



# Superhydrophilic surface modification of copper surfaces by Layer-by-Layer self-assembly and Liquid Phase Deposition of TiO<sub>2</sub> thin film

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## ABSTRACT

A new method has been developed for the superhydrophilic surface modification of copper using versatile solution-based fabrication techniques. The high surface area of TiO<sub>2</sub> nanoparticles was exploited to create a thin film with increased surface energy that transformed copper materials from relatively hydrophobic to superhydrophilic. Copper exposed to ambient conditions resulting in a thin layer of copper oxide has a water contact angle near 90°, but following TiO<sub>2</sub> modification, the contact angle dropped to 0°. The thin film responsible for this drastic improvement in wettability proved durable by retaining its excellent properties throughout an extended application of thermal stress. SEM and Raman Spectroscopic analysis confirmed the structural integrity of the film before and after a durability test.

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## 1. Introduction

Many of the most successful commercial applications of nanoparticles in recent years have involved titanium dioxide. A major thrust in TiO<sub>2</sub> nanoparticle research is thin film design, which has led to an abundance of not only intriguing, but also useful new technologies. Examples include anti-fogging glass coatings, surface modification of microfluidic devices, anti-microbial films, and even novel air purification systems [1–10]. A number of the more popular applications, such as the anti-fogging glass film, depend primarily on the hydrophilic nature of TiO<sub>2</sub>.

One of the few ways to make the hydrophilic behavior of a surface more robust is to increase its roughness and exposed surface area [11,12]. Naturally, the surface area of a film will be large when its component particles are small. Therefore, thin films fabricated with nanoparticles can be highly hydrophilic. This is especially true when considering TiO<sub>2</sub> nanoparticles [13]. Perhaps the most common use for hydrophilic TiO<sub>2</sub> coatings is the surface modification of glass [2–6,8,18]. Indeed, the possible applications of glass coatings have been thoroughly explored. However, there currently exists enormous undeveloped potential for TiO<sub>2</sub> coatings on materials other than glass (or silicon), specifically on non-optical devices.

Reported here for the first time is the application of hydrophilic TiO<sub>2</sub> thin film technology to copper surfaces for the specific purpose of increasing the efficiency of heat sinks, heat pipes, and other cooling devices. Such devices rely on the rapid transport of water or other liquids across warm surfaces to increase their rate of heat

transfer. This action is greatly assisted by hydrophilic coatings designed to overcome the more hydrophobic nature of bare copper. Copper metal exposed to ambient conditions is covered by a thin layer of copper oxide and normally has a water contact angle of approximately 90° (Fig. 1). This hydrophobic behavior can be improved greatly by fabricating a TiO<sub>2</sub> thin film on the copper's surface. In fact, the surface modification described here transformed the copper from relatively hydrophobic to superhydrophilic with a contact angle of 0° (Fig. 2). The use of Layer-by-Layer (LbL) self-assembly and Liquid Phase Deposition (LPD) enhances the appeal of this technology for industrial applications due to its scalability and effectiveness in coating surfaces with complex morphologies.

