Interfacial Effects of *In Situ*-Synthesized Ag Nanoparticles on Breath Figures

Xiaoli Jiang,[†,‡] Xuefeng Zhou,[‡] Yu Zhang,[†] Tianzhu Zhang,[†] Zhirui Guo,[†] and Ning Gu*[,†,‡]

[†]*Jiangsu Key Laboratory for Biomaterials and Devices, State Key Laboratory of Bioelectronics, School of Biological Science and Medical Engineering, Southeast University, 4 Sipailou, Nanjing 210096, China, and* [‡]*Suzhou Key Lab of Biomedical Materials and Technology, Research Institute of Southeast University in Suzhou, 150 Ren Ai Road, Suzhou Industrial Park, Suzhou 215123, China*

In the present study, we introduced Ag nanoparticles into polymer and found for the first time that Ag nanoparticles can induce the formation of breath figure (BF) arrays on polymer surfaces. The effect of Ag nanoparticles has a balance with the BF process, which is influenced by humidity levels and polymers. These nanoparticle-induced BF process involves an interesting interaction between two self-assembly processes on different length scales. The aggregation of Ag nanoparticles on the water/polymer interface might be the key to their inducing ability. Hence, the interfacial-active Ag nanoparticles can be utilized to widen the applications of the BF method and to fabricate a wide variety of novel functionalized porous polymer films.

1. Introduction

Polymer films with highly ordered pores have been studied long because of their wide uses in electronics,[1] photonics,[2] and catalysis.[3] Recently, they also continue to generate considerable interest as novel cell culture substrates.[4] The breath figure (BF) method has attracted more attention because of the availability and the simple process for fabricating porous polymer films, compared with those of other templating methods where colloidal particles[5,6] or macroporous silica[7] were used as templates. BF utilize the solvent-evaporation-induced condensation of water vapor on the surface of a polymer solution. The droplets of the condensed water self-assemble into a hexagonally ordered array at the air/solution interface. After the evaporation of solvent and water droplets, the well-ordered honeycomb structure is left on the film surface.[8-11] However, this method is known to require precise control over the processing environment conditions, and the polymer used in BF usually should be specially designed and synthesized to obtain better quality in pore size and distribution.[12-16] Therefore, the development of simpler and more controllable processes for the patterning of polymer films remains a great challenge to material science. Meanwhile, the exact mechanism of BF formation is not fully understood, and the mechanism of droplet stabilization is also under debate.

In the current research, we introduce Ag nanoparticles into polymers by a facile *in situ* reduction method, and Ag nanoparticles act as a novel influence factor for the fabrication of nanocomposite films with ordered porous surface pattern. In this approach, the promoting effect of nanoparticles in the BF process is observed for the first time. The effect of nanoparticles has a balance with the BF process, which is determined by the humidity levels and polymers. The interactions between the BF process and Ag nanoparticles, which are assembled at the liquid−liquid interface, are discussed. Meanwhile, nanoparticles can functionalize these BF holes with potential applications related to their electronic, chemical, or optical properties.

2. Experimental Section

2.1. Materials. Silver nitrate (AgNO$_3$, 99%), sodium borohydride (NaBH$_4$, 99%), and hydrogen tetrachloroaurate (HAuCl$_4$) were purchased from Shanghai Chemical Reagent Co. Poly(L-lactic acid) (PLLA) ($M_W = 100,000$) was purchased from Shandong Institute of Medical Instrument. Polyurethane (PU) (Tecothane, Lubrizol) was purchased from Dow Chemical Co. in Shanghai. All solvents, ethanol, chloroform (CHCl$_3$), and tetrahydrofuran (THF), were dried carefully according to the standard procedure.

2.2. Preparation of Nanoparticle/Polymer Suspension. (a) Four wt % suspension of PU in THF/ethanol containing 1% of Ag nanoparticles: 0.2 mL of AgNO$_3$ absolute ethanol solution (1 mmol/L) was first mixed with 50 mL of THF solution containing 2 g of PU to obtain a PU/AgNO$_3$ solution in THF/ethanol, and then 0.2 mL of freshly prepared NaBH$_4$ ethanol solution (0.02 mol/L) was added to the above PU/AgNO$_3$ solution with vigorous stirring. The bright-brown suspension was obtained after the reaction was complete. PU with 0.2% and 5% Ag nanoparticles were also prepared as described in the above procedure, while the concentrations of AgNO$_3$ absolute ethanol solution changed to 0.2 mmol/L and 5 mmol/L, respectively.

(b) Ten wt % suspension of PLLA in CHCl$_3$/ethanol containing 1% of Ag nanoparticles: 0.5 mL of AgNO$_3$ absolute ethanol solution (1 mmol/L) was first mixed with 50 mL of CHCl$_3$ solution containing 5 g of PLLA to obtain a PLLA/AgNO$_3$ solution in CHCl$_3$/ethanol, and then 0.5 mL of freshly prepared

*Corresponding author. Phone: +86-(0)25-83272460. Fax: +86-(0)25-83272476. E-mail: guning@seu.edu.cn.

