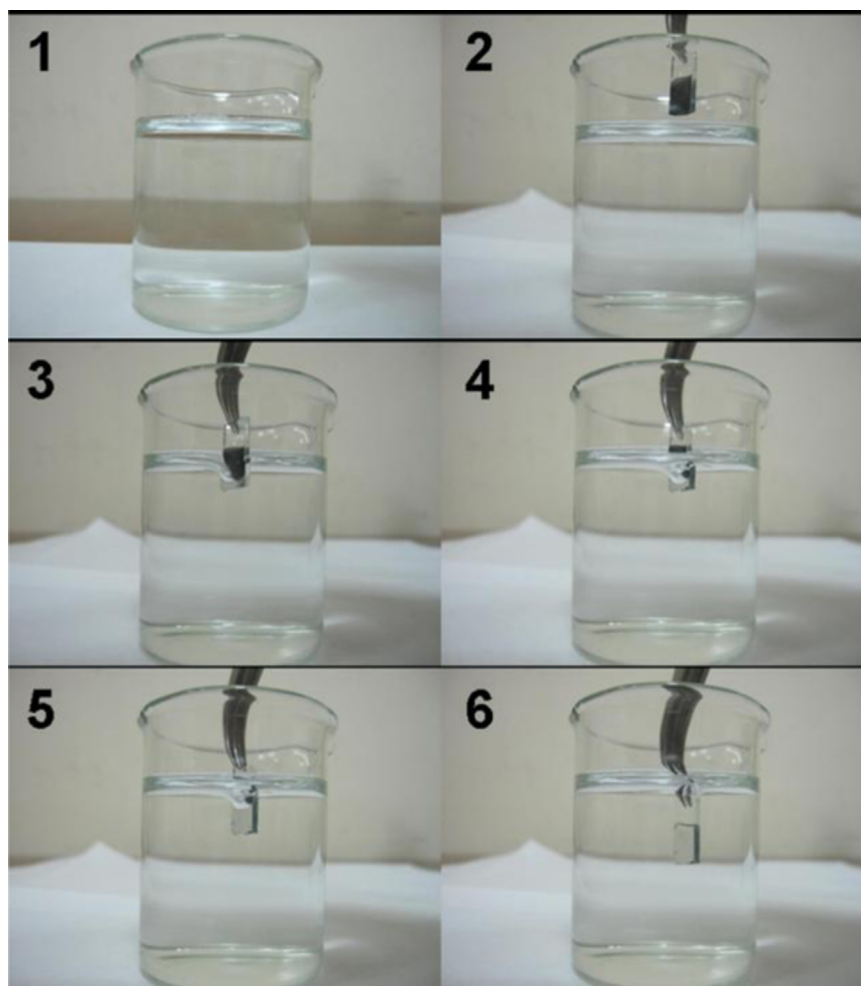

Fig. 3. Photographs of sample C in water taken at an angle which past the critical angle.
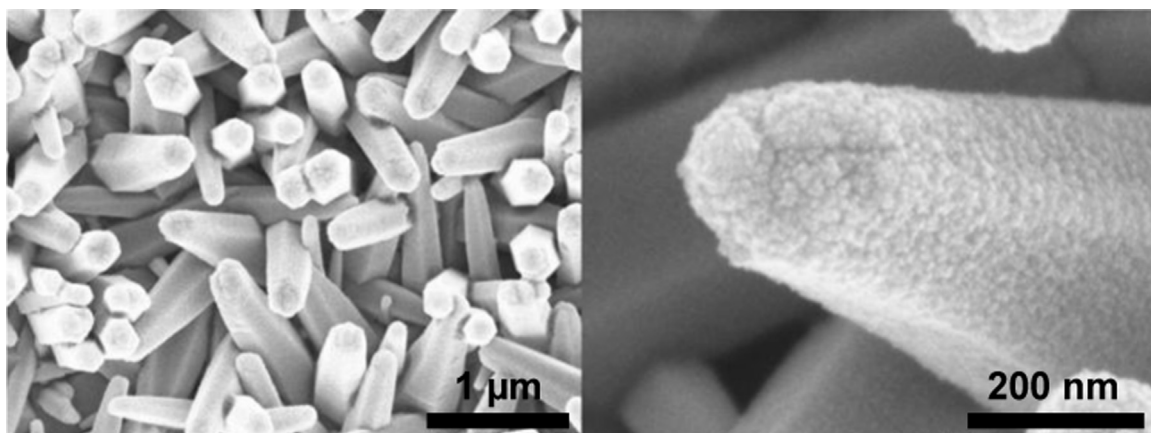
Fig. 4. Top view SEM images of ZnO/Ni NRs (sample D) prepared by magnetron sputtering method.
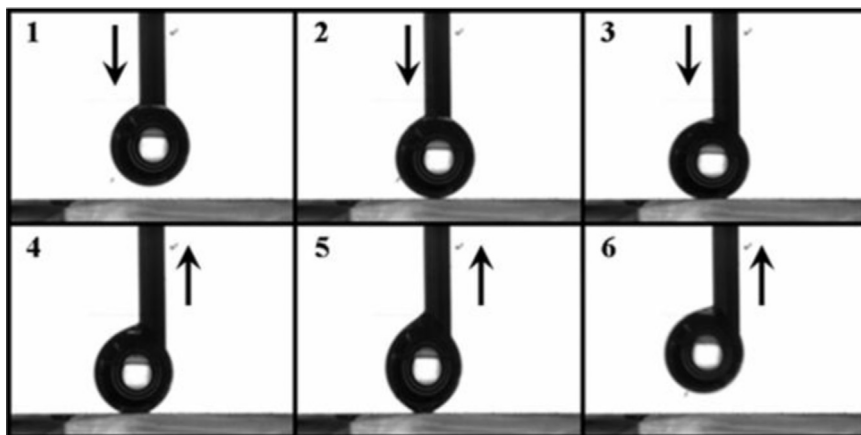

