

# An Efficient Substrate-Free Method of Producing SiO<sub>2</sub>-Based Nanoparticles for Superhydrophobic Applications

Lucas D. C. de Castro,\* Nelson M. Larocca, Osvaldo N. Oliveira, Jr., and Luiz A. Pessan



Cite This: *ACS Omega* 2022, 7, 1259–1263



Read Online

ACCESS |



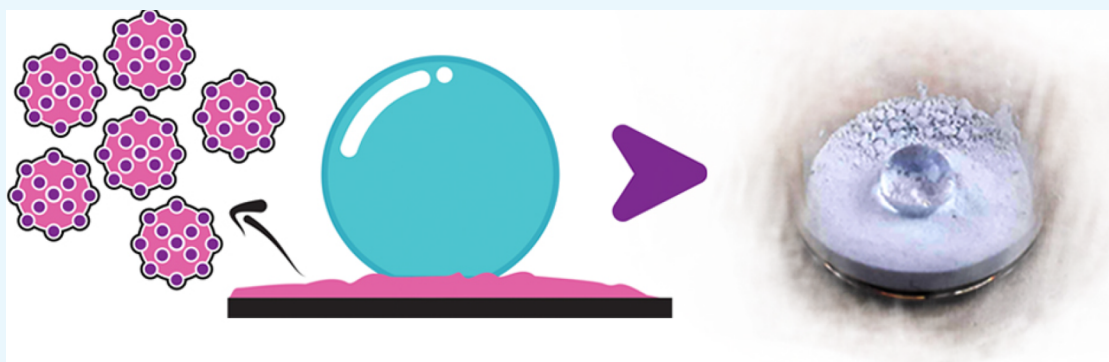
Metrics & More



Article Recommendations



Supporting Information



**ABSTRACT:** We report on the preparation of SiO<sub>2</sub>-based nanoparticles readily available for superhydrophobic applications. In contrast to usual approaches, our process is substrate-free and based on electrostatic adsorption of small SiO<sub>2</sub> particles onto large SiO<sub>2</sub> cores with the aid of poly(diallyldimethylammonium chloride) followed by calcination and chemical modification with trichlorododecylsilane. The as-prepared nanoparticles are in powder form and exhibit stable superhydrophobic behavior at room temperature because of the unique combination between the hierarchical raspberry-like structure and low surface energy. If properly stored, the nanoparticles retain their functional properties for several months.

## INTRODUCTION

Biological materials are generally organized from the nano- to the macroscale, often in hierarchical structures with intricate nanoarchitectures that are difficult to mimic in industrial processes. Building blocks are assembled into multiscale structures and respond cooperatively to external stimuli, resulting in unusual properties—an advantage that boosted the interest in bioinspired designs.<sup>1</sup> The leaves of *Nelumbo nucifera* (lotus flower), for example, have inspired the development of water-repellent surfaces<sup>2–5</sup> due to their superhydrophobic properties with the synergy between the hierarchical structure and low surface energy.<sup>6–8</sup> Systematic methods of preparing hierarchical nanoparticles may thus enhance biomimetics with suitable building blocks for bioinspired structures.

Nanoparticles with superhydrophobic properties can be fabricated in different ways. For instance, hierarchical structures were prepared via layer-by-layer (LbL) deposition of small particles over already-deposited large particles on a glass substrate, from which superhydrophobic coatings were obtained after proper chemical modification.<sup>9</sup> However, the LbL route is time-consuming, being limited to substrates that can withstand high temperatures since a calcination step is required. Furthermore, the formed particles may exhibit intrinsic defects during the assembly cycles. These limitations

are overcome in the present work, in which we present an efficient method of preparing substrate-free nanoparticles in powder form readily available for superhydrophobic applications. The hierarchical structure of SiO<sub>2</sub>-based nanoparticles is built-up in an aqueous medium via electrostatic assembly of small particles onto a large core with a strong polycation. This electrostatic adsorption is advantageous compared to the usual chemical approach based on the functionalization of one or more components.<sup>10–14</sup> It does not require expensive or extremely controlled reactors, being amenable to the use of different materials; it is also safer/cleaner as hazardous chemicals are not required.