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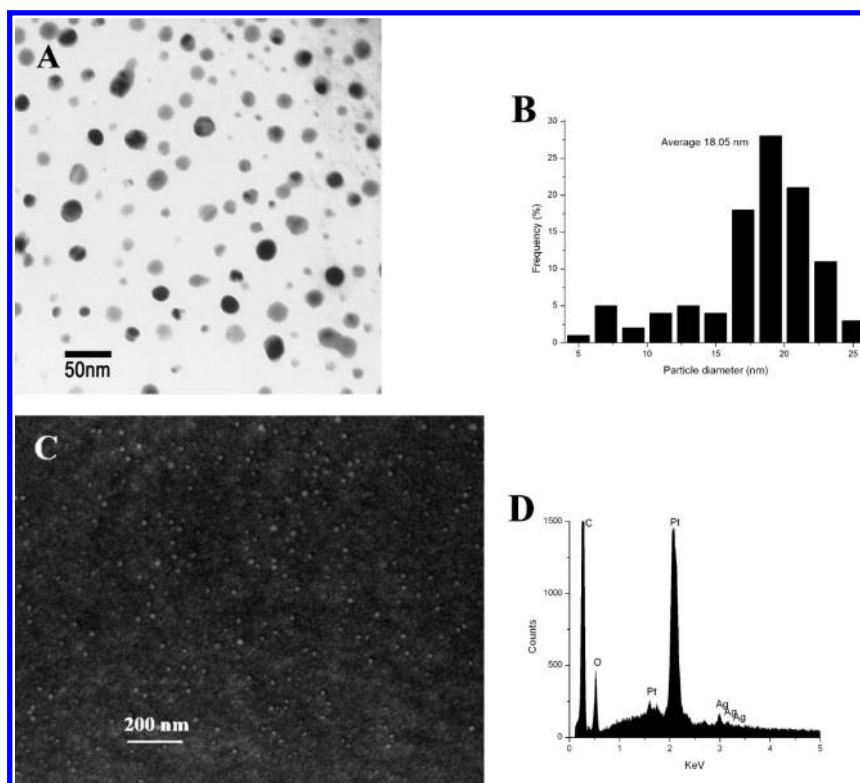(16) Stenzel-Rosenbaum, M. H.; Davis, T. P.; Fane, A. G.; Chen, V. *Angew. Chem., Int. Ed.* **2001**, *40*, 3428.

Figure 1. (A) TEM image of Ag nanoparticle-impregnated polyurethane. (B) Size distribution of Ag nanoparticles. (C) SEM image of the Ag/PU polymer surface, cast under 10% RH. (D) EDX spectrum of the surface of Ag/PU film coated with platinum.

$NaBH_4$ ethanol solution (0.02 mol/L) was added to the above PLLA/AgNO$_3$ solution with vigorous stirring. The bright-brown suspension was obtained after the reaction was complete.

(c) Ten wt % suspension of PLLA in CHCl$_3$/ethanol containing 1% Au nanoparticles: The preparation procedure is similar to process b where 0.5 mL of AgNO$_3$ absolute ethanol solution (1 mmol/L) was replaced with 0.5 mL of HAuCl$_4$ absolute ethanol solution (3 mmol/L). A pink composite suspension was obtained.

2.3. Formation of Polymer−Nanoparticle Composite Films. One hundred microliters of polymer−nanoparticle suspension was cast on a cover glass in a silica-gel desiccator at room temperature (25 °C) with 30% relative humidity (RH). The suspensions were directly utilized without purification. To check if residuals have any influence on the formation of porous films, a control experiment was designed as follows: the polymer solution, ethanol/polymer solution, AgNO$_3$/polymer solution, and NaBH$_4$/polymer solution were used to cast polymer films under the same conditions as those described above. High humidity conditions (90%) are achieved by placing the cover glasses in a sealed chamber half filled with water. The relative humidity of the atmosphere was measured by hygrometers in each of the chambers. After complete evaporation of the solvent, the films were first washed with ethanol and then dried overnight.

2.4. Characterization. The dispersion of nanoparticles inside the polymer matrix was observed by transmission electron microscopy (TEM; JEOL, JEM2000EX). The sample was prepared by dropping 0.01 mL of PU/Ag composite suspension on the TEM grid. The surface morphologies of the flat films were investigated by using a scanning electron microscope (SEM; JEOL, JSM-5610LV) equipped with an energy-dispersive X-ray (EDX; NORAN, VANTAGE) microanalysis system. The samples were coated with platinum under reduced pressure with a sputter coater prior to examination. The surfaces of the porous films were probed by atomic force microscopy (AFM; Agilent, PicoPlus). The contact angles of the flat polymer−nanoparticle films were measured by a dynamic contact angle measuring system (DCA; KSV, CAM200).

3. Results and Discussion

3.1. Characterization of Polymer−Nanoparticle Composites. The polymer−nanoparticle composite was prepared by a one-step *in situ* reduction method. There are many methods to prepare polymer−nanoparticle composites. However, a great stumbling block to the production of well-dispersed nanocomposites is the aggregation of nanoparticles, which negates the benefits associated with the nanoscopic dimension.[17] In this work, the *in situ* formation of nanoparticles in the polymer matrix promotes uniform nanoparticle dispersion. The morphology of Ag nanoparticles in the PU matrix is shown in Figure 1A. The monodispersive colloids show that the PU matrix embedding Ag nanoparticles prevented coagulation, although the polymer cannot be observed because of its lower electron density. It is evident from the histograms (Figure 1B) that the average diameter of Ag nanoparticles in PU is 18.05 nm. The size distributions were obtained by measuring the diameters of 200 particles in arbitrarily chosen areas of TEM images. The SEM image of the surface of a flat composite film shows that the Ag nanoparticles are well dispersed with an average size of about 20 nm (Figure 1C). The presence of silver was also clearly exhibited in the EDX spectrum as shown in Figure 1D.

