Supporting Information

Interfacial Polymerization of Dopamine in a Pickering Emulsion: Synthesis of Cross-Linkable Colloidosomes and Enzyme Immobilization at Oil/Water Interfaces

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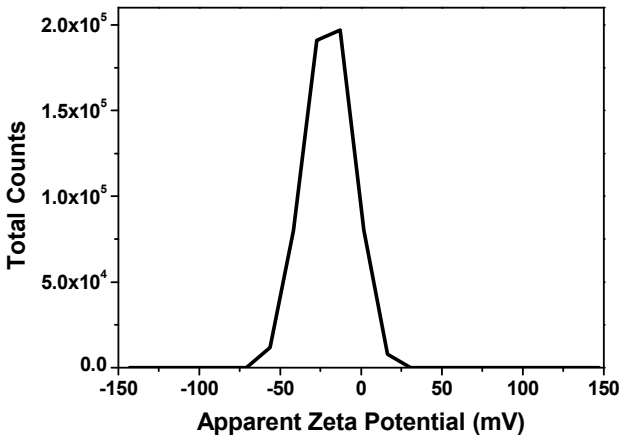

Figure S1. Zeta potential of the hydrophobic silica NPs.The zeta potential of the hydrophobic silica NPs is -20.2mV.

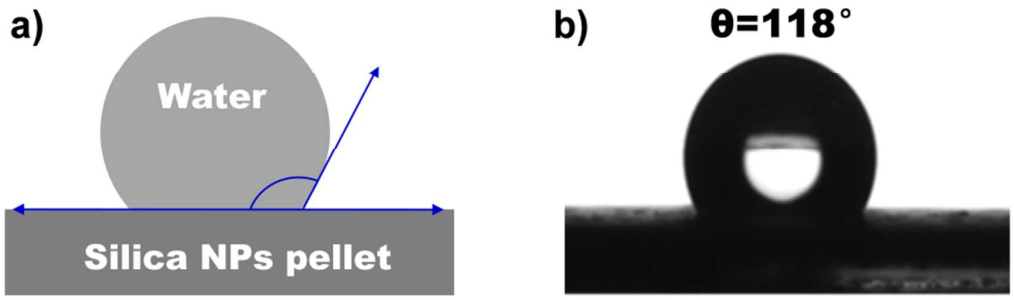

Figure S2. a) Scheme of the contact angle on the flake of SiO_2 NPs pellet. b) Photographs of a 2μL water droplet, resting on the surface of thin slice of the hydrophobic silica NPs.

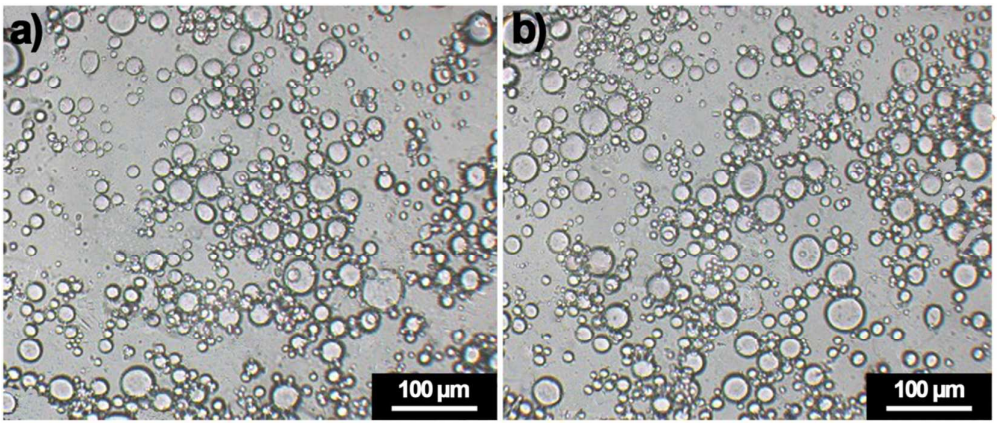

Figure S3. a) Optical micrograph of SiNDs in water/heptane media. b) Optical micrograph of SiN/PDACs in water/heptane media.

