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Title Page

Title: One-Step Synthesis of Superhydrophobic and Multifunctional Nano Copper Modified Bio-polyurethane for Controlled-Release Fertilizer with "Multilayer Air Shields": New Insight of Improvement Mechanism

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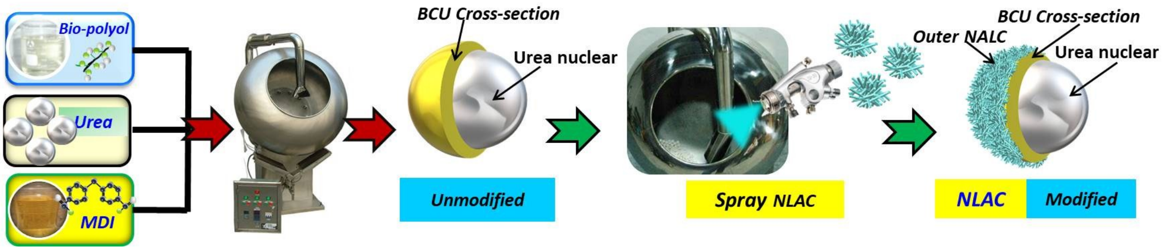
Experimental section

Materials. Lauric acid (99.8%) was purchased from Tianjin Bodi Chemical Industry Co., Ltd. (Tianjin, China). Copper hydroxide (98%) was obtained from Chengdu Aikeda Chemical Reagent Co., Ltd. (Sichuan, China). Biopolyol produced from castor oil and MDI were purchased from Aladdin Industrial Co., Ltd. (Shanghai, China). NaCl, Methylbenzene, and petroleum ether were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Commercially available palm oil, soybean oil, and silicone oil were purchased from local markets. Agar powder was purchased from Beijing Solarbio Sicence & Techonology Co., Ltd. (Beijing, China). Trypticase Soy Broth was obtained from Qingdao Hope Bio-techonogy Co., Ltd. (Shandong, China). Lactose Bile Fermentation Tube was purchased from Tianjin Yingbo Biochemistry Reagent Co., Ltd. (Tianjin, China).

Preparation of Nano Lauric Acid Copper. The 4g (0.02 mol) lauric acid and 0.98g (0.01mol) was mixed in a 100-mL beaker with 50 mL mixture of alcohol and water (50% v/v). The mixture was treated by sonication and stirring for one hour under room temperature condition. Nano lauric acid copper was obtained after drying.

Preparation and Release Characteristics of BCU and SBCU. The BCU was synthesized using a multistep assistant strategy, which was showed in Schema 1. 1.0 kg urea prills were first preheated to 65± 1°C in a drum. 6g biopolyol and 4g MDI were then added into the drum after fully mixing. The coating process was repeated three times to obtain the BCU, and the bio-polyurethane weight was about 3% of the total fertilizer weight. The pretreatment of SBCU was the same as that of BCU. After the urea was coated with 2.5% bio-polyurethane, 5g nano lauric acid copper was sprayed in the drum to obtain the SBCU.



Schema1 Preparation Process of BCU and SBCU

The release characteristics of BCU and SBCU were determined in water at 25°C. 10 g of BCU or SBCU were put into a plastic bottle containing 200 mL of deionized water at 25 ± 0.1°C (each had three replicates). Nitrogen concentration of water samples from each bottle at 1, 3, 5, 7, 10, 14, 21, and 28 days or until the cumulative nitrogen release reached over 80% were determined using the Kjeldahl method [2]. After each sampling, all the water in the bottles was poured out and 200 mL deionized water was then added again. At same time, the Cu^{2+} content was also determined using atomic absorption spectrometer (AA-7000, Japan) at 1, 3, 5, 7, 10, 14, 21, 28, 35, 42, 49 and 60 days.

Oil/Water Separation. The 30 mL oil/water mixture (50% v/v, and the water was dyed green) was poured into the separation funnel setup with the nano lauric acid copper coated 100 mesh and nonwoven fabric. The separated liquids were gathered to test the separation efficiency, and five kinds of oil and organic solvents including soya-bean oil, palm oil, methylbenzene, silicone oil and petroleum ether were used to perform the experiment.