3.2. Effects of Humidity Level: BF Process with Ag Nanoparticles in Polyurethane. In recent years, BF process with nanoparticles has received increasing interest in fabricating honeycomb-structured composite films.[18−20] The study of a BF process with CdSe nanoparticles has been reported.[21] The hierarchical assembly of nanoparticles with BF was studied. However, the effects

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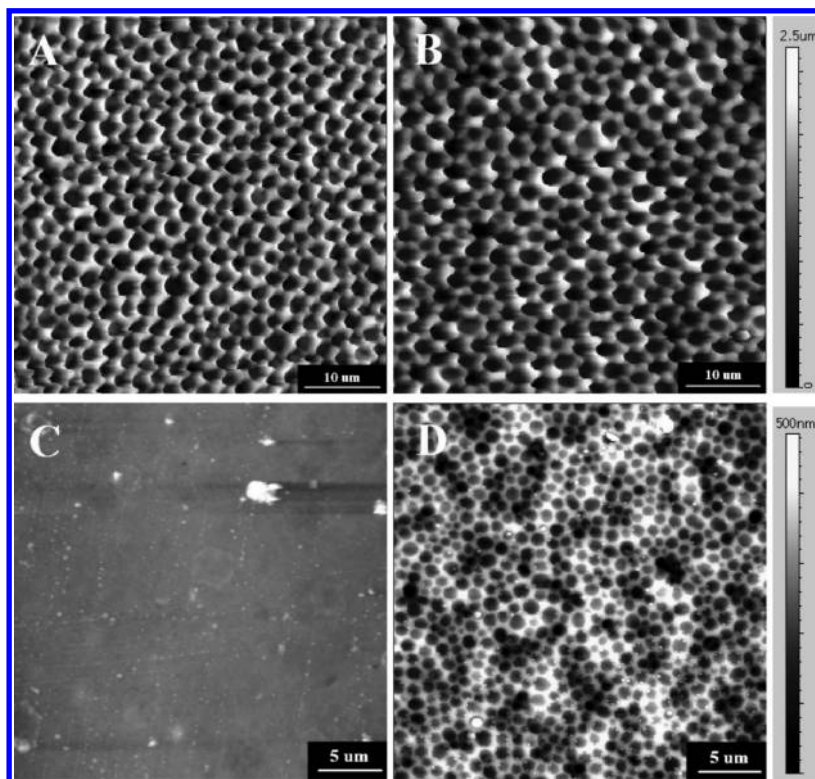(20) Yonezawa, T.; Onoue, S.; Kimizuka, N. *Adv. Mater.* **2001**, *13*, 140.

Figure 2. AFM images of polyurethane films. (A) The pure PU film and (B) Ag nanoparticle-added PU film obtained at 90% RH. (C) The pure PU film and (D) Ag nanoparticle-added PU film obtained at 30% RH.

of nanoparticles on BF were not observed. In this study, by *in situ* reduction method, Ag nanoparticles in polymers can influence the formation of regular pore arrays on the surface depending upon the humidity levels, contents of Ag nanoparticles, and polymers.

The BF process with Ag nanoparticles was first carried out in PU. Whether Ag nanoparticles can influence the BF process in PU depends on the humidity level. First, in 90% RH, the nanoparticle−polymer composite suspension was cast in a silica-gel desiccator RH at room temperature. Meanwhile, pure PU films were fabricated under the same conditions without adding Ag nanoparticles. The surface structures of the films were observed by AFM. As can be seen in Figure 2A and B, there are no significant differences between the films with and without Ag nanoparticles. The size scales and characteristics of the BF pattern on PU films do not depend on the presence of the Ag nanoparticles under humid conditions.

However, when RH decreased to 30% and the other factors remained invariable, Ag nanoparticles began to influence the BF process. Generally, the pure PU film is flat with no pores on it when cast in a dry environment (Figure 2C). With the presence of Ag nanoparticles, a relatively regular macroporous polymer film is observed as shown in Figure 2D. The average diameter of the honeycomb pore is 2.3 μm. Polymers rarely form a BF pattern in dry conditions (RH < 50%)[22] but rather only with the addition of extra water into solvent and by spin-cast technology.[23,24] The use of Ag nanoparticles to promote BF formation at low humidity is observed for the first time here.

Therefore, the humidity level determines whether Ag nanoparticles can induce regular pores on the PU film surface. In 90% RH, where PU can form BF patterns by itself, the effect of nanoparticles is inhibited by the BF process. In 30% RH, where PU cannot form porous films, nanoparticles can induce the formation of honeycomb structure on the surface. Thus, in the case of PU, Ag nanoparticles showed a kind of promoting ability for BF when RH is lower.