## RESULTS AND DISCUSSION

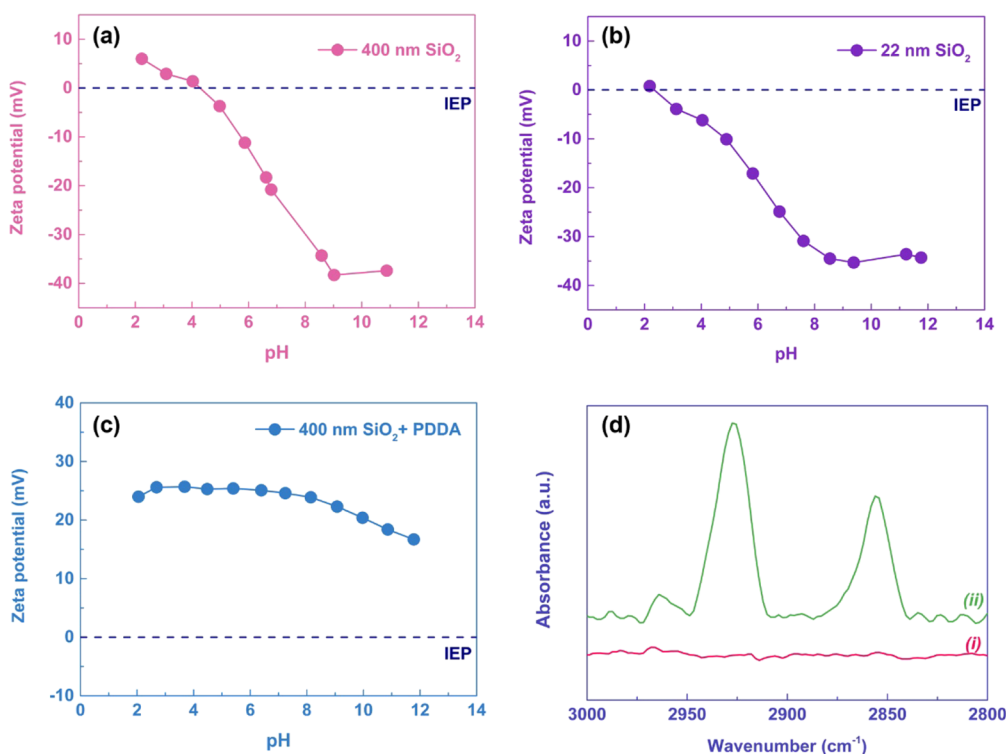
Electrostatic adsorption in aqueous solutions requires all the system components to be charged; surface charge is reversed in each adsorption step, and flocculation should be avoided. Since