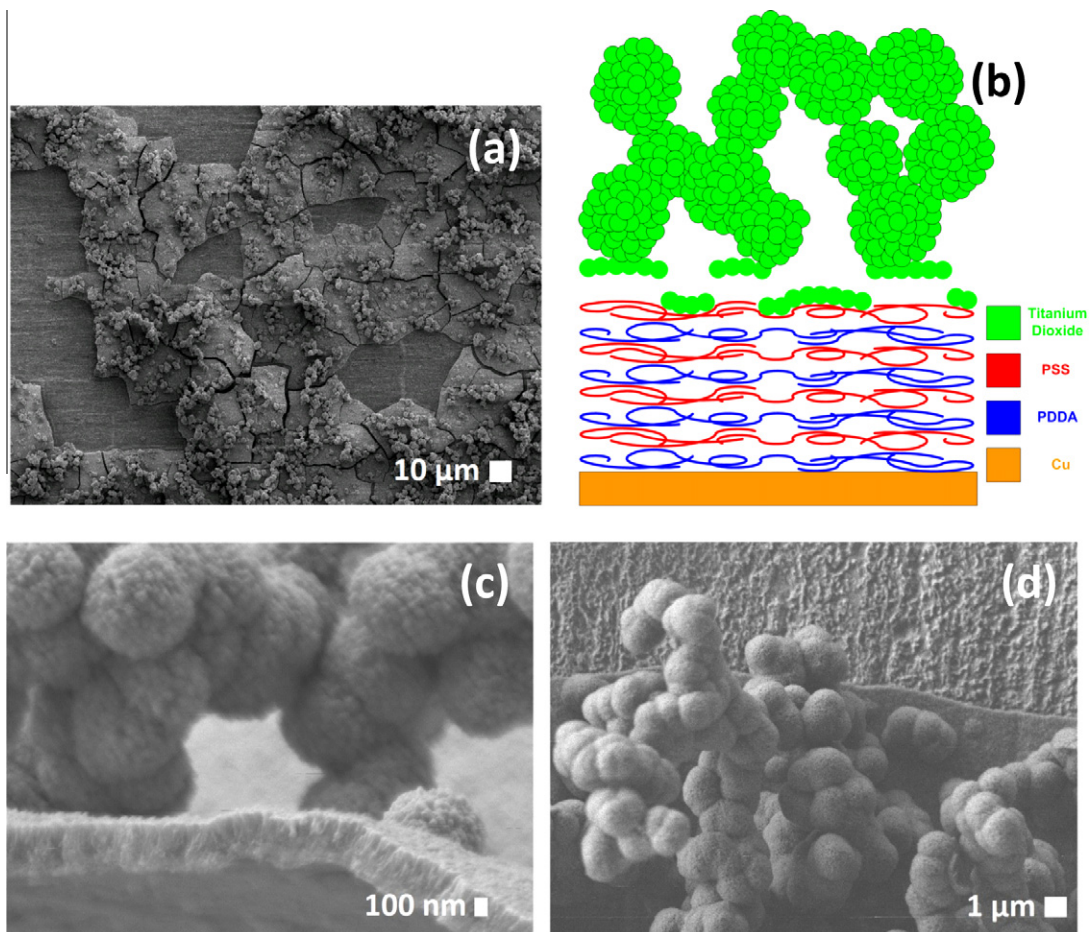
## 2. Methods

### 2.1. Layer-by-Layer self-assembly and Liquid Phase Deposition

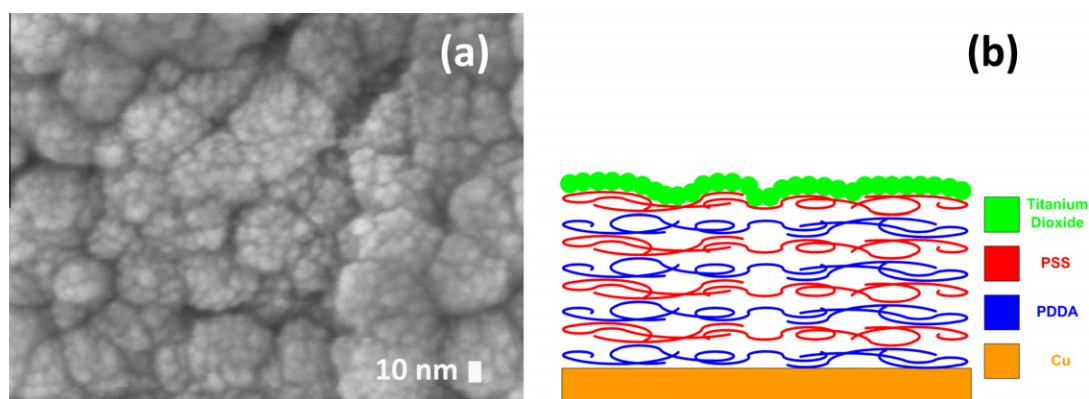
LbL self-assembly is a solution-based fabrication technique that relies on the simple electrostatic attraction between species of opposite charge [14–17]. A charged substrate is placed in a solution containing particles of the opposite charge. By diffusion and electrostatic attraction, the charged particles in solution come to rest on the substrate, forming a monolayer. After this has occurred, the substrate is removed from the solution, rinsed, and then dried in a stream of nonreactive gas, such as N<sub>2</sub>. The rinsing and blow drying are important steps in the process because they remove weakly attached particles. If such particles remain on the substrate, they prevent future layers from forming a tight bond. Next, the coated substrate is placed in another solution of particles with the charge opposite that of the previous solution. Then the second