Antibacterial Ability. To prepare LB solid culture medium, 1g trypticase soy broth, 2g lactose bile fermentation tube, 1.5g agar powder, 0.5 NaCl, and 95 mL deionized water was mixed in 250-mL triangular flasks. After sealing, the flasks were added into a high temperature sterilizer at 120 °C for 0.5 hour. When the temperature cold to 70°C, triangular flasks were taken out, and the liquid was poured into plastic petri dishes in a bacteria-free operating environment. Each culture dish contained nearly 25 mL LB. When it cooled to room temperature, the LB solid culture media were obtained.

The LB solid culture medium was cut into square pieces. Some of them were soaked into the nano lauric acid for 0.5 hour, and then taken out for natural air drying in a bacteria-free environment. After that, three unmodified and three modified pieces were put into LB solid culture media in the plastic petri dishes. 2 uL *E. coli* cells were then inoculated on the LB solid culture media, smearing uniformity with glass spreading rod. After sealing, the plastic petri dishes were incubated in a biochemical incubator at 37°C. All the operations were in a bacteria-free environment.

Characterization. SEM (SU8010 EDS：Model 550i, Japan) and TEM (Tecnai G2 F30 S-TWIN 300KV, American) were used to observe the morphology of the samples. Surface elemental distribution of the samples was analyzed through an energy dispersive X-ray spectroscopy (EDS) detector and XPS (Thermo escalab 250Xi, American). WCA was tested through a contact angle meter (KINO SL200KS, American). FTIR (Nicolet 6700, American) was used to characterize the surface functionalities.

Oil/Water Separation and Antibacterial Ability. The multifunctional nano lauric acid copper was also used for oil/water separation and antibacterial performance. Because the nano lauric acid copper is superhydrophobic and superoleophilic, it has great potential to remove oils or other organic compounds from water. To evaluate the oil/water separation capacity ability of the nano lauric acid copper, the coated non-woven fabric was attached to a self-regulating funnel as a filter/separator in a laboratory test (Figure 5A). When 30 mL oil/water mixture (soyabean oil, 50% v/v) was poured into the funnel, the green water layer was repelled and retained above the fabric. At the same time, the yellow soya-bean oil quickly passed through the filter into the beaker. During the oil/water separation process, there was no external force except the gravity and no green water drop was observed in the yellow oil layer (Video 3), indicating low energy consumption and high separation efficiency of this nano lauric acid copper coated filter. Five kinds of oil and organic solvents were used to further evaluate the separation capacity and efficiency of nano lauric acid copper coated materials. The separation efficiency of the filter to soya-bean oil, palm oil, methylbenzene, silicone oil, and petroleum ether were 99.86%, 99.76%, 99.56%, 99.77%, and 99.87%, respectively (Figure 5B), confirming that nano lauric acid copper coated materials have high separation capacity and efficiency for oils and organic pollutants. Furthermore, the coated filter showed excellent stability and recyclability for separation of oil/water. As shown in Figure 5C, the filter maintained stable separation ability for five cycles to separate the five substances from water with efficiencies all over 99%. The nano lauric acid copper coated 100 mesh nylon net was also used to separate oil from water and showed high separation efficiency as well

(Video 4). These results indicated that nano lauric acid copper has great potential to improve the surface properties of low-cost porous materials including nets and fabrics to enable them as filter materials to separate oils and other organic compounds from water.

