

CuO/NiO core/shell nanowire arrays directly synthesised on copper foam with promising superhydrophobic property

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Published in *Micro & Nano Letters*; Received on 31st October 2013; Revised on 23rd December 2013; Accepted on 27th February 2014

A report is presented on the synthesis of a novel nanoscale core/shell heterostructure with CuO nanowires as the core and NiO nanoparticles as the shell directly grown on copper foam by a two-step solution method. The heterostructures are investigated and analysed by scanning electron microscopy and an X-ray diffractometer. The results indicate that the secondary growth of NiO nanoparticles around CuO nanowires leads to the creation of CuO/NiO hetero-hierarchical core/shell nanowire arrays. The wettability of the CuO/NiO core/shell nanowire arrays after being modified by trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane is studied. The CuO/NiO core/shell nanowire arrays on copper foam present promising superhydrophobic properties with high water contact angles up to $164 \pm 2^\circ$.

1. Introduction: One-dimensional (1D) heterostructured nanomaterials have received much attention both for fundamental research and for practical applications in nanoscale electronics, optoelectronics, chemical/bio/optical sensors/detectors and energy harvesting/conversion devices [1–5]. Substantial attention has been paid to the development of new synthetic methodologies for well-controlled growth of novel core/shell nanowire heterostructures [1, 4, 5]. Up to now, a great variety of core/shell nanowire heterostructures with promising properties have been demonstrated [1, 4–9]. However, a great challenge still exists in the rational design and facile synthesis of core/shell nanowire heterostructures with controlled morphology and desired function in large scale at low cost. Compared with vapour-phase strategies [10–12], the solution-based techniques are regarded as low-cost effective approaches in preparing various interesting nanomaterials with the advantages of low process temperature, environmental friendliness and process simplicity [1, 4, 5].

Among the various nanomaterials, transition metal oxides are indisputably the prerequisite for developing different novel materials with functionality and smartness. Among them, CuO and NiO have been intensively studied separately for various applications such as lithium ion batteries [13, 14], gas sensors [15], energetic materials [16, 17] and superhydrophobic surfaces [18, 19]. To enhance the performance for these applications, the integration of CuO and NiO into core/shell nanowire structures is regarded as one promising avenue to achieve improved properties via the synthetic effect of each other. Recently, the hydrothermal growth of ZnO nanorods on CuO nanowires pre-synthesised by thermal annealing of Cu foil has been reported and remarkably enhanced superhydrophobic performance has been demonstrated [7]. Nevertheless, it needs a very high temperature to prepare CuO nanowires on Cu foil and time-consuming hydrothermal process for integrating ZnO nanorods on CuO nanowires. Saadat *et al.* [9] reported the synthesis of coaxial Fe₃O₄/CuO hybrid wires grown directly on a copper substrate by the electrochemical method and significantly enhanced electrochemical performance was achieved. However, the electrochemical method requires special apparatus. To the best of our knowledge, there is no report in the literature for synthesising CuO/NiO core/shell nanowire arrays directly on copper foam by facile and effective two-step method and investigating their wettability properties.

In this Letter, we present the synthesis of CuO/NiO core/shell nanowire arrays based on CuO nanowires arrays directly grown

on copper foam by a simple two-step solution method. To demonstrate the potential applications, the resulting CuO/NiO core/shell nanowire arrays are used to fabricate a superhydrophobic surface. It is found that these unique hierarchical arrays have promising superhydrophobic performance with high water contact angles (CAs) of up to $164 \pm 2^\circ$.