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**Fig. 1.** (a) LPD at 45 °C produced a film that quickly chipped away during rinsing when large agglomerates that had bonded to the dense base layer pulled off the substrate; (b) schematic drawing of  $\text{TiO}_2$  agglomerates breaking away from the surface and ripping off sections of the desired  $\text{TiO}_2$  thin film, not drawn to scale; (c) SEM image showing a cross-section of the thin film being ripped away from the surface and (d) overhead perspective of agglomerate-covered thin film and exposed copper surface following the loss of the film as described in (b) and (c).



**Fig. 2.** (a) SEM image detailing the structure of the tightly-packed nanoparticles composing the base layer of  $\text{TiO}_2$  and (b) a schematic drawing of the film's proper structure without any undesired agglomerates.

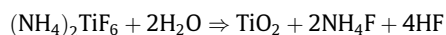
monolayer is grown in the same fashion as the first. This process is repeated as necessary to build up the desired type of film.

In the surface modification of copper described here, LbL self-assembly was employed to build up a “buffer layer” similar to what Tsuge used in his optical coating [18]. This served as the film's foundation, a series of alternately-charged monolayers that assisted in providing a tight electrostatic bond between bare copper

and the  $\text{TiO}_2$  particles deposited on top. The charged monolayers were composed of highly ionic polymer nanoparticles with diameters less than 5 nm. Since copper generally holds a negative charge, poly(dimethyldiammonium chloride) (PDDA), a positively charged particle, was used for the first layer of the film. Next, poly(sodium 4-styrenesulfonate) (PSS), a strongly negative polymer, formed the second layer. This sequence repeated several times, ending with

PSS. The negative charge of PSS was necessary for the proper adhesion of the positively-charged  $\text{TiO}_2$  particles, which were finally attached using Liquid Phase Deposition.

LPD is another convenient, room temperature, solution-based method of creating highly uniform, thin layers of nanoparticles on the surface of an object [19,20]. With this technique,  $\text{TiO}_2$  nanoparticles precipitate out of a hydrolysis reaction of ammonium hexafluorotitanate,  $(\text{NH}_4)_2\text{TiF}_6$ , assisted by boric acid,  $\text{H}_3\text{BO}_3$ . Lin provided a reasonable and fairly detailed model for the reaction mechanism [21]. In summary, the reaction proceeds in this manner [21,22].



The addition of  $\text{H}_3\text{BO}_3$  shifts the equilibrium of this reaction to the right, as boric acid reacts with hydrofluoric acid according to the following equation.



## 2.2. Experimental

An Ameriwater Ultra-Pure Laboratory Deionizer produced water of 20 M $\Omega$  purity for all aqueous solutions and for the rinsing of samples after the deposition of each layer.  $(\text{NH}_4)_2\text{TiF}_6$ ,  $\text{H}_3\text{BO}_3$ , PDDA, and PSS were all obtained from Sigma–Aldrich and used without any further purification. Industrial grade planar copper sheets were diced for test substrates.