**Received:** October 20, 2021

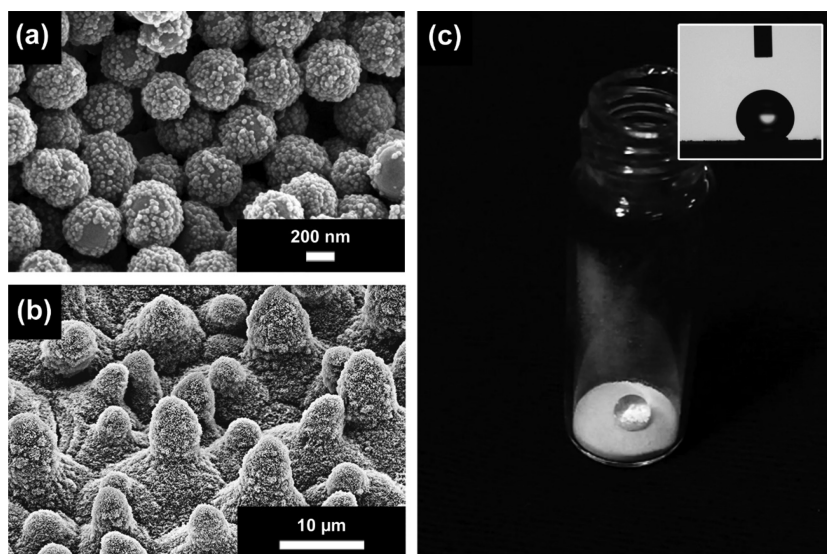
**Accepted:** December 14, 2021

**Published:** December 22, 2021





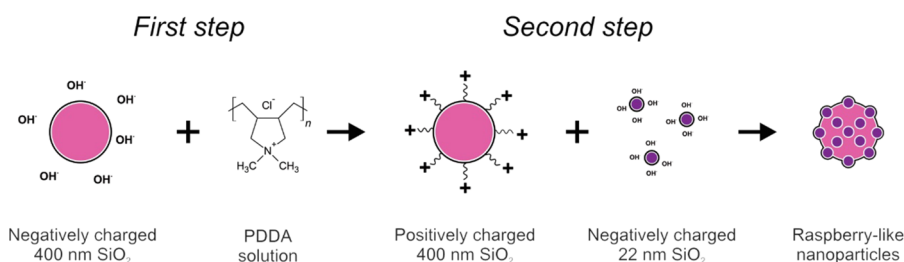
**Figure 1.** Zeta potential measurements for (a) 400 nm SiO<sub>2</sub>, (b) 22 nm SiO<sub>2</sub>, and (c) 400 nm SiO<sub>2</sub> + PDPA aqueous suspensions. (d) Excerpts of the FTIR spectra in the C–H stretching region of (i) non-treated and (ii) treated raspberry-like nanoparticles.



**Figure 2.** SEM images of (a) the superhydrophobic nanoparticles and (b) surface of a lotus leaf adapted from Ensikat et al.<sup>19</sup> distributed under the Creative Commons Attribution 2.0 Generic License (<http://creativecommons.org/licenses/by/2.0/>). (c) Water droplet over our nanoparticles and its respective WCA analysis.

the surface charge of particles in contact with water is normally pH-sensitive,<sup>15</sup> we determined stabilities of 22 and 400 nm SiO<sub>2</sub> using Zeta potential measurements over a wide pH range. Figure 1a and Figure 1b show a negative character for 400 and 22 nm SiO<sub>2</sub> suspensions over almost the entire pH range, respectively. Stability of SiO<sub>2</sub> suspensions could be observed above pH ~8;<sup>15,16</sup> therefore, pH ~9 was fixed for all coating steps. Surface modification of negatively charged 400 nm SiO<sub>2</sub> was performed with PDPA, which was chosen because it is a water-soluble strong polycation, i.e., the degree of dissociation of its ionic groups is nearly pH-independent.<sup>17</sup> This feature is

useful since there is no pH range limitation for using PDPA. The successful PDPA adsorption on 400 nm SiO<sub>2</sub> is indicated in Figure 1c, with its positive charge from the ammonium groups overcompensating the SiO<sub>2</sub> negative charge. Hence, adsorption of 22 nm SiO<sub>2</sub> is made possible on a 400 nm SiO<sub>2</sub> + PDPA surface. The as-prepared raspberry-like nanoparticles were calcinated and modified with trichlorododecylsilane. The success of the chemical treatment was confirmed in the FTIR spectra of Figure 1d, where a comparison is made for the C–H stretching region of the non-treated and treated nanoparticles. There is no peak for non-treated nanoparticles in the region of



**Figure 3.** Scheme of the electrostatic adsorption process.

2800–3000 cm<sup>−1</sup>. On the other hand, three peaks are seen for the treated nanoparticles, which are assigned to be 2960 cm<sup>−1</sup> =  $\nu_a$  asymmetric CH<sub>3</sub> stretching vibration, 2921 cm<sup>−1</sup> =  $\nu_a$  asymmetric CH<sub>2</sub> stretching vibration, and 2852 cm<sup>−1</sup> =  $\nu_s$  symmetric CH<sub>2</sub> stretching vibration.<sup>18</sup> The methyl and methylene stretching vibrations arise from grafted trichlorododecylsilane molecules on the treated nanoparticles, confirming the chemical modification.

An SEM image of the nanoparticles is shown in Figure 2a and compared to the surface of a lotus leaf, our source of inspiration, in Figure 2b. Despite the difference in scale, both surfaces are conceptually similar, exhibiting dual-scale roughness governed by a hierarchical structure. After calcination and chemical modification, the nanoparticles form a homogeneous powder, exhibiting water repellency and low hysteresis, as illustrated in Figure 2c and Movie S1. From our experiments, the water contact angle (WCA) of the raspberry-like SiO<sub>2</sub> nanoparticles in powder form is ca. 150°. We note, nevertheless, that our substrate is a powder, and thus, one cannot ensure the same topography in every measurement as required by the water contact angle definition. Therefore, the WCA value should be regarded just as an indicator of the superhydrophobic effect of the raspberry-like SiO<sub>2</sub> nanoparticles and not as an absolute value. Despite the technical limitations, one may infer that the nanoparticles are highly stable with no significant change in the WCA during 15 min (see Movie S1). Finally, if the nanoparticles are properly stored (i.e., away from sunlight and at room temperature), then the superhydrophobic effect can last for several months.