2. Experimental: A two-step solution method was used to prepare CuO/NiO core/shell nanowire arrays. First, Cu(OH)₂ nanowires arrays were synthesised on copper foam by surface oxidation with alkali assistance using the similar method developed in [20]. The copper foam sample was cleaned in ethanol with ultrasonic assistance and then using deionised (DI) water for 5 min. The copper foam was then immersed in a solution containing 2.5 mol l⁻¹ sodium hydroxide and 0.1 mol l⁻¹ ammonium persulphate at around 25°C for approximately 20 min. The sample was taken out from the solution, rinsed with DI water for several times and dried by N₂ gas. In the second stage, the as-prepared Cu(OH)₂ nanowires arrays were directly used as the skeleton for growing the NiO nanoparticles in a chemical bath. The as-prepared Cu(OH)₂ nanowire arrays on copper foam were immersed in a mixing solution of 40 ml of 1 M nickel sulphate (Alfa Aesar), 30 ml of 0.25 M potassium persulphate (Aldrich), 10 ml of aqueous ammonia (28–30% NH₃, EM Science) and 20 ml of DI water in a 250 ml Pyrex beaker at room temperature for 5–10 min [4]. The substrates were then taken out of the solution and rinsed with DI water. The as-fabricated samples were annealed at 300°C in air for 2 h to prepare CuO/NiO core/shell nanowire arrays. The PFOCTS-modified surface was obtained by putting the as-prepared CuO/NiO core/shell nanowire arrays synthesised on copper foam into 1 mM PFOCTS [molecular formula: CF₃(CF₂)₅CH₂CH₂-Si(Cl)₃] in hexane for half an hour at around 25°C. Finally, the sample was washed and then dried at 150°C for 10 min [19].

Scanning electron microscopy (SEM) and X-ray diffraction (XRD) are employed to characterise the as-synthesised CuO/NiO core/shell nanowire arrays. The static CA and adhesion to the CuO/NiO core/shell nanowire arrays on copper foam of DI water droplets were tested by a Rame-Hart Model 500 at around 25°C. CAs were measured at five different places of one sample and then the average value of the five CAs was defined as the final CA value.

3. Results and discussion: SEM analysis of the morphologies of CuO nanowire arrays before and after NiO growth is shown in Fig. 1. The low magnification SEM image shown in Fig. 1a displays that CuO nanowire arrays grow uniformly on the surface of copper foam in a large area. The high magnification SEM image in Fig. 1c indicates that the CuO nanowire arrays have relatively smooth surfaces with a diameter of 100–500 nm. After the growth of NiO, it can be clearly seen that the surfaces of CuO nanowire arrays are covered by the NiO nanoparticles causing them to become thicker and have rougher surfaces as shown in Fig. 1b. As indicated in a high magnification SEM image of CuO nanowire array after NiO growth (see Fig. 1d), many small size NiO nanoparticles cover the surface of CuO nanowires, forming CuO/NiO core/shell nanowire arrays, which could play an important role in improving the wettability.

Fig. 2 shows the XRD pattern of synthesised CuO/NiO core/shell nanowire arrays. The diffraction peaks for CuO are clearly seen in the pattern. The diffraction peaks for Cu₂O are mainly because of the oxidation of the copper foam substrate. The diffraction peaks for NiO are also observed in the pattern, suggesting that NiO has been integrated around the CuO nanowire arrays. The weak diffraction peaks for NiO are because of the fact that only a very thin layer (~0.5 μm) of NiO (compared with the 0.5 mm-thick oxidised substrate) is deposited on the CuO nanowire arrays as indicated in Figs. 1b and d. Another possible reason is that the NiO nanoparticles are not well-crystallised and/or polycrystalline.

To evaluate the wettability of the CuO nanowire arrays before and after NiO integration, CA measurements were performed using a water droplet having a volume of 4–5 μl. Water droplets

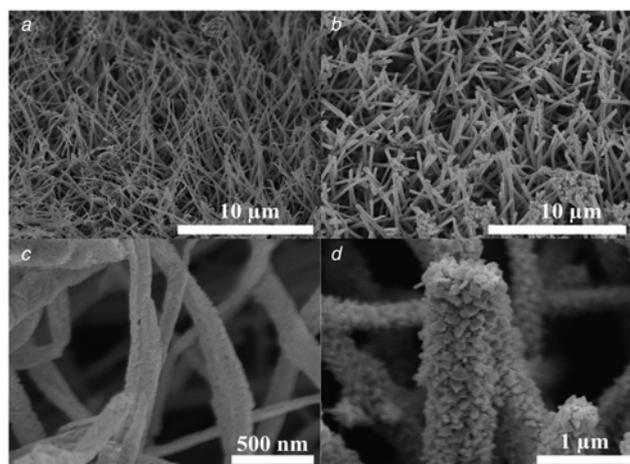


Figure 1 SEM images
a and c CuO nanowires arrays
b and d CuO/NiO core/shell nanowires arrays