3.3. Effects of the Residuals. Because the suspensions were cast into polymer films without purification, whether the properties of casting solution are altered with the presence of residuals was investigated. Absolute ethanol, $AgNO_3$ ethanol solution, and $NaBH_4$ solution were added to PU solution to investigate whether they have any influence on the formation of porous films at 30% RH. The concentrations of $AgNO_3$ and $NaBH_4$, and total volumes of ethanol in three groups were the same as those of the Ag/PU suspension.

As can be seen from Figure 3, different residual-added PU films all formed without the honeycomb structure. The surface of the absolute ethanol-added PU film as shown in Figure 3A appears almost the same as that of the pure PU film in Figure 2C. In Figure 3B, it was discovered that the film with $AgNO_3$ is fully covered with nanoscale spicules, which might be the crystals of silver salts. In Figure 3C, few random small holes are seen on the $NaBH_4$ solution-added PU film. This suggests that the presence of residuals do not influence the formation of well-ordered bubble arrays on PU in dry conditions. Therefore, the addition of Ag nanoparticles is the only case in which PU films formed with BF arrays on the surface.

3.4. Effects of Ag Nanoparticle Content. The influence of the amount of Ag nanoparticles in PU on BF formation was also examined. Figure 4 shows the relationship between the capability of the honeycomb-patterned structure and the Ag nanoparticle concentration at 30% RH. At low Ag contents, for example,
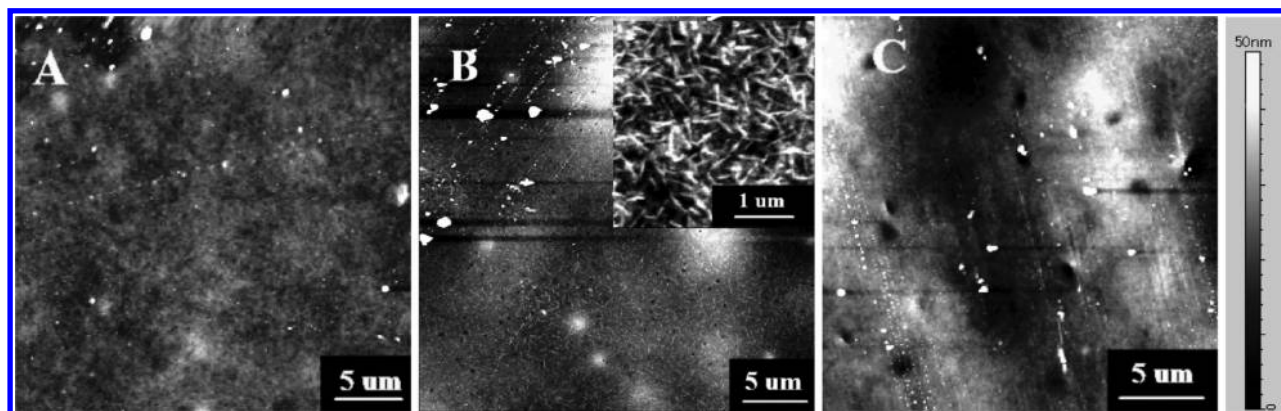
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Figure 3. AFM images of residual-added PU films cast at 30% RH. (A) Absolute ethanol added PU film. (B) AgNO$_3$ ethanol solution added PU film. (C) NaBH$_4$ solution added PU film.
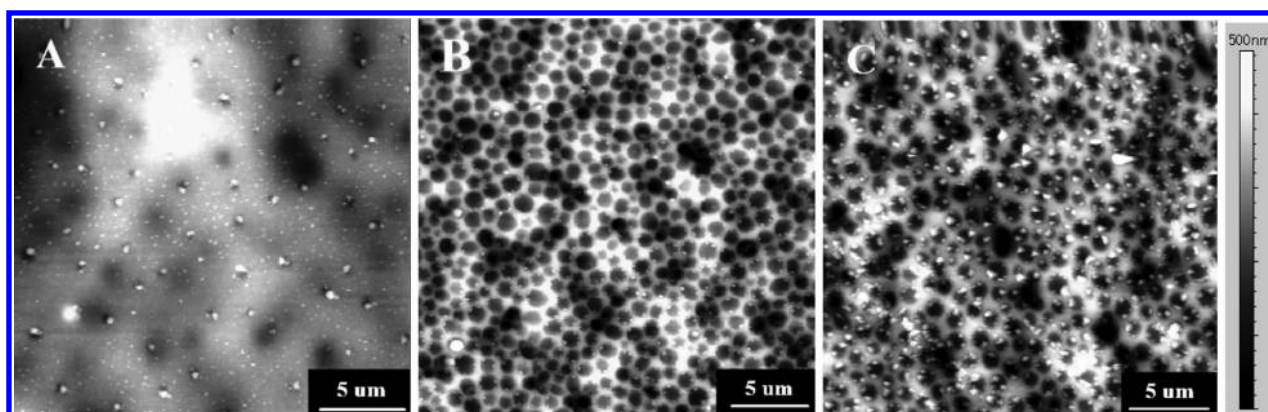

Figure 4. AFM images of Ag/PU nanocomposite films cast at 30% RH with Ag nanoparticle content of (A) 0.2%, (B) 1%, and (C) 5% based on the weight of PU.

