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Supplementary Materials for

Ultrasensitive nanoparticle enhanced laser-induced breakdown spectroscopy using a super-hydrophobic substrate coupled with magnetic confinement

Daming Dong*, Leizi jiao, Xiaofan Du and Chunjiang Zhao*

National Engineering Research Center for Information Technology in Agriculture, Beijing Academy of Agriculture and Forestry Sciences

*Correspondence and requests for materials should be addressed to: D.D (damingdong@hotmail.com; dongdm@nercita.org.cn);

S1. Materials and Methods

Super-hydrophobic substrate preparation.

The majority aim of this study is to demonstrate the enhancement effect of super-hydrophobic substrate coupled with magnetic confinement to laser-induced breakdown spectroscopy (LIBS), while the fabrication method of super-hydrophobic material is not the keynote. Therefore, we used a simple way to produce the super-hydrophobic interface with adhered metal nanoparticles. A commercial super-hydrophobic coating, Ultra-ever Dry (Florida, USA) was used to form hydrophobic layers[1-5]. We also used a commercial solution (prod No. 13705-20, TED PELLA, INC) to supply 20 nm gold nanoparticle. The nanoparticle solution was washed 3 times using a centrifuge (H1650W, cence company, Changsha, China) to remove stabilizers.

The preparation processes are as follows: 1) Take 10 ml Ultra-ever Dry solutions (top layer), and mix it with 1 ml nanoparticle solution, and stir uniformly. The reason of using 10:1 ratio are given in S2 part of supplementary materials. 2) Spray the bottom layer of Ultra-ever Dry solutions

onto a glass slide (25.4 mm * 76.2 mm) and drying in the air for 20 mins. 3) Then spray the mixer solutions onto the glass side after it is dried. 4) After 30 mins of drying in air, the super-hydrophobic interface with adhered metal nanoparticles was formed.

The sample container with super-hydrophobic nanoparticles and magnetic confinement.

As shown in figure.2, a sample container was developed to realize nanoparticle enhanced LIBS with both super-hydrophobic interface and magnetic confinement. The latter was provided by a magnetic sheet, which is 6 mm thick with a 5 mm conical hole. When the solution to be measured was dropped and dried on the glass side-based super-hydrophobic substrate, it will be inserted between the magnetic sheet and the metal plate.

The experimental system.

The LIBS experimental system was composed of laser, spectrometer, 3-dimensional moving platform and a precise delay generator. The laser we used was a Q-Switched Nd: YAG Laser-CFR200 laser generator (Quantel Ltd., France). Its wavelength was 1064 nm and the pulse width was 9 ns with the repetition frequency of 10 Hz. The beam divergence angle was less than 1 mrad and the maximum output energy was 200 mJ. The spectrometer was HR2000+ produced by Ocean Optics Company. Its spectral range was from 200 to 1100 nm with the spectral resolution of 0.2 nm and the signal-to-noise ratio of 250:1. A 3-dimensional moving platform was developed to adjust the appropriate position during the measurements, with a positioning accuracy of 200 nm. We also developed a FPGA based delay generator to output trigger signals for the delay between the laser shot and the spectrometer. In this experiment, the laser energy was set to 150 mJ, the spectral range was 200-850 nm, and the spot size was 200 μ m.

The experimental methods.

The experiment was carried out according to the steps as following: 1) Prepare a glass side-based super-hydrophobic substrate with adhered metal nanoparticles using the method described above. 2) Drop the solution to be measured onto the substrate surface and put it into a drying oven. In this study, when we dropped 200 μ L solutions onto the substrate and dried it under 50 °C conditions, it cost 40 mins for drying. 3) Insert the substrate into the sample container and keep

the aggregates in the middle hole of the magnetic sheet, as shown in figure 2. 4) Put the sample container on the 3-dimensional moving platform of LIBS system, focus the laser spot on the aggregates and measure the LIBS spectra.

S2. Performance of the super-hydrophobic substrate

The hydrophobic properties of the substrate

We dropped 200 μL water onto the substrate we prepared and used a SL200B Static and Dynamic Optical Contact Angle Goniometer (USA Kino Industry Co., Ltd) to evaluate the contact angle. Figure S1 showed the contact angles of an entire super-hydrophobic substrate. The contact angle was 155.7 ±3.1°. It was obviously in Cassie state with high contact angle and low hysteresis characteristic. We dropped 200 μL aqueous solution onto a glass slide without hydrophobic properties, a large aggregate of approximately 2 cm in diameter was formed, as shown in Figure 1b. When the same solution was dropped on the super-hydrophobic substrate we prepared, the diameter of the aggregate is about 200 μm, which indicates the concentrating factor of our substrate is 4-fold higher than glass slide.