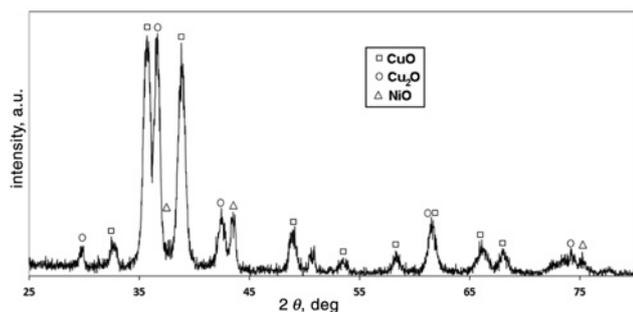


Figure 2 XRD pattern of the CuO/NiO core/shell nanowire arrays

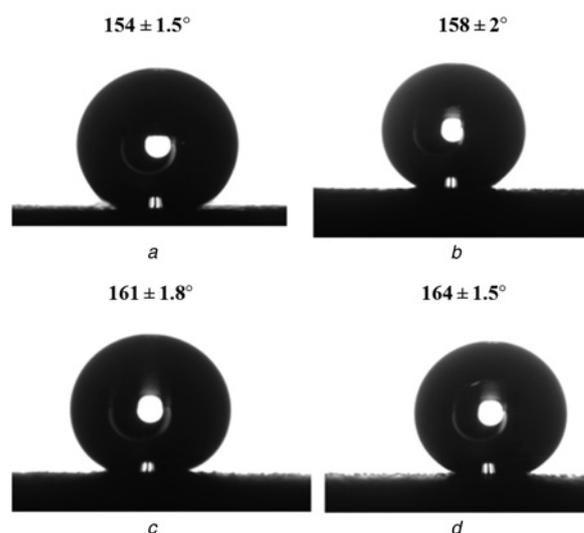


Figure 3 Images and CAs of water droplets on different surfaces
a NiO on copper foam
b CuO nanowire arrays on copper foam
c CuO/NiO nanowire arrays by deposition of NiO for 5 min
d CuO/NiO nanowire arrays by deposition of NiO for 10 min

were first dropped on the CuO/NiO core/shell nanowire array samples that are not modified by PFOCTS. It is observed that the water droplets spread fast on the samples with CAs close to 0, which indicates that the CuO/NiO core/shell nanowire array samples are superhydrophilic. However, the surface of the sample changes from superhydrophilic to superhydrophobic after being modified by PFOCTS. As shown in Fig. 3, the CAs on the surfaces of NiO on copper foam substrate and the growth of CuO nanowire arrays directly on copper foam are measured to be $154 \pm 1.5^\circ$ and $158 \pm 2^\circ$, respectively. The growth of the NiO nanoparticle shell on the CuO nanowire arrays is found to present a higher static CA. When the growth time of NiO increases, the CA also increases and achieves a maximum value of $164 \pm 1.5^\circ$ as can be seen from Fig. 3d. This result indicates that the growth of NiO on CuO nanowire arrays can enhance the surface roughness. It is well known that higher surface roughness of a sample can trap more air, which is beneficial for achieving higher CAs and superhydrophobicity. However, if the growth time of NiO is increased further, the CAs will decrease. This is attributed to the fact that the higher density of NiO nanoparticles growth on CuO nanowire arrays is not beneficial for the superhydrophobic property because air cannot be trapped in the hierarchical roughness.