Antibacterial activity of a filtration membrane is critical because biofouling can greatly reduce its efficiency. The antibacterial performance of the nano lauric acid copper was also qualitatively assessed using *E. coli* cells as the probe. The Luria–Bertani (LB) solid culture medium was used to inoculate the E. coli cells using spread plates with glass spreading rods. As shown in Figure 5, the unmodified LB culture medium was clear at the very beginning (Figure 5D), then turned into muddy (Figure 5E) after incubation for two days, indicating the growth and reproduction of E. coli cells. The modified LB lump with nano lauric acid copper was also clear at first. Incubation for two and five days, however, did not show the obvious signs of *E. coli* cells, which was confirmed by repetitions (Figure S6, Supporting Information). When further incubation of *E. coli* cells in two solid culture media, the unmodified one showed booming of bacteria, while the modified one had much less bacterial growth, indicating the antibacterial ability of the nano lauric acid copper. This antibacterial ability of nano lauric acid copper is probably inherited from Cu^{2+} and similar results have been reported in a previous study.[27] In addition to preventing biofouling of coated filtration membranes, the antibiotic effect of the nanomaterial can help treating soil borne disease when the coated fertilizer is applied in soils.

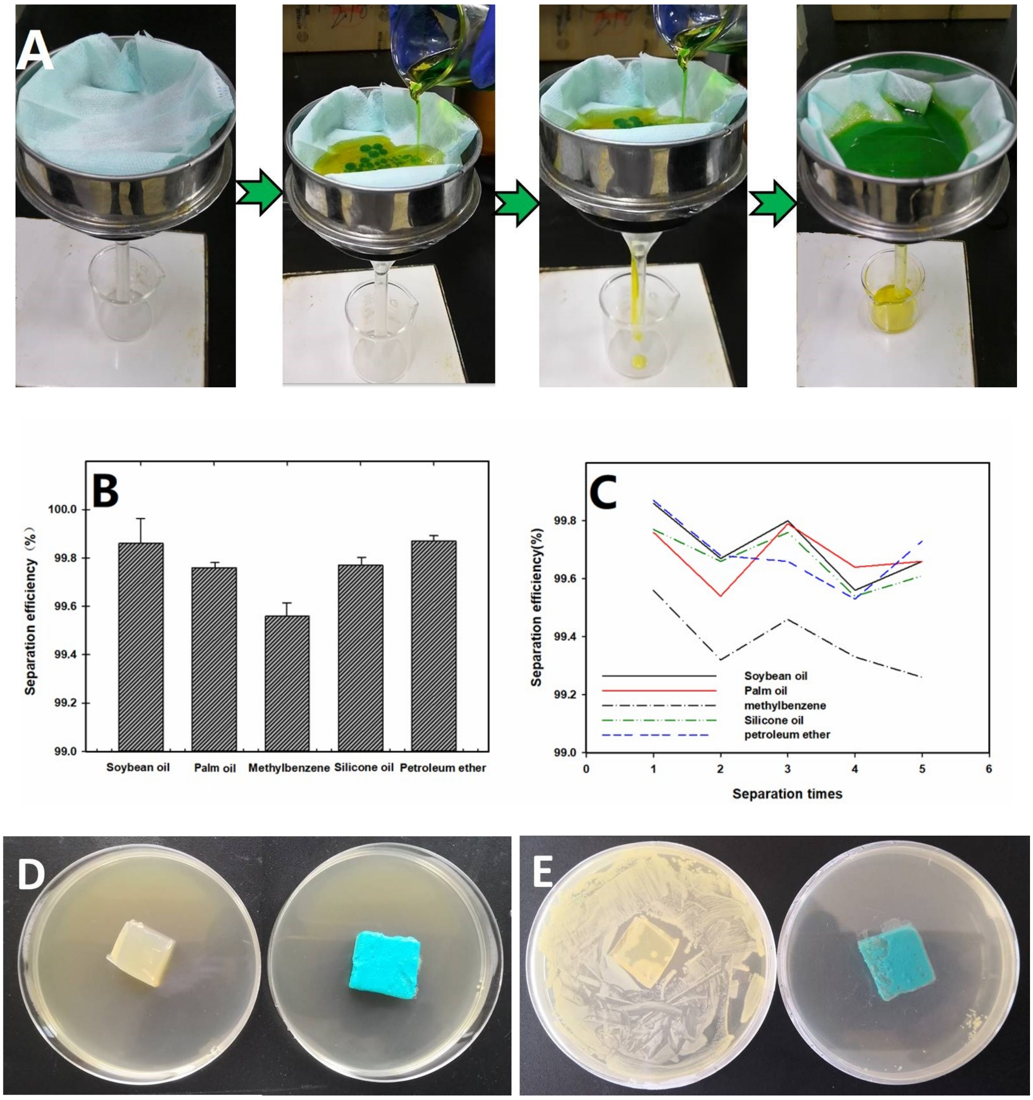


Fig. S1 Oil/water separation process using lauric acid copper coated non-woven fabric (oil is yellow and water is green) (A); Common organic solvent separation efficiency (B); and its repeated separation efficiencies (C). Antibacterial activity of nano lauric acid copper modified AGAR block (right) and AGAR block without modification (left). Photographs show E. *coli* colonies growing on solid culture mediums, and the incubation times are zero day (D), two days E)

Fig. S2 EDS spectra of nano lauric acid copper

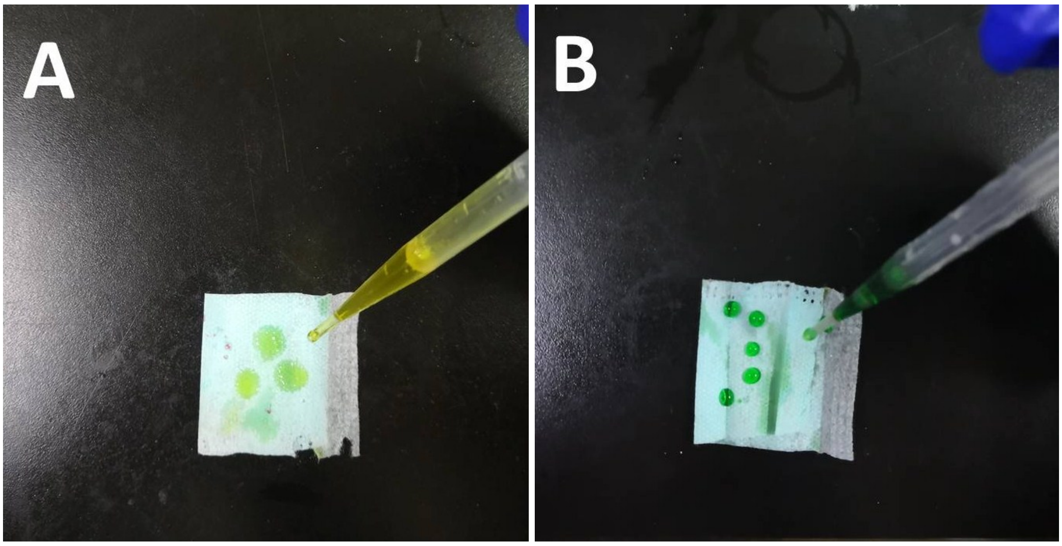


Fig.S3 Photographs show the oil contact with nano lauric acid copper coated non-woven fabric (A) and water contact with nano lauric acid copper coated non-woven fabric (B).