We analyzed the surface topography of the substrate, which was shown in figure 1a. For the nanoparticle solutions was washed before the spray, the golden particles had a uniform distribution on the super-hydrophobic layer, without aggregates and islands. We counted the distribution of the nanoparticles on the substrate for a 10 μm*10 μm area, and the number was about 85±12. Wang *et. al* studied the chemical composing of the super-hydrophobic layers formed by Ultra-ever Dry using X-ray photoelectron spectroscopy and found that the elemental compositions were C, O, F, Si and Cl[5]. To more clearly demonstrate that the chemical compositions had no interfere to the Cu and Cd measurement in this experiment, figure S2 and figure 2d compared the LIBS signal of pure water and 100 *ppt* Cu solution and 400 *ppt* Cd solution, respectively.

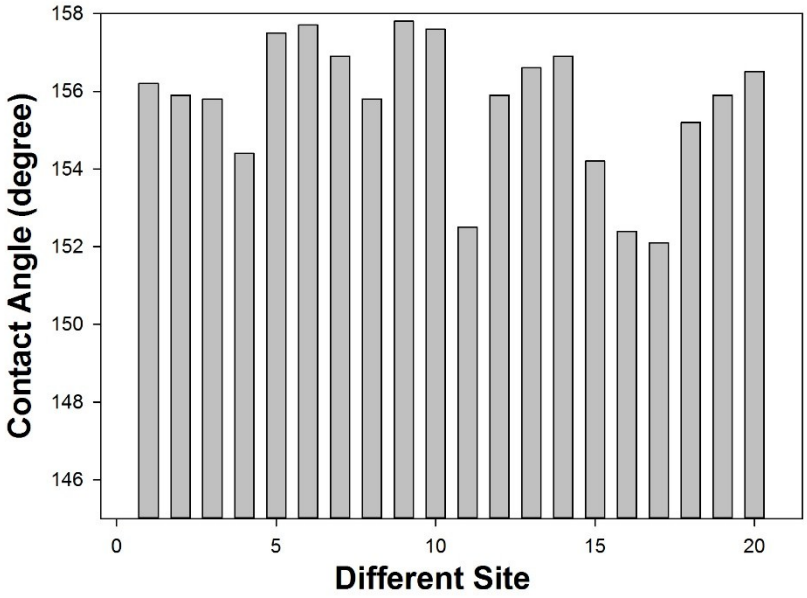

Figure S1. The contact angles of an entire super-hydrophobic substrate

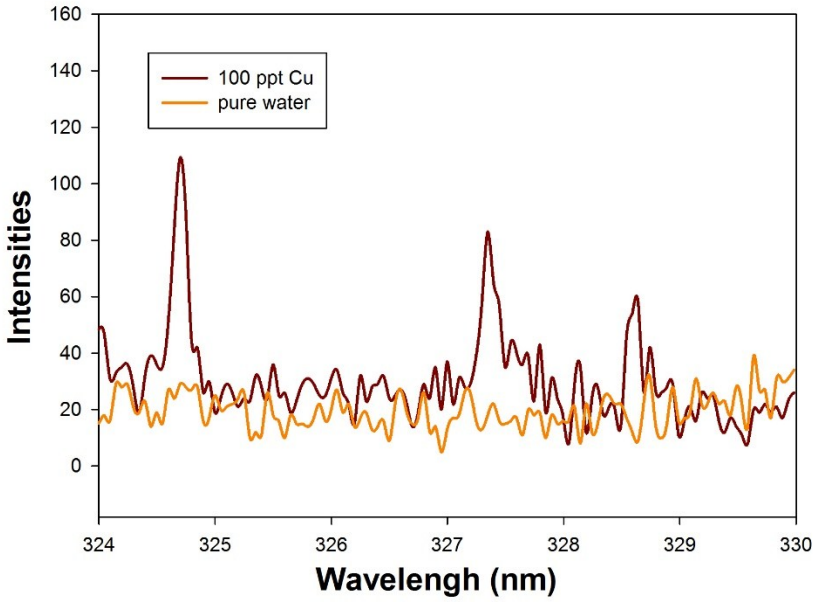

Figure S2. The LIBS signal of pure water and 100 *ppt* Cu solution using the sample container with super-hydrophobic substrate

Determination of the ratio between super-hydrophobic coating and nanoparticle solution