0.2%, irregular small pores combined with individual nanoparticles are observed on the surface of the obtained film (Figure 4A). When the amount of Ag nanoparticles was increased to 1%, a uniform honeycomb-patterned structure is observed on the surface (Figure 4B). However, if too many Ag nanoparticles were embedded in PU, for example, 5%, not only regular pores were observed on the film but also some particles were found on the framework and on the bottom of the cavities (Figure 4C). Ag nanoparticles are unable to induce the formation of the BF pattern on the surface when the Ag concentration was low. As more Ag nanoparticles were introduced in PU, the segregation of nanoparticles might happen.

3.5. Effects of Polymer: BF Process with Ag Nanoparticles in Poly(L-lactic acid). Besides the casting humidity, the choice of polymer is also essential for the construction of regular bubble arrays. PLLA is one of the most widely used synthetic polymeric materials for bone tissue engineering.[25] Since the microsize structure on the material surface is important to control cell behavior, much attention has been directed toward technology for fabricating the material surface. The effects of Ag nanoparticles on PLLA to form well-ordered bubble arrays was investigated here.

Ag nanoparticle/PLLA composite suspension was prepared by the same method as that used for Ag/PU. Then, the polymer–nanoparticle composite suspension and PLLA solution were cast in a silica-gel desiccator at 90% RH and room temperature. The morphologies of PLLA films (without and with Ag nanoparticles)

are represented, respectively, in Figure 5A and B. As can be seen, the pores on the pure PLLA film surface are irregular in size and distribution, while the pores on the Ag/PLLA film surface have a better quality in array and monodispersion of diameter. The averaged diameter of the pores without Ag nanoparticles is 1.75 μm with a standard deviation of 0.69. However, for the Ag nanoparticle/PLLA film, although the averaged diameter of pores is still 1.75 μm, the standard deviation of the diameters of pores is decreased from 0.69 to 0.46, which means the regularity of pore size has been improved remarkably. However, when cast at a low humidity (RH = 30%), the PLLA film and Ag nanoparticle-added PLLA film did not form with honeycomb structure (Figure 5C and D). The Ag nanoparticles with a size of about 20 nm can be seen clearly on the flat film surface (Figure 5D).

Whether nanoparticles can influence the BF process in PLLA also depends on the humidity level. Different from Ag nanoparticles in PU, at 90% RH where PLLA cannot form regular bubble arrays by itself, Ag nanoparticles in PLLA affect and induce the microporous bubble array formation. However, in dry conditions when the trend of BF formation is too weak, Ag nanoparticles cannot affect the BF process any more. Some polymers cannot form honeycomb-structured films at high humidity, which can be known as BF-disable polymers. In most cases, PLLA fails to form regular patterns under common surfactant-free BF conditions.[26] Therefore, in the case of PLLA, Ag nanoparticles show

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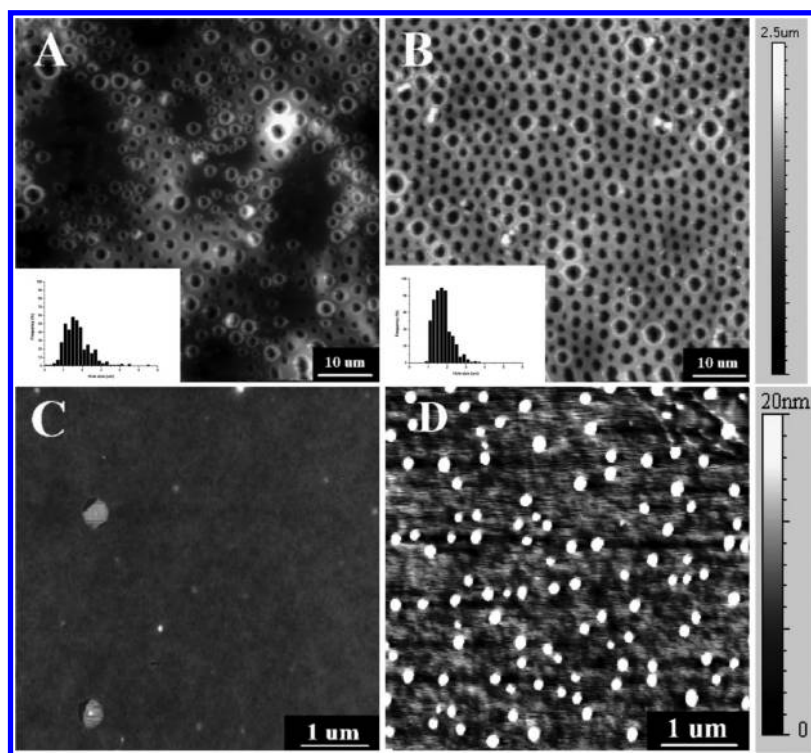
Figure 5. AFM images of poly (ʟ-lactic acid) films. (A) The pure PLLA film and (B) Ag nanoparticle-added PU film obtained at 90% RH (inset: the distribution of hole size). (C) The pure PLLA film and (D) Ag nanoparticle-added PU film obtained at 30% RH.

the ability to induce the formation of well-ordered bubble arrays at high humidity.