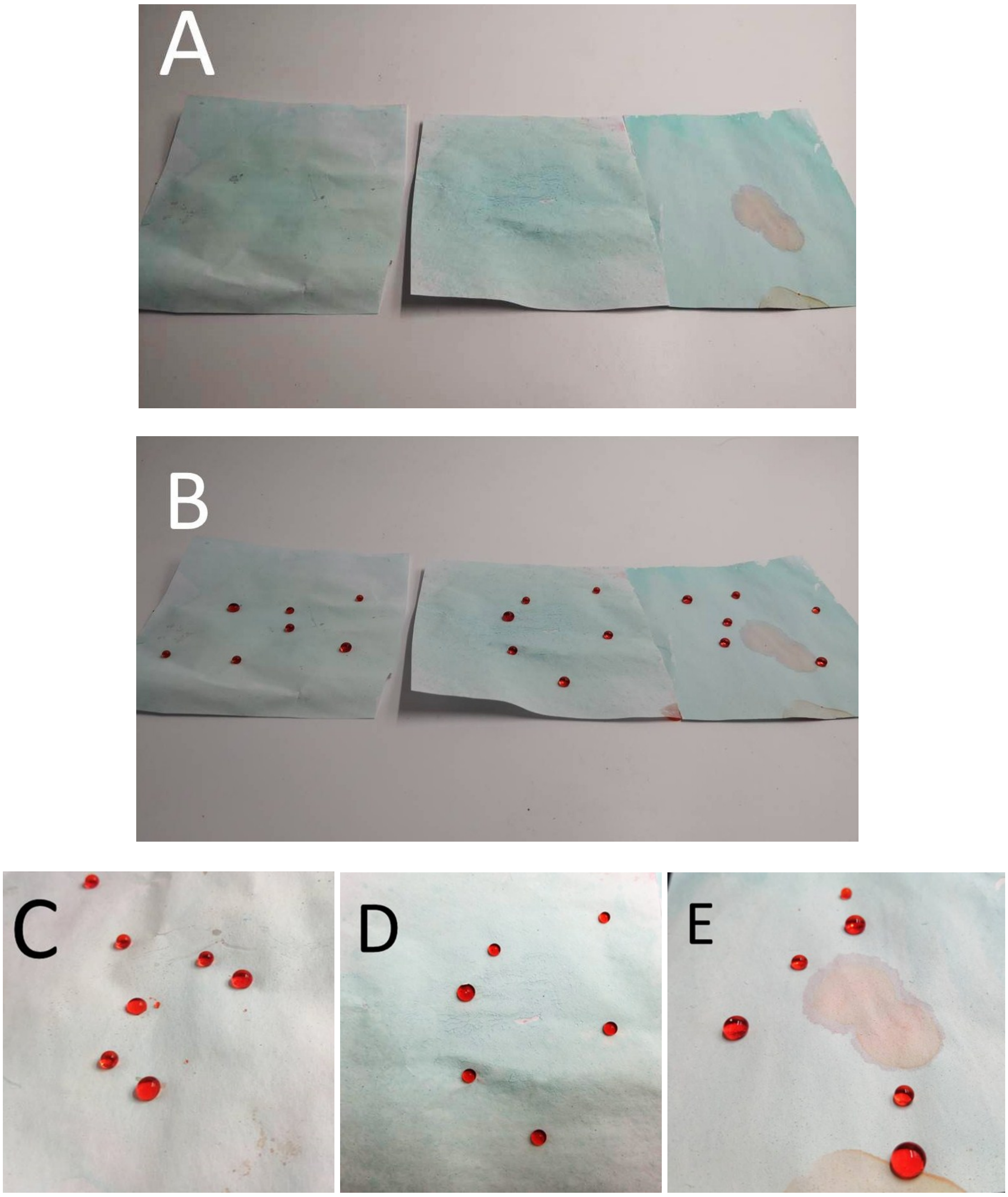


Fig.S4 Photographs showing different spraying amounts of nano lauric acid copper on the paper (A, from left to right, 1mmol, 2mmol, 3mmol); water contact with materials (B, from left to right, 1mmol, 2mmol, 3mmol) and close shot figure (C, 1 mmol; D, 2mmol; E, 3mmol).

Fig. S5 Photographs showing BCU(left) and SBCU(right)