## CONCLUSIONS

Substrate-free raspberry-like nanoparticles were successfully prepared via electrostatic adsorption of negatively charged 22 nm SiO<sub>2</sub> nanoparticles onto positively charged 400 nm SiO<sub>2</sub> + PDDA cores. After calcination and chemical treatment with trichlorododecylsilane, a powder with stable superhydrophobic behavior at room temperature was obtained. The synergy between the hierarchical structure and low surface energy is the key for the superhydrophobicity of the nanoparticles. We believe that the simplicity of the proposed process allied to its low-cost might inspire a new set of technological applications, permitting widespread use of the superhydrophobic phenomenon.

## MATERIALS AND METHODS

Tetraethyl orthosilicate (TEOS, 99%); aqueous ammonia solution (25%); trichlorododecylsilane; poly(diallyldimethylammonium chloride) (PDDA, Mw = 200,000–350,000, 20 wt % aqueous solution); and Ludox TM-40 (40 wt % SiO<sub>2</sub> suspension in water, 22 nm average diameter) were purchased from Sigma-Aldrich. SiO<sub>2</sub> particles

(~400 nm average diameter) were synthesized via the Stöber method.<sup>20</sup> Milli-Q water was used in all aqueous suspensions/solutions and rinsing steps. The stability of the colloidal suspensions was evaluated with Zeta potential measurements performed in a Dispersion Technology DT1200 equipment over a wide pH range. Evidence of chemical modification was investigated by Fourier transform infrared spectroscopy (FTIR) in a Nicolet Nexus 470 FTIR ESP spectrometer using samples prepared in KBr pellets. The morphology of nanoparticles was studied with scanning electron microscopy (SEM) images obtained using a Zeiss LEO 1530 FESEM. Contact angle measurements were performed in a CAM 200 (KSV NIMA) equipment using a 6  $\mu$ L droplet deposited over a certain amount of our superhydrophobic nanoparticles in powder form.<sup>21</sup> The water contact angle (WCA) was estimated using the LB-ADSA, a freely available plugin for ImageJ.<sup>22</sup>

The fabrication of raspberry-like nanoparticles was based on the electrostatic adsorption of negatively charged coating particles (22 nm SiO<sub>2</sub>) onto the positively charged cores (400 nm SiO<sub>2</sub>), as shown schematically in Figure 3. The experimental procedure was carried out with the batch technique using a similar procedure to Phan et al.,<sup>23</sup> where all components are employed in aqueous media. The concentration of aqueous solutions/suspensions is not fixed and should be defined for each system; however, the coating component must always be in excess compared to the core. Here, assuming a close-packed monolayer coverage, the maximum theoretical number of small particles  $N_{\max}$  on a single large particle is calculated from the geometry with eq 1.<sup>24</sup>

$$N_{\max} = \frac{2\pi}{\sqrt{3}} \left[ 1 + \left( \frac{R}{r} \right) \right]^2 \quad (1)$$

where  $r$  and  $R$  are, respectively, the radii of small and large nanoparticles.

$N_{\max}$  was estimated, assuming that nanoparticles of both sizes are monodispersed and amorphous (i.e.,  $\rho \sim 2.2$  g/cm<sup>3</sup>). As an attempt to achieve a satisfactory coverage of the raspberry-like nanoparticles, we applied a multiplier of 100× to the theoretical  $N_{\max}$  value (see the Supporting Information). The concentrations and volumes of aqueous solutions/suspensions employed are shown in Table 1.

The deposition of the polyelectrolytes and/or coating particles on the cores was conducted by dropwise addition of component A to component B under vigorous stirring for several hours. To minimize the bridging effect, the following mixing protocol was adopted: particle suspension (A) into polymer solution (B) for particle/polymer systems and small particle suspension (A) into large particle suspension (B) for particle/particle systems. After each adsorption step, the suspension obtained was centrifuged, washed/dispersed several



**Table 1. Concentrations and Volumes Employed in Preparing the Nanoparticles<sup>a</sup>**

	first step (pH 9)		second step (pH 9)	
	<sup>A</sup> 400 nm SiO <sub>2</sub>	<sup>B</sup> PDDA	<sup>A</sup> 22 nm SiO <sub>2</sub>	<sup>B</sup> 400 nm SiO <sub>2</sub> + PDDA
concentration (wt %)	0.5	1.0	4	0.1
volume (mL)	100	200	100	100

<sup>a</sup>Dropwise addition of component A to component B under vigorous stirring for several hours.

times in water, and dried in vacuum overnight at room temperature. The as-prepared nanoparticles were calcinated at 500 °C for 4 h to remove PDDA and consolidate the raspberry-like structure. The product was powdered with a mortar and pestle, dispersed in a 0.25 wt % trichlorododecylsilane solution in chloroform for 1 h, centrifuged/washed in chloroform, and dried in vacuum overnight at room temperature.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c05878>.