3.6. Au Nanoparticles in the BF Process. The *in situ* reduction method and the nanoparticle-induced pore-forming process also can be applied to other nanoparticle systems. Au nanoparticle/PLLA composites can be prepared by this method. The nanoparticles were also homogenously dispersed in PLLA with an average size of 20 nm (Supporting Information). Porous films of Au nanoparticle/PLLA composite were deposited from chloroform under the same BF conditions as those of the Ag nanoparticles system at 90% RH. The size and the uniformity of the pore were almost the same as those of the corresponding pores in the Ag nanoparticles system (Supporting Information). The averaged diameter of pores is still 2.3 *μ*m, and the standard deviation of the diameters of pores is decreased from 0.69 to 0.45 when compared with that of PLLA film formed without Au nanoparticles, which means that the regularity of pore size has been improved.

3.7. Interfacial Effects of Nanoparticles. The BF arrays are honeycomb structures formed during solvent evaporation from a polymer solution with the condensation of water droplets on the surface. When nanoparticles are introduced into the system, they absorb and self-assemble at the fluid−fluid interface[27,28] and form a mechanically resistant layer encapsulating the water droplet. With continuous evaporation of organic solvent, this ordered arrangement of water droplets is fixed, and the immobilized nanoparticles stay at the interface, as shown in the schematic illustration of interfacial segregation of nanoparticles in Figure 6A.

AFM images of the Ag/PU film formed at 30% RH and the Ag/PLLA film formed at 90% RH were taken and shown in Figure 6B−E. In Ag/PU, as shown in Figure 6B, nanoparticles

with different sizes are observed on the internal surface of the holes showing the absorption of Ag nanoparticles on the air/polymer interface. In the magnified image (Figure 6C), some individual particles with quite larger size than the primary particle diameter (20 nm) are observed. This may be the reason that since THF is a water-miscible solvent, nanoparticles can resist the coalescence of water droplets and the THF solvent but cannot totally partition water and THF/polymer. Therefore, the dissolution of the polymer−nanoparticle composite in water leads to nanoparticles in irregular sizes.

In the AFM image of Ag/PLLA (Figure 6D), no particle is observed on the surface. However, the magnified image (Figure 6E) reveals the presence of nanoparticles. But the contours of Ag nanoparticles are not clear, which is considered as caused by Ag nanoparticles immersed more in the PLLA matrix. THF is totally miscible in water as $CHCl_3$ is immiscible, but the *in situ* reduction method to prepare Ag nanoparticles in these two solvents might lead to different surface properties of nanoparticles. This might be the reason why it was discovered that Ag nanoparticles reside more in the water in the PU/THF system, while residing more in the polymer in the PLLA/$CHCl_3$ system.

The contact angles of water on the surface of the flat polymer−nanoparticle composite films are shown in Figure 7. All of the films were cast at 30% RH. The Ag/PU and Au/PU films were cast by the spinning coating method to achieve a flat surface of the polymer film. PU is more hydrophilic than PLLA; therefore, the contact angles of the PU group are smaller than those of the PLLA group. The water contact angles of the two groups decrease with the addition of nanoparticles. So the surfaces of the polymer−nanoparticle composite films are supposed to be more hydrophilic than pure polymer films. This might be the result of the reduction of surface energy caused by the presence of nanoparticles.[29] Additionally, the water contact

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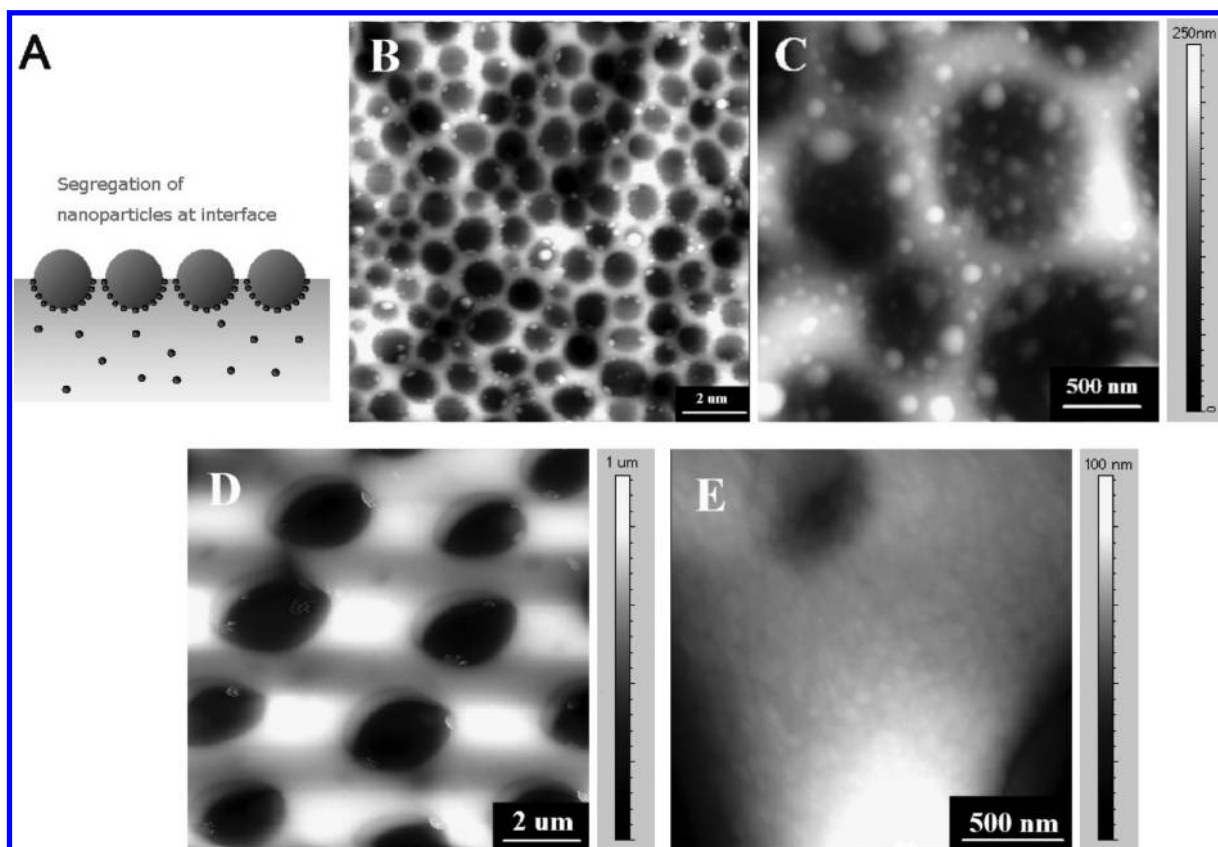(29) Binks, B. P.; Clint, J. H. *Langmuir* **2002**, *18*, 1270.