The adhesive characteristics of water droplets on the CuO nanowire arrays with PFOCTS modification before and after NiO growth were also investigated. Fig. 4 shows a sequence of images of CuO/NiO core/shell nanowire arrays with PFOCTS modification approached to a water droplet with a volume of 4 μl suspending on a syringe. It can be clearly seen that the sample is effortlessly separated from the water droplet and the separation force is very small, even though severe deformation occurs in this case. On the contrary, as the sample of CuO nanowire arrays without the growth of NiO is slowly separated from the suspending water droplet as illustrated in Fig. 5, an adhesion between the surface of the sample and water droplet can be clearly observed. An obvious separation force is needed to move the surface away from the water droplet. This result indicated that the CuO/NiO core/shell nanowire array sample has a promising remarkable superhydrophobic property without adhesive force between the surface and the water droplet. This should be attributed to the fact that the novel CuO/NiO core/shell nanowire arrays have a hierarchical rough surface, which can trap more air

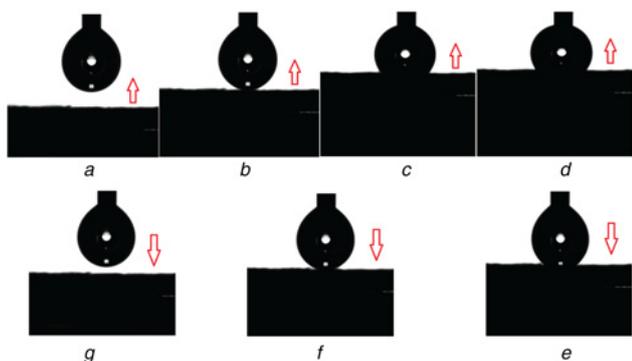


Figure 4 Sequential images of CuO/NiO core/shell nanowire arrays with PFOCTS-modification that gradually contact and then depart from a water droplet hanging on a syringe; moving direction of substrate indicated by red arrows

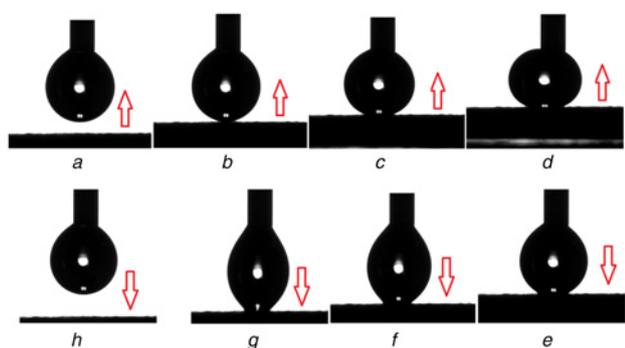


Figure 5 Sequential images of CuO nanowire arrays with PFOCTS-modification that gradually contact and then depart from a water droplet hanging on a syringe; moving direction of substrate indicated by red arrows

than that of the bare CuO nanowire array with a regular rough surface.

4. Conclusion: A facile effective two-step solution method is presented for the direct synthesis of CuO/NiO core/shell nanowire arrays on copper foam substrate. In the core/shell structure, the CuO nanowire arrays are scaffolds that are uniformly and compactly coated with a thin layer of NiO nanoparticles. Excellent superhydrophobic performance is observed in such unique core/shell nanowire arrays with an achieved water CA as high as $164 \pm 2^\circ$. Furthermore, very little water adhesion and drag resistance is observed for the CuO/NiO core/shell nanowire arrays. The improvement could be caused by a synergistic effect between CuO and NiO as well as the unique feature of core/shell heterostructures, which provide increased hierarchically rough surfaces. Such CuO/NiO core/shell nanowire array composites grown directly on conductive copper foam substrates will find potential applications in various areas including self-cleaning coatings, corrosion and surface protections, liquid transport, and separation between water and oil.

5. Acknowledgment: This work was supported by the National Natural Science Foundation of China (grant nos 11002128, 11272292 and 11172276).

6 References

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