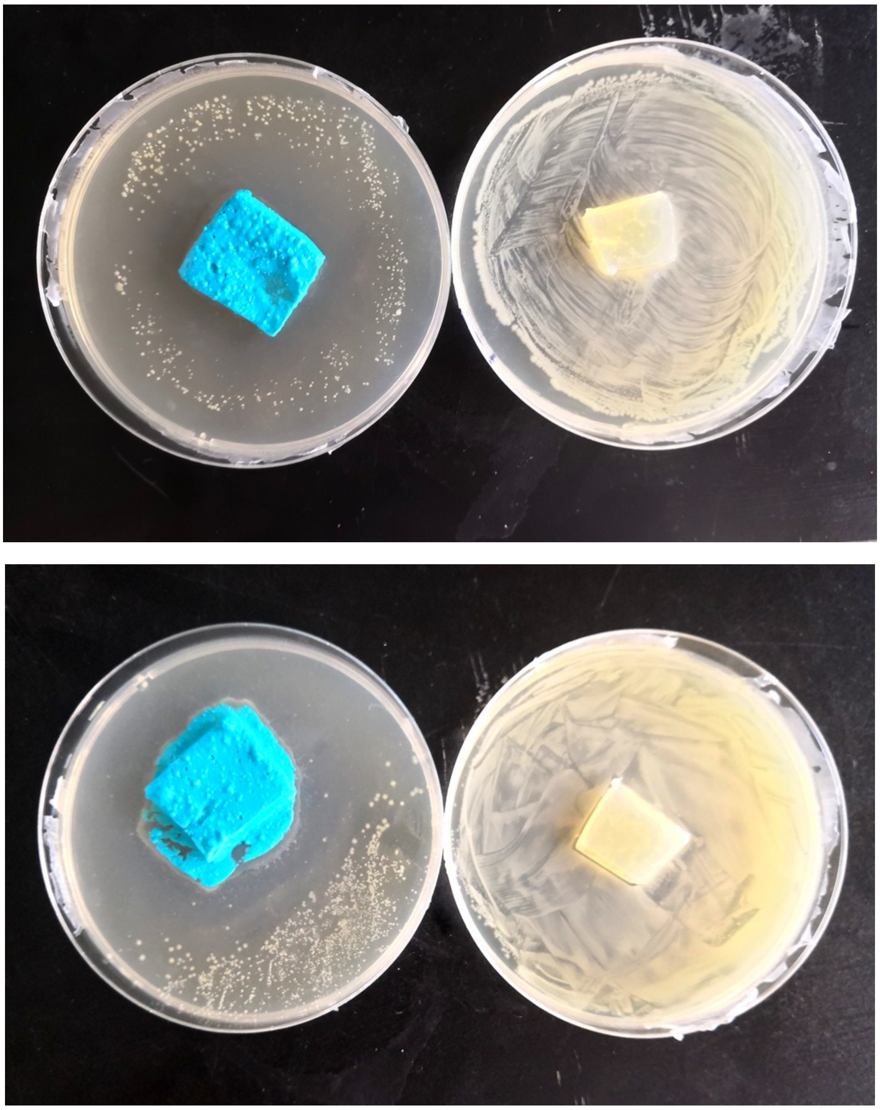


Fig.S6 Digital photographs showing repetition treatment of the antibacterial activity of nano lauric acid copper