S1. Control of surface coverage of SiO<sub>2</sub> raspberry-like nanoparticles (PDF)

Movie S1. Superhydrophobic effect of the substrate-free SiO<sub>2</sub> nanoparticles and the stability test, showing the contact angle of a water droplet deposited on substrate-free SiO<sub>2</sub> nanoparticles for 15 min (AVI)

## ■ AUTHOR INFORMATION

### Corresponding Author

Lucas D. C. de Castro – São Carlos Institute of Physics,  
University of São Paulo, 13566-590 São Carlos, SP, Brazil;  
orcid.org/0000-0002-7757-3726;  
Email: [lucasdanielcastro@hotmail.com](mailto:lucasdanielcastro@hotmail.com)

### Authors

Nelson M. Larocca – Federal University of São Carlos,  
Graduate Program in Materials Science and Engineering,  
13565-905 São Carlos, SP, Brazil

Oswaldo N. Oliveira, Jr. – São Carlos Institute of Physics,  
University of São Paulo, 13566-590 São Carlos, SP, Brazil;  
orcid.org/0000-0002-5399-5860

Luiz A. Pessan – Federal University of São Carlos, Graduate  
Program in Materials Science and Engineering, 13565-905  
São Carlos, SP, Brazil

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsomega.1c05878>

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brasil (CAPES) (finance code 001), CNPq, INEO, and FAPESP (2015/20052-0, 2020/02938-0, and 2018/22214-6). The authors thank Prof. André Rocha Studart and Complex Materials group – ETH Zürich for the support.