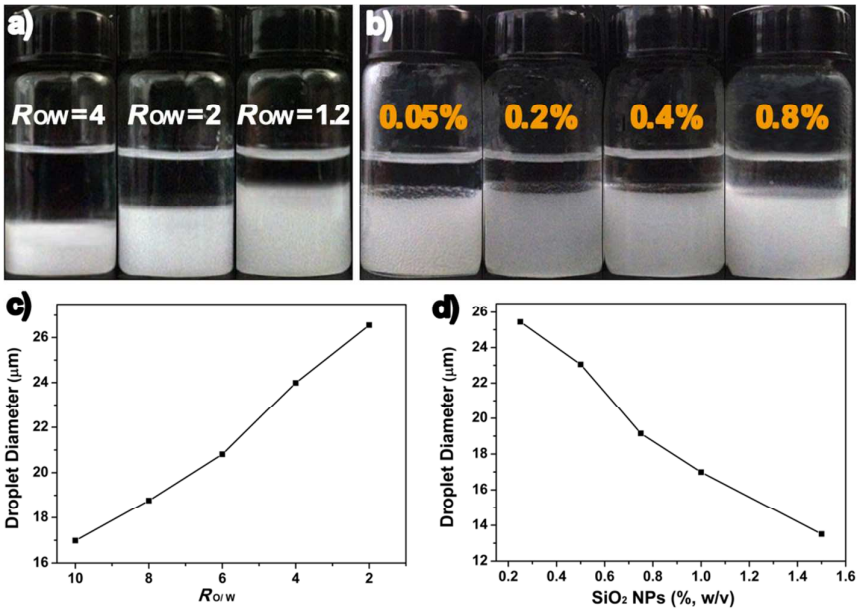

Figure S4. a) Photographs of silica-stabilized droplets (SiNDs) formed at different $R_{o/w}$ values. b) Photographs of SiNDs at different SiO_2 NPs loadings. c) The change in the average diameters of emulsion droplets at different $R_{o/w}$ values. The SiO_2 NPs loading was held constant at 1% (w/v). d) The change in the average diameters of emulsion droplets at different SiO_2 NPs loadings. The $R_{o/w}$ value was held constant at 10.

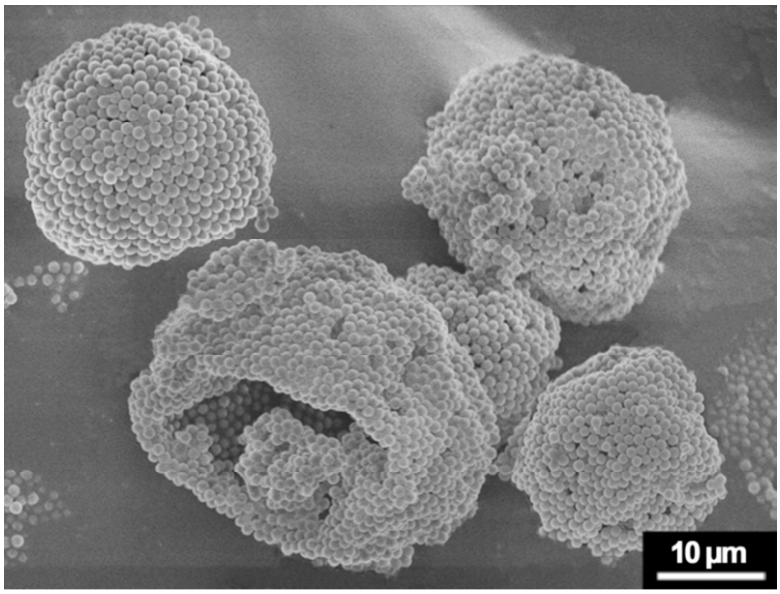

Figure S5. SEM images of the SiN/PDACs with 2 mg dopamine mL^{-1} Tris-buffer and $R_{o/w}$=6.