First, copper substrates were cleaned of organic contaminants with acetone, isopropyl alcohol, and then water. Next, a stream of nitrogen gas dried the copper samples before the initial deposition. After drying, substrates were submerged in solutions of 4.29 ( $10^{-5}$ ) M PDDA, which also contained NaCl at a concentration of 0.50 M. Following a 10 min deposition period, samples were removed from the PDDA solution, thoroughly rinsed in deionized water, and dried again with  $\text{N}_2$  gas. The deposition process was then repeated for 10 min in a 4.29 ( $10^{-5}$ ) M PSS solution, also containing NaCl with a concentration of 0.50 M. Then once more, samples were rinsed and dried. Alternating layers of PSS and PDDA in

this manner continued until four layers of each had been built on the copper surface. This construction served as a foundation for the  $\text{TiO}_2$  particles.

Equal volumes of 0.20 M  $(\text{NH}_4)_2\text{TiF}_6$  and 0.60 M  $\text{H}_3\text{BO}_3$  were heated to 70 °C, then combined and maintained at this temperature. The copper substrates coated in PDDA and PSS were submerged in this solution immediately upon mixing the  $(\text{NH}_4)_2\text{TiF}_6$  and  $\text{H}_3\text{BO}_3$ . After 6 h, the copper substrates were removed from the mixture and rinsed thoroughly in deionized water to remove loose particles. A gentle jet of nitrogen gas dried samples following the rinse. At the conclusion of this process, a uniform, faint white haze remained on the copper samples, indicative of the thin film strongly adhered to all surfaces.

To analyse the structural characteristics of the film, images of coated copper substrates were obtained using a JEOL 6700 scanning electron microscope. Then Raman spectra of the film were examined to understand the chemical properties of this LbL/LPD hybrid. In the interest of developing a useful coating for microfluidic applications involving elevated temperatures, the film's durability was tested in boiling water for a period of 88 h. At the conclusion of this time, SEM and Raman analyses were repeated. In addition, water contact angles were determined before and after the boiling with an OCA-15 contact angle meter and video-based measurement software from DataPhysics. Average contact angles were recorded from four measurements taken at random locations on each film sample. All contact angle measurements were made with 5.0 mL drops of deionized water. A stream of nitrogen gas dried samples after each contact angle measurement.

## 3. Results and discussion

SEM images revealed that two main components made up the  $\text{TiO}_2$  film, a thin base layer and a much thicker, rough deposit on top, shown in Fig. 1. As the LPD hydrolysis reaction proceeded and  $\text{TiO}_2$  precipitated out of the solution, a film approximately 300 nm thick formed directly on top of the PDDA and PSS. This thin film was a carpet of tightly packed particles between 15 and 50 nm in diameter. Then, a jumbled collection of relatively large agglomerates