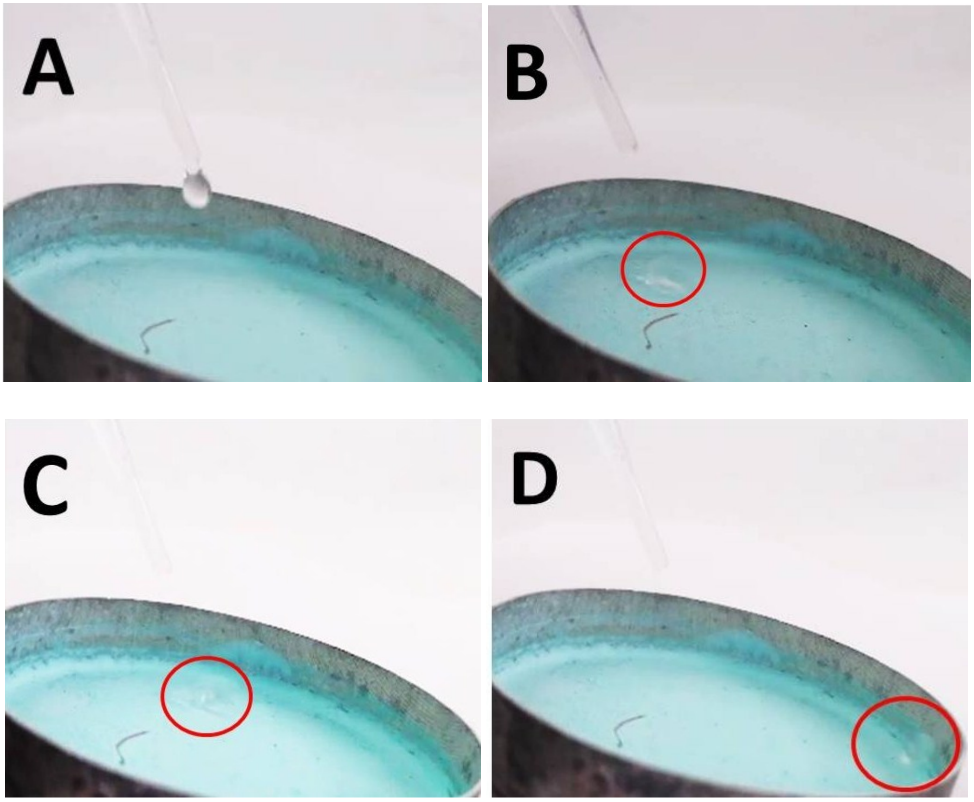


Fig. S7 Photo to show the sliding angle of the nano lauric acid copper coating

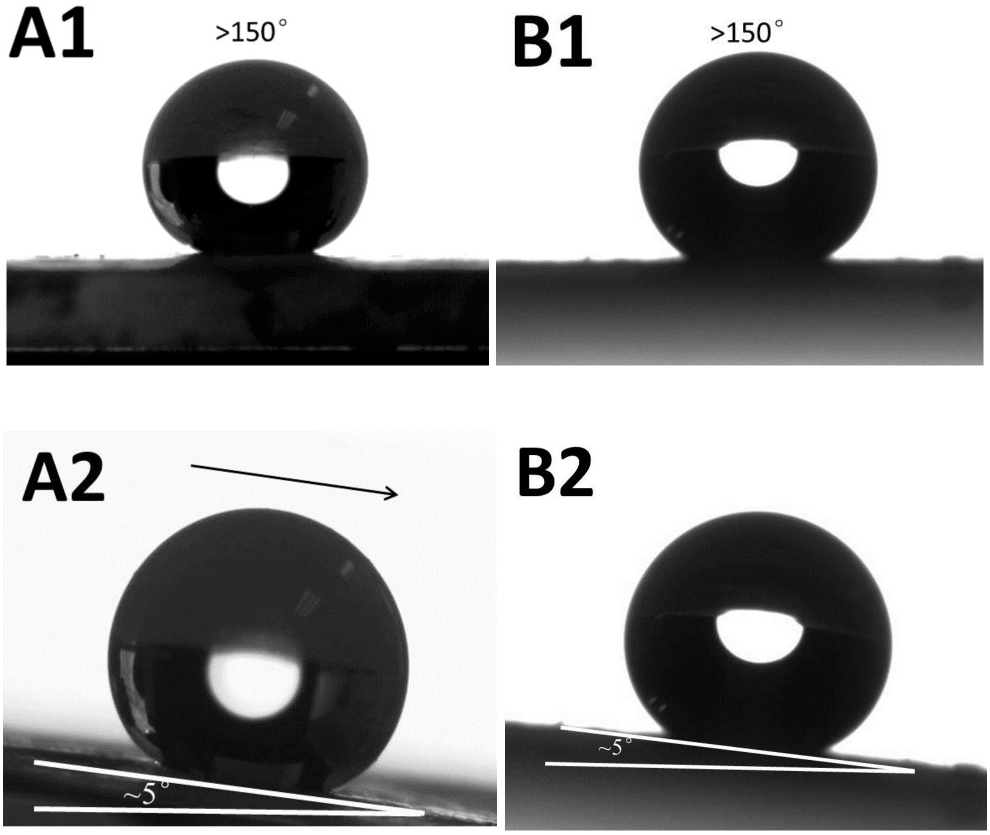


Fig. S8 WCA (A1and B1) and sliding angles (A2 and B2) of the coating materials before and after water incubation.