Figure 6. (A) Cross-sectional schematic diagram of nanoparticle assembly at the water droplet−solution interface during BF formation. (B) AFM images of Ag/PU films cast at 30% RH. In the magnified image (C), Ag nanoparticles can be seen embedding on the caves on the PU film. (D and E) AFM images of Ag/PLLA films cast at 90% RH.
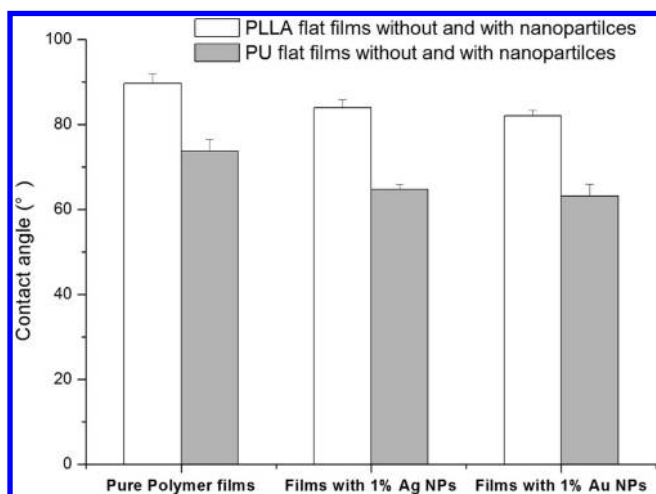

Figure 7. Changes in water contact angles of PLLA and PU films without and with Ag and Au nanoparticles. Data were expressed as the mean value with average standard deviations (SD), $n = 6$.

angles of Ag nanoparticle-added polymer films are greater than those of Au nanoparticle-added polymer films.

3.8. Proposed Mechanism for the Effects of Nanoparticles on the BF Process. At the liquid−liquid interface, wetting behavior of the water droplet determines whether the honeycomb structure can be formed. The spreading coefficient S (the work done in spreading water droplets over a unit area of polymer solution surface) equals the surface tension of the polymer solution, minus the surface tension of the spreading water droplet, minus the interfacial tension between the liquids, as shown in

Figure 8a. The definition of the spreading coefficient S is shown in eq 1, which is never greater than zero.[30]

$$S = -\Delta G = -[(\sigma_{\text{sus/w}} + \sigma_{\text{g/w}}) - \sigma_{\text{g/sus}}] \qquad (1)$$

$$\cos\theta = (\sigma_{\text{g/sus}} - \sigma_{\text{sus/w}})/\sigma_{\text{g/w}} \qquad (2)$$

$$S = \sigma_{\text{g/w}}(\cos\theta - 1) \qquad (3)$$

In eq 1, $\sigma_{\text{sus/w}}$ is the interfical tension between suspension and water, $\sigma_{\text{g/w}}$ is the interfical tension between air and water, and $\sigma_{\text{g/sus}}$ is the interfical tension between air and the suspension. $S < 0$ indicates partial wetting, and $S = 0$ means complete wetting.[31] S determines the size and depth of porous holes.

S changes continuously in the BF process during solvent evaporation and solid film formation. The contact angle can be calculated from eq 2, which is also changing. In two situations, which have been discussed previously, Ag nanoparticles can influence BFs (PU in THF at 30% RH and PLLA in CHCl₃ at 90% RH) with different effects on the interface. As for the case of PLLA in CHCl₃ at 90% RH, the water droplets grow fast to a large volume and immerse deeply into the polymer solution, resulting in the irregular pore pattern on the surface. As can be seen in Figure 6, the final status contact angle of the Ag/PLLA film is smaller than that of the PLLA film (from 89.75° to 83.98°),