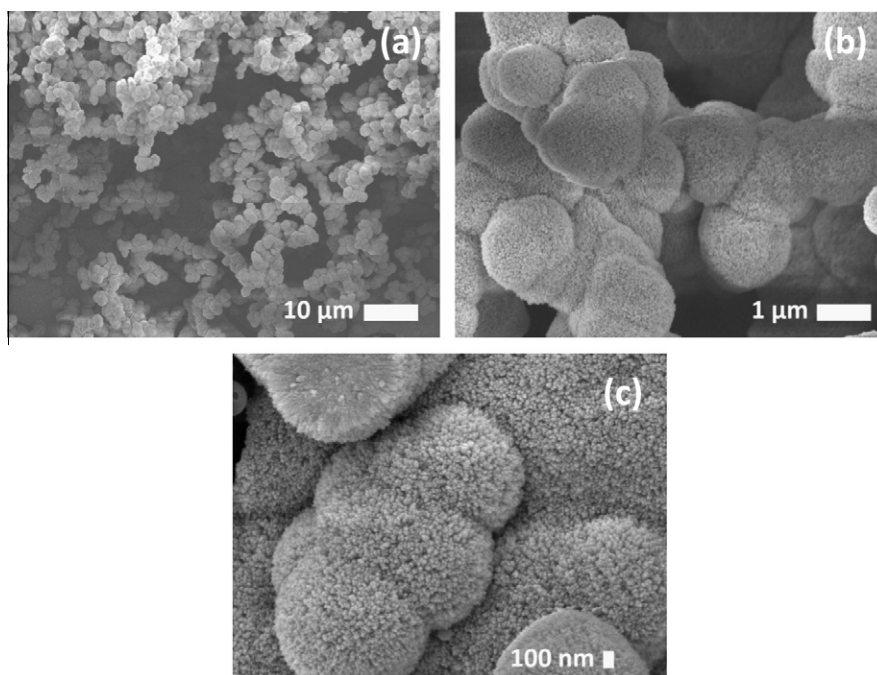


Fig. 3. Additional SEM images showing the structure of the film: (a and b) agglomerates on top of the thin film and (c)  $\text{TiO}_2$  agglomerates attached to the base film.



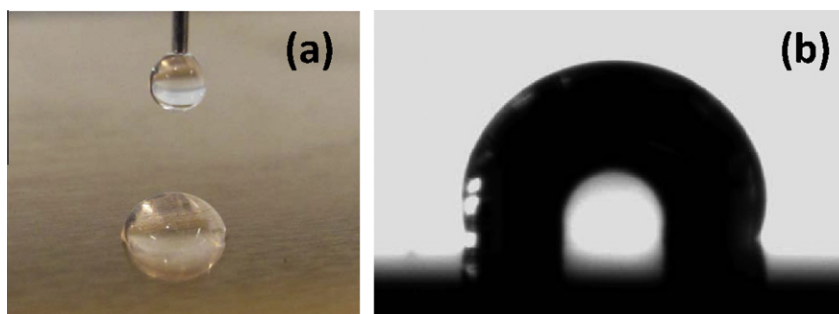


Fig. 4. (a) Drop of water on a bare copper plate and (b) contact angle slightly above 90°.

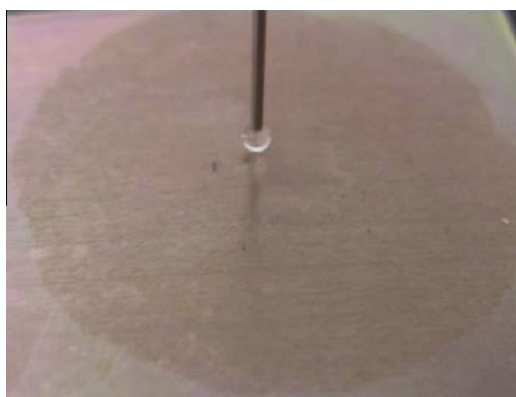


Fig. 5. Drop of water spreading rapidly immediately upon hitting the coated copper surface.

with low density formed on top of the thin film. Because the large agglomerates were normally on the order of microns, they were visible as an opaque white coating on the copper substrate. Ideally, to minimize thermal resistance and to enhance the precision of the film's coverage, the large particle agglomerates should be removed. However, under the wrong deposition conditions, these unwanted agglomerates bonded to the thin layer of TiO<sub>2</sub> nanoparticles and it was impossible to remove them without severely damaging the desired thin film underneath.

When the reactant solutions were not heated above room temperature before their combination, the hydrolysis reaction proceeded slowly and the large agglomerates bonded with the thin film as it formed on the substrate. In contrast, when reactant solutions were heated prior to their combination, the reaction occurred

rapidly, as indicated by almost immediate precipitation of TiO<sub>2</sub>. Further, when this happened, the large agglomerates of TiO<sub>2</sub> did not attach firmly to the thin film growing on the substrate's surface. Rather, these giant collections of TiO<sub>2</sub> particles detached easily from the surface of the film during rinsing, leaving only a uniform, superhydrophilic thin layer of tightly-packed TiO<sub>2</sub> nanoparticles (Fig. 2).