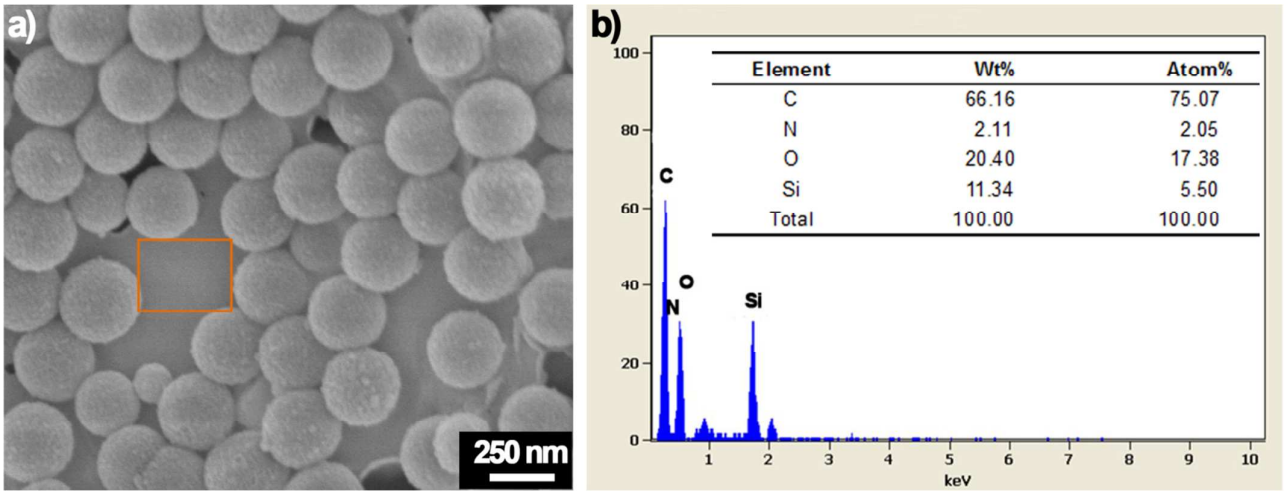

Figure S6. EDS analysis of the PDA layer localized on the shell of SiN/PDACs. a) SEM image of the scanning area on the surface of the colloidosome. b) The EDS spectrum of PDA layer showing the elements distribution.

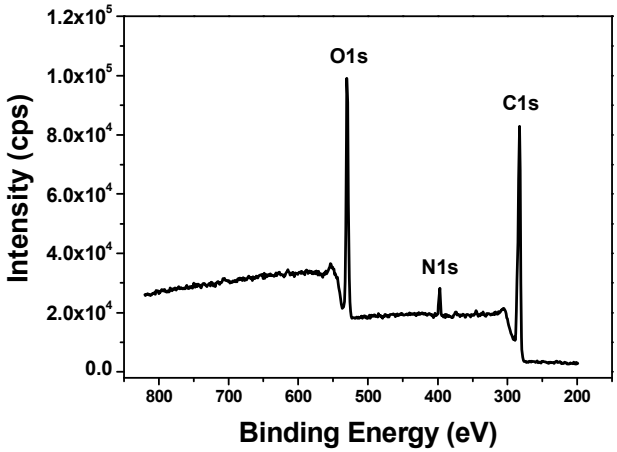

Figure S7. XPS survey spectra of the detached SiO_2 NPs, which were collected from SiN/PDACs after repeated high-speed centrifugation, ultrasonic and cleaning treatment with water and ethanol for multiple cycles.

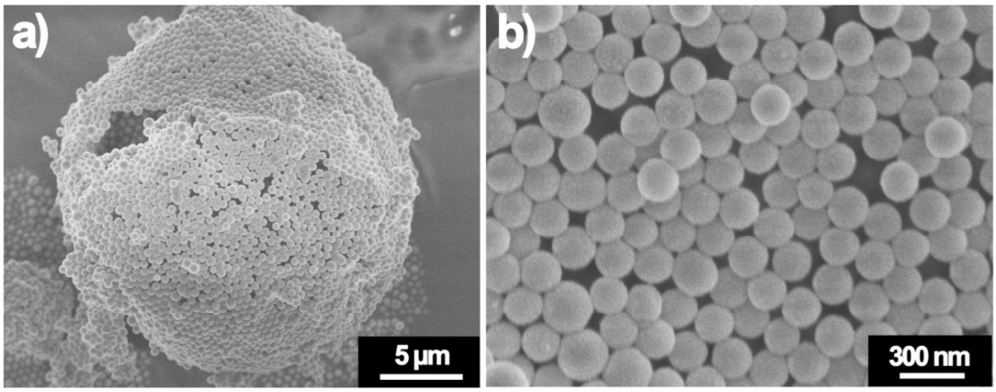

Figure S8. a) SEM image of the SiNDs and b) its outer surface formed with no addition of dopamine at $R_{o/w}$=6 and 1% (w/v) SiO_2 NPs loading.