Fig. 5. Photographs of water droplet shape as it contacted and separated from the surfaces of sample D before UV irradiation. The arrows represent the moving direction of the water droplet.

irradiated with UV light, the photogenerated holes and electrons will create surface oxygen vacancies and zinc defective sites. Water molecules are adsorbed and coordinated kinetically to these oxygen vacancies, which lead to adsorption of the water molecules on the surface of ZnO NRs [2,23]. This process greatly enhances the surface hydrophilicity of ZnO NRs, which is disadvantageous to outdoor applications. Therefore, in order to obtain a UV-durable super-hydrophobic surface, we should prevent ZnO from contacting water. In our experiment, Ni nanoclusters act as this role to cut relation between ZnO NRs and the water droplets. The water droplets could only contact Ni nanoclusters instead of ZnO NRs, thus avoided the photoinduced wettability conversion.

Finally, the UV irradiation effect on the sample A, B and C were investigated. Upon UV irradiation ($\sim$ 1 mW cm^{-2}) of 2 h, the water CA of sample A was reduced to about 87° (as shown in Fig. 6A), indicating that the wettability changed from hydrophobicity to hydrophilicity. But sample B and C showed almost unchanged wettability after UV irradiation of 2 h, exhibiting UV-durable property (Fig. 6B-5, C-5). In addition, sample C still exhibits super-hydrophobicity after 8 months. The super-hydrophobic ZnO/Ni NR arrays have potential applications in daily life, as the intensity of UV irradiation in this measurement is much stronger than that in sunlight.

4. Conclusions

In summary, we have successfully prepared a UV-durable super-hydrophobic surface through a simple two-step electrodeposition method without modification of organic materials. The method could effectively control the density of Ni nanoclusters and tune the morphology of the surface via changing the deposition time. The super-hydrophobicity of this surface comes from the coexistence of triple-level roughness and high density Ni nanoclusters. The introducing of Ni nanoclusters not only cause the surface roughness but also avoid the photoinduced wettability conversion of ZnO NR, thus ensuring the UV-durable super-hydrophobicity. This surface still exhibited super-hydrophobicity and self-cleaning effect after 8 months. This simple method can be universally applied to various electric conductive substrates such as copper, aluminum and may also provide interesting insight into the design of novel super-hydrophobic surfaces.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ceramint.2016.07.162.
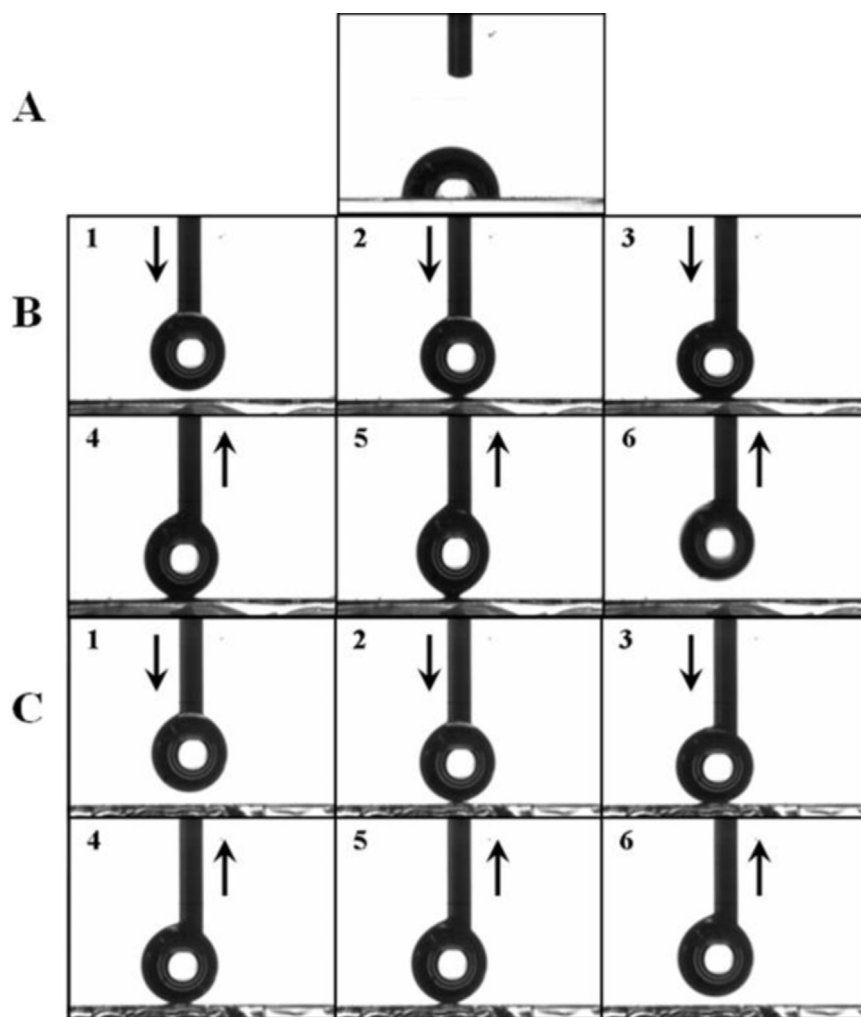
Fig. 6. (A) Photograph of water droplet shape on the surface of sample A after UV irradiation with CA value about 87°. (B, C) Photographs of water droplet shape as it contacted and separated from the surfaces of sample B and C, respectively (after UV irradiation). The arrows represent the moving direction of the water droplet.

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