The different modes of particle growth during a TiO<sub>2</sub> LPD reaction, as described by Katagiri et al., shed some light on these results [23]. According to Katagiri's group, small primary particles begin to precipitate before the larger "raspberry-like" agglomerates form in the solution (Fig. 3a and b). These large collections of primary particles tend to grow much faster at temperatures near 70 °C than they do at temperatures below 50 °C. Though not emphasized by Katagiri, his data suggest that the different phases of growth are more distinct from one another at higher temperatures. Assuming this model of particle growth, it is likely that increased thermal excitation prompted the quick deposition of primary particles to form the dense base layer before the large agglomerates began to develop. However, at lower reaction temperatures, the base layer grew slowly alongside the agglomerates and both structures became joined as they shared primary particles (Fig. 3c).

The TiO<sub>2</sub> thin film reduced the water contact angle of copper samples consistently from approximately 90° to 0° (Fig. 4a and b). Drops of water that landed on the coated copper fell to 0° in a small fraction of a second before spreading out across the surface rapidly in all directions (Fig. 5). Therefore, the film was superhydrophilic. Such performance allows water to flow across the copper quickly, making it a better dissipater of heat in many cooling applications.

Also important for heat dissipation purposes is the film's ability to withstand relatively harsh temperatures over time. While higher

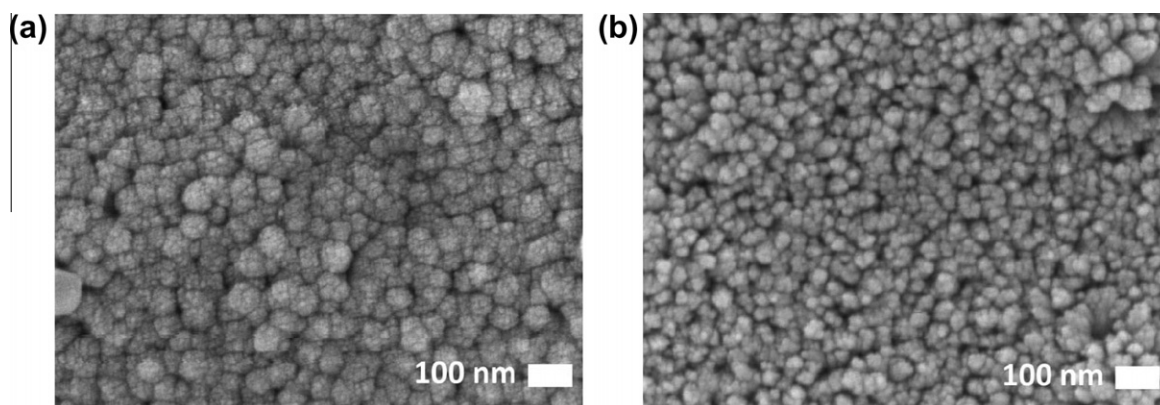
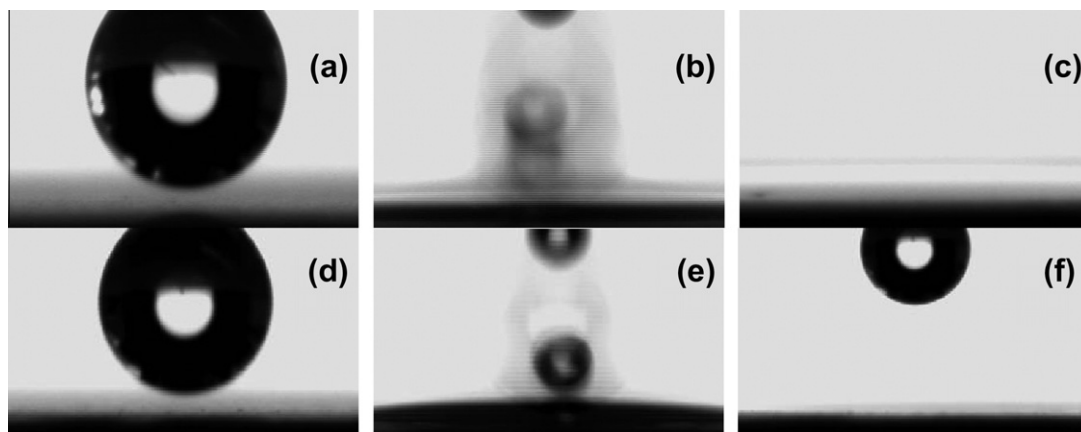
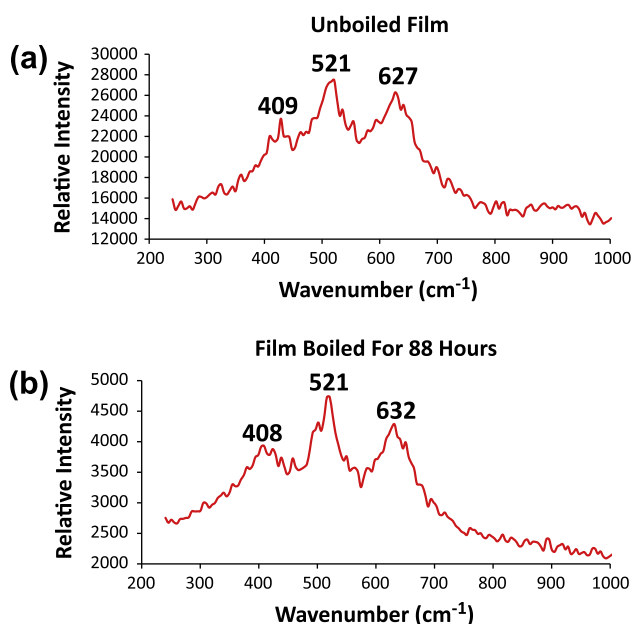