As described in the experimental part, to create a super-hydrophobic interface with adhered metal

nanoparticles, we mixed Ultra-ever Dry and the nanoparticle solution at a 10:1 ratio. This ratio was determined through studying the hydrophobic properties and enhancement effect among various ratios. Figure S3 showed the contact angles of different ratios of mixer, which indicated that the hydrophobic properties become worse with more nanoparticle solutions. It is obvious that the contact angle of 10:1 was only a little smaller than that of 50:1 and 100:1, while the contact angle of 5:1 sharply decreased. We also developed the sample containers with both super-hydrophobic substrate and magnetic confinement of different ratios. When we dropped 200 μ L Cu solution in the sample container, the one with 10:1 ratio showed the highest LIBS signal intensity at 324.7 nm, as shown in figure S4. The signal of 100:1 and 50:1 were weak, for the number of nanoparticles was not enough for the enhancement, though they have good hydrophobic properties. The signal of 5:1 and 1:1 ratio were also weaker than that of 10:1, because their hydrophobic properties were limited.

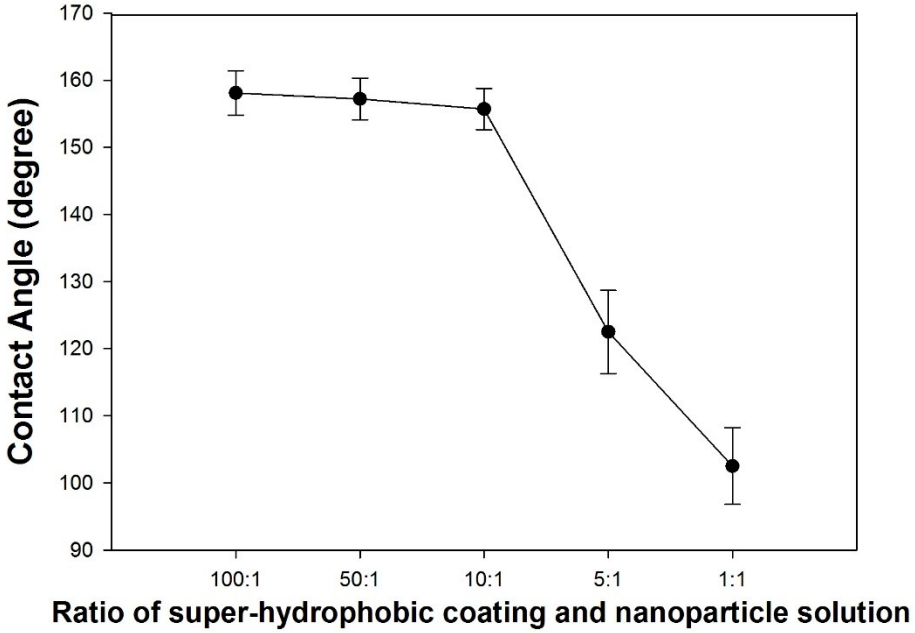

Figure S3. The contact angle of different ratio of super-hydrophobic coating and nanoparticle solution

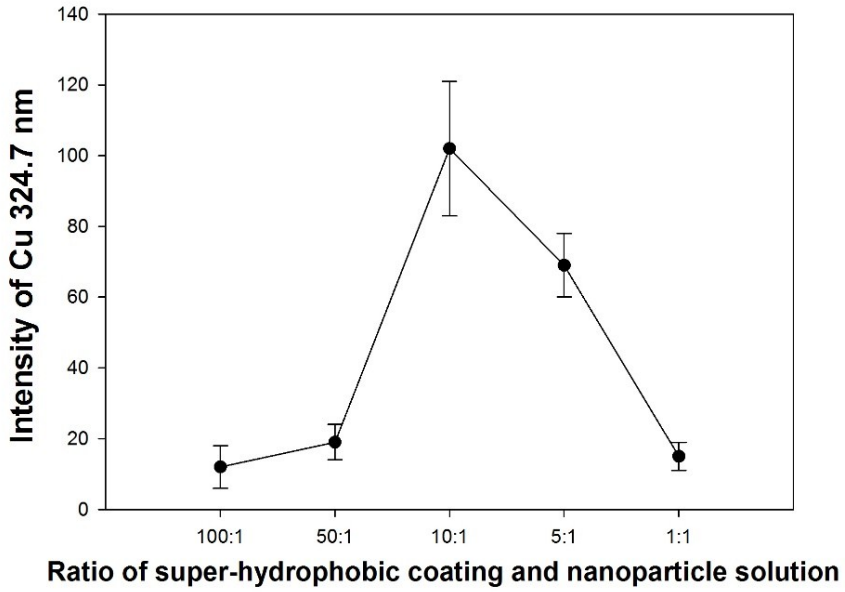

Figure S4. The LIBS intensity of Cu 324.7 nm line (100 *ppt* Cu solution) of different ratio of super-hydrophobic coating and nanoparticle solution

Notes and references

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