## ■ REFERENCES

- (1) Studart, A. R. Towards High-Performance Bioinspired Composites. *Adv. Mater.* **2012**, *24*, 5024–5044.
- (2) Zhao, X.; Park, D. S.; Choi, J.; Park, S.; Soper, S. A.; Murphy, M. C. Robust, Transparent, Superhydrophobic Coatings Using Novel Hydrophobic/Hydrophilic Dual-Sized Silica Particles. *J. Colloid Interface Sci.* **2020**, *574*, 347–354.
- (3) Li, G.; Jiang, B.; Liu, H.; Ning, L.; Yi, D.; Wang, X.; Liu, Z. Superhydrophobic Surface with Lotus/Petal Effect and Its Improvement on Fatigue Resistance of Heat-Resistant Steel. *Prog. Org. Coat.* **2019**, *137*, 105315.
- (4) Tong, W.; Xiong, D.; Zhou, H. TMES-Modified SiO<sub>2</sub> Matrix Non-Fluorinated Superhydrophobic Coating for Long-Term Corrosion Resistance of Aluminium Alloy. *Ceram. Int.* **2020**, *46*, 1211–1215.
- (5) Li, J.; Wan, H.; Ye, Y.; Zhou, H.; Chen, J. One-Step Process to Fabrication of Transparent Superhydrophobic SiO<sub>2</sub> Paper. *Appl. Surf. Sci.* **2012**, *261*, 470–472.
- (6) Barthlott, W.; Neinhuis, C. Purity of the Sacred Lotus, or Escape from Contamination in Biological Surfaces. *Planta* **1997**, *202*, 1–8.
- (7) Koch, K.; Barthlott, W. Superhydrophobic and Superhydrophilic Plant Surfaces: An Inspiration for Biomimetic Materials. *Philos. Trans. R. Soc., A* **2009**, *367*, 1487–1509.
- (8) Cheng, Y. T.; Rodak, D. E.; Wong, C. A.; Hayden, C. A. Effects of Micro- and Nano-Structures on the Self-Cleaning Behaviour of Lotus Leaves. *Nanotechnology* **2006**, *17*, 1359–1362.
- (9) Castro, L. D. C.; Larocca, N. M.; Pessan, L. A. Effect of Structural Features on the Superhydrophobicity of SiO<sub>2</sub>-Based Coatings. *Langmuir* **2021**, *37*, 124–131.
- (10) Ming, W.; Wu, D.; van Benthem, R.; de With, G. Superhydrophobic Films from Raspberry-like Particles. *Nano Lett.* **2005**, *5*, 2298–2301.
- (11) Pureskiy, N.; Ionov, L. Synthesis of Robust Raspberry-like Particles Using Polymer Brushes. *Langmuir* **2011**, *27*, 3006–3011.
- (12) Carcouët, C. C. M. C.; Esteves, A. C. C.; Hendrix, M. M. R. M.; van Benthem, R. A. T. M.; de With, G. Fine-Tuning of Superhydrophobicity Based on Monolayers of Well-Defined Raspberry Nanoparticles with Variable Dual-Roughness Size and Ratio. *Adv. Funct. Mater.* **2014**, *24*, 5745–5752.
- (13) Du, X.; Liu, X.; Chen, H.; He, J. Facile Fabrication of Raspberry-like Composite Nanoparticles and Their Application as Building Blocks for Constructing Superhydrophilic Coatings. *J. Phys. Chem. C* **2009**, *113*, 9063–9070.
- (14) Siddiqui, A. R.; Li, W.; Wang, F.; Ou, J.; Amirfazli, A. One-Step Fabrication of Transparent Superhydrophobic Surface. *Appl. Surf. Sci.* **2021**, *542*, 148534.
- (15) Xu, R. Progress in Nanoparticles Characterization: Sizing and Zeta Potential Measurement. *Particuology* **2008**, *6*, 112–115.
- (16) Júnior, J. A. A.; Baldo, J. B. The Behavior of Zeta Potential of Silica Suspensions. *New J. Glass Ceram.* **2014**, *04*, 45415.
- (17) Zhitomirsky, I. Cathodic Electrodeposition of Ceramic and Organoceramic Materials. Fundamental Aspects. *Adv. Colloid Interface Sci.* **2002**, *97*, 279–317.
- (18) Ruehe, J.; Novotny, V. J.; Kanazawa, K. K.; Clarke, T.; Street, G. B. Structure and Tribological Properties of Ultrathin Alkylsilane Films Chemisorbed to Solid Surfaces. *Langmuir* **1993**, *9*, 2383–2388.
- (19) Ensikat, H. J.; Ditsche-Kuru, P.; Neinhuis, C.; Barthlott, W. Superhydrophobicity in Perfection: The Outstanding Properties of the Lotus Leaf. *Beilstein J. Nanotechnol.* **2011**, *2*, 152–161.
- (20) Stöber, W.; Fink, A.; Bohn, E. Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range. *J. Colloid Interface Sci.* **1968**, *26*, 62–69.
- (21) Alghunaim, A.; Kirdponpattara, S.; Newby, B. Z. Techniques for Determining Contact Angle and Wettability of Powders. *Powder Technol.* **2016**, *287*, 201–215.
- (22) Stalder, A. F.; Melchior, T.; Müller, M.; Sage, D.; Blu, T.; Unser, M. Low-Bond Axisymmetric Drop Shape Analysis for Surface Tension and Contact Angle Measurements of Sessile Drops. *Colloids Surf., A* **2010**, *364*, 72–81.

(23) Pham, T.; Bui, T.; Nguyen, V.; Bui, T.; Tran, T.; Phan, Q.; Pham, T.; Hoang, T. Adsorption of Polyelectrolyte onto Nanosilica Synthesized from Rice Husk: Characteristics, Mechanisms, and Application for Antibiotic Removal. *Polymers* **2018**, *10*, 220.

(24) Bao, Y.; Li, Q.; Xue, P.; Huang, J.; Wang, J.; Guo, W.; Wu, C. Tailoring the Morphology of Raspberry-like Carbon Black/Polystyrene Composite Microspheres for Fabricating Superhydrophobic Surface. *Mater. Res. Bull.* **2011**, *46*, 779–785.



ACS IN  
FOCUS

Cellular Agriculture  
Lab-Grown  
Dilek Erilliç  
Dorothee E.

Machine Learning in Chemistry  
Jon Paul Janet &  
Heather J. Kulik

bacterials  
Lidia Cheng Jaramillo  
William M. Wuest

ACS Publications

ACS In Focus ebooks are digital publications that help readers of all levels accelerate their fundamental understanding of emerging topics and techniques from across the sciences.



[pubs.acs.org/series/infocus](https://pubs.acs.org/series/infocus)

ACS Publications  
Most Trusted. Most Cited. Most Read.