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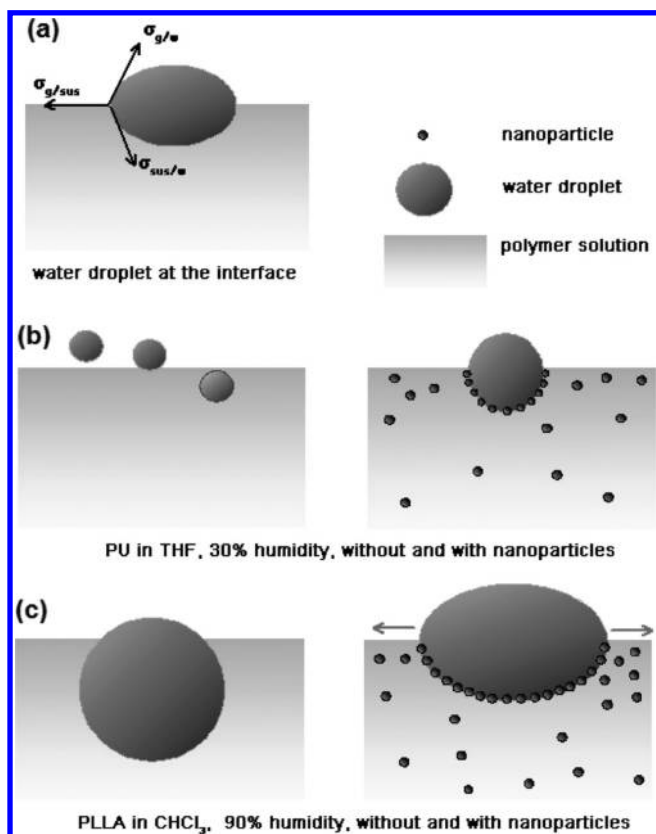(31) Dobbs, H.; Bonn, D. *Langmuir* **2001**, *17*, 4674.

Figure 8. Cross-sectional schematic diagram of water droplets stabilized at the interface during breath-figure formation. (a) Wetting behavior of the water droplet. (b) When PU is in THF at 30% RH, the presence of Ag nanoparticles in the polymer forms a mechanically resistant layer preventing the water droplet from dissolving in the polymer solution. (c) As for the case of PLLA in CHCl₃ at 90% RH, the water droplets grow fast to a large volume and immerse deeply into the polymer solution. With the addition of Ag nanoparticles, S increases by the reduction of the contact angle of the Ag/PLLA film. Therefore, the water droplet spreads over a larger area on the interface and immerses less into the solution.

resulting in the increase of S according to eq 3. While S is smaller than zero, this leads to the spreading of the water droplet over a larger area on the interface and lower immersion into the solution (Figure 8c). Therefore, a more regular bubble pattern with larger sizes formed on the surface.

As for the case of PU in THF at 30% RH, since THF is totally immersible in water, the water droplet which grows slowly in dry conditions cannot stay at the interface and will immerse into the THF solvent. Therefore, S is zero at the beginning of the BF process. With the addition of Ag nanoparticles in the polymer, the nanoparticles absorb at the interface and stabilize the water−solvent interface, forming a mechanically resistant layer preventing the water droplet from dissolving with the polymer solution. Therefore, the honeycomb structure can be left on the PU film surface (Figure 8b).

The effects of nanoparticles have a balance with the BF process. The polymers and humidity levels determine the trend of the BF process. The polymer, which can form the BF pattern under standard conditions without extra help, such as PU, combined with a high humidity level results in a strong trend to form BF arrays. Otherwise, a BF-disabled polymer, such as PLLA, plus dry conditions are difficult for forming BF. Nanoparticles can interact with the BF process between these two situations, where PU was cast at 30% RH, and PLLA was cast at 90% RH.

Such a nanoparticle-induced BF process represents a novel alternative to the conventional surfactant-added one and may prove to be more advantageous. The behavior of nanoparticles and surfactants in the BF process is similar in some ways. However, nanoparticles are strongly held at interfaces and have a much more condensed nature of an insoluble monolayer compared with that of a soluble surfactant.[32] Additional stabilization arises when the particle−particle interactions are such that a three-dimensional network of nanoparticles develops in the continuous phase surrounding the drops.[33]

The interfacial effects of nanoparticles may widen the application of the BF method. With the addition of nanoparticles, some BF-disabled polymers can be utilized to form honeycomb-structured films, and therefore, the casting conditions for BF will not be restricted to a high RH. Nanoparticle-decorated macroporous polymer films will be multifunctional with the properties of nanoparticles. For instance, a Ag/PLLA honeycomb-structured material is being developed into a novel cell growth substrate with antibacterial ability. Although the metal nanoparticles comprise the bulk of the discussion, the concepts that are discussed can be applied to a wider variety of other nanoparticle compositions.

4. Conclusions

In summary, we found for the first time that Ag nanoparticles have interfacial effects on the BF formation in the present work. The *in situ*-synthesized Ag nanoparticles act as novel influence factors of BF formation. The effects of nanoparticles have a balance with the BF process, which is determined by humidity levels and polymers. The research of interactions between the BF process and Ag nanoparticles, which are assembled at the liquid−liquid interface, is beneficial in gaining a better understanding of the mechanism of BF. With the assistance of Ag nanoparticles, BF can be carried out under dry conditions, and more polymers can be utilized to form BF arrays. Meanwhile, nanoparticles can functionalize these BF holes with potential applications. The influences of the properties of nanoparticles on BFs, such as the particle diameter, shapes, and surface properties, need to be investigated further.

Supporting Information Available: Characterization data of Au nanoparticle−polymer composite as well as the AFM image of film casting with Au nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org

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