Fig. 6. (a) Before and (b) after boiling the film for 88 h.



**Fig. 7.** (a) Immediately before (b) during and (c) after a drop's contact with the film's surface before boiling; (d) before (e) during and (f) after drop contact with film after boiling test.



**Fig. 8.** (a) Raman spectrum of  $\text{TiO}_2$  film before boiling and (b) Raman spectrum of  $\text{TiO}_2$  film after boiling.

temperatures could have been used, this study subjected the film to boiling water at  $100^\circ\text{C}$  for 88 h (Fig. 6a and b). Such a test was relevant when considering the moist, hot environment of a water-cooled heat sink. Fig. 7a–c shows a drop of water immediately before, during, and after contact with the  $\text{TiO}_2$  film, prior to the boiling period. This performance was duplicated almost exactly following the boiling, as seen in Fig. 7d–f. The consistency of the film's effectiveness despite severe test conditions is in accord with SEM observations, which show that the structure did not suffer serious harm during the boiling, though it did appear to have experienced a slight reduction in density.

Raman spectral analysis bolstered the observations made with both contact angle measurements and also SEM images. According to the measured Raman spectra, the  $\text{TiO}_2$  originally deposited on the copper surface survived the harsh, boiling environment. This was indicated by three peaks distinctive of crystalline anatase  $\text{TiO}_2$ , which appeared before and after the boiling (Fig. 8). The absence of rutile and brookite spectra in the Raman analysis showed that neither of these phases were present in the film [24–28].

#### 4. Conclusion

A new application of  $\text{TiO}_2$  thin film technology has been developed to transform bare copper covered by a thin layer of its naturally occurring oxide from hydrophobic ( $\text{CA} = 90^\circ$ ) to superhydrophilic ( $\text{CA} = 0^\circ$ ). With this innovation comes great potential to radically improve heat dissipation devices such as microfluidic cooling systems and heat pipes, which often rely on efficient fluid flow across copper surfaces. The coating method detailed here takes advantage of the scalability and versatility of LbL self-assembly and Liquid Phase Deposition, making the implementation of this technology more practical for current manufacturing processes.

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