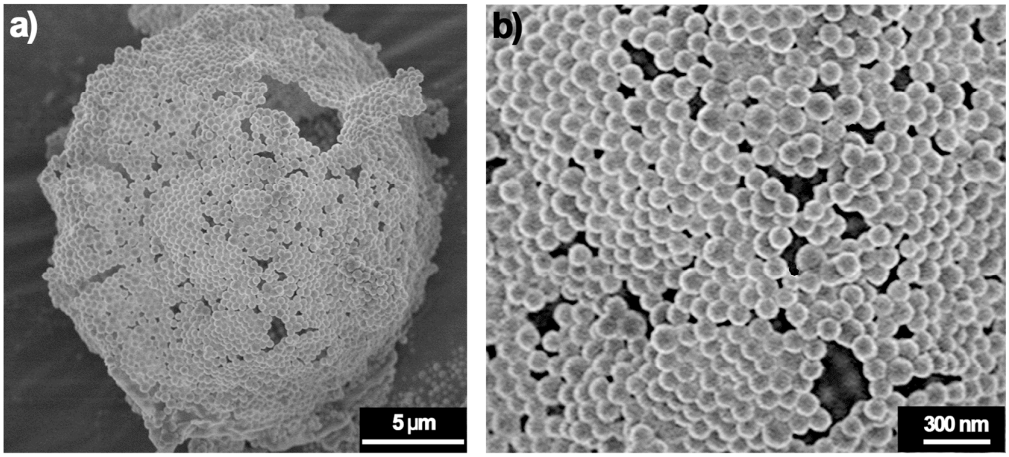

Figure S9. a) SEM image of the colloidosomes (denoted as SiN/PDAiCs) and b) its outer surface formed by directly emulsifying an aqueous solution of dopamine with heptane at $R_{o/w}$=6, 5 mg dopamine mL^{-1} Tris-buffer, 1% (w/v) SiO_2 NPs loading.

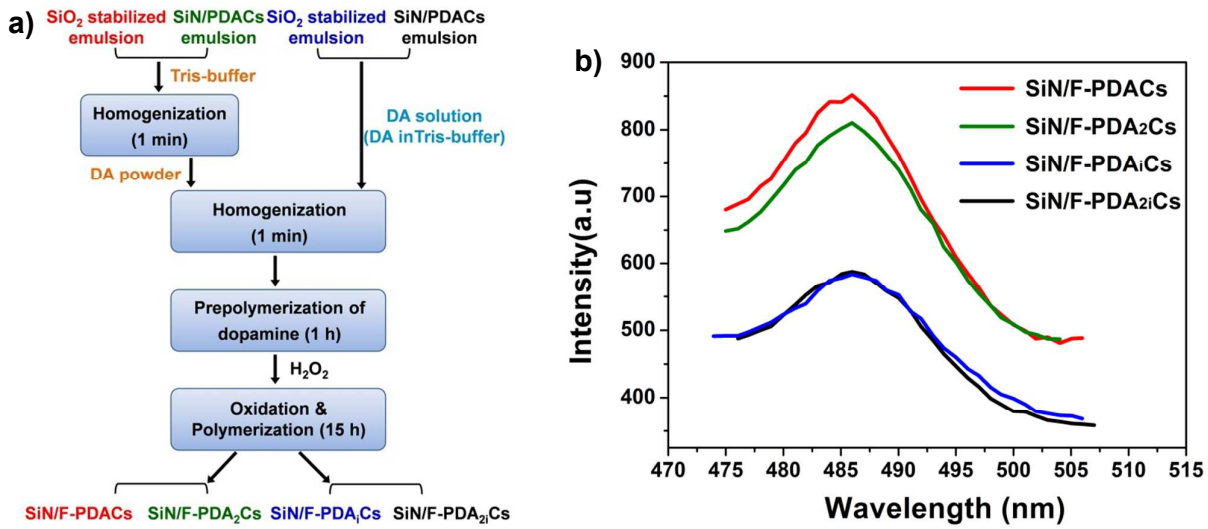

Figure S10. a) The fluorescent labeling of PDA via the polymerization of dopamine in the presence of H_2O_2. In these cases, the $R_{o/w}$ of the initial emulsion was held constant as 10, while the final $R_{o/w}$ of fluorescent emulsion was held constant as 5.3. b) Fluorescence emission spectra of the fluorescent colloidosomes prepared at different operational reaction conditions as described in Figure S10a.

Fluorescence analysis: The fluorescently labeled SiN/F-PDACs were prepared following the procedure as shown in Figure 10a. Briefly, dopamine powder was added to the SiO2 stabilized Pickering emulsion for 1 h pre-polymerization. Then, an aqueous H_2O_2 solution was added, homogenized and allowed to react for another 15 h at 20 °C, forming the fluorescently labeled colloidosomes. The SiN/F-PDACs were then characterized by fluorescence spectroscopy. As shown in Figure S10b, the emulsion of SiN/F-PDACs exhibits bright blue luminescence with a maximum emission wavelength of ca.486 nm under excitation at 405 nm. This fluorescence property is consistent with previously reported results, indicative of the formation of F-PDA.

When the aqueous solution of dopamine was used, the fluorescent colloidosomes, denoted as SiN/F-PDAiCs, were also prepared following a similar procedure to that mentioned above (Figure S10a). Excitation of a suspension of SiN/F-PDAiCs at 405 nm also leads to a fluorescence emission at ca. 486 nm but shows a significant decrease in fluorescence intensity (Figure S10b), which can be attributed the polymerization of dopamine in the aqueous core (the inner of the colloidosomes) rather than at oil/water interfaces. In addition, the SiN/PDACs were also used as templates to synthesize fluorescent PDA by adding dopamine powder or aqueous dopamine solution (Figure S10a). As expected, a higher fluorescence intensity was observed in the case of SiN/F-PDA_2Cs due to the interfacial polymerization of dopamine and thus more fluorescent molecules incorporated into the colloidosome shell (Figure S10b). Compared to the SiN/F-PDACs, the SiN/F-PDA_2Cs have a slightly lower fluorescence intensity, possibly attributed to the existing PDA layer speeding up the polymerization of dopamine and thus lead to fewer fluorescent molecules. In this study, we also found that no fluorescence was observed when the SiN/PDACs were treated with H_2O_2 alone (no dopamine added).

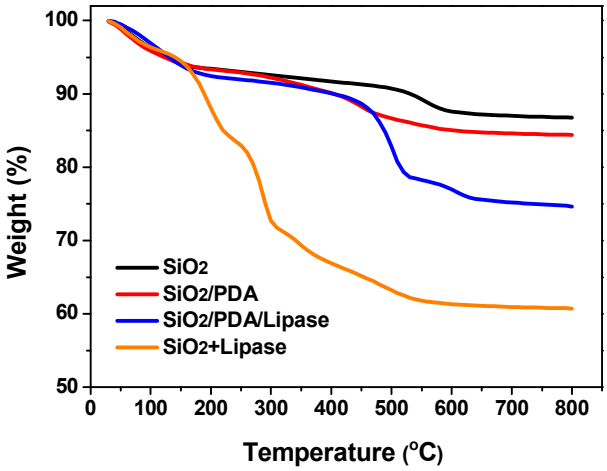

Figure S11. Thermogravimetric data of the mixture of SiO_2 NPs and lipase (SiO_2+Lipase), the detached SiO_2 NPs, SiO_2 NPs coated with PDA (SiO_2/PDA), SiO_2 NPs coated with PDA and immobilized lipase (SiO_2/PDA/Lipase), which were collected from SiNDs, SiN/PDACs and lipase-SiN/PDACs after repeated high-speed centrifugation, ultrasonic and cleaning treatment with water and ethanol for multiple cycles.

As shown in Figure S11, for the mixture of silica and lipases, the mass loss from 250 to 300 ℃ should be attributed to the degradation of lipases. For the SiO2/PDA/Lipases, the degradation of PDA and lipase was observed from 300 to 500 ^{o}C. In this case, the physical and chemical protection derived from SiN/PDACs likely contribute to a higher degradation temperature for lipase. Additionally, the mass loss started from 500 ^{o}C was due to the degradation of hydrophobic siloxane groups connected on SiO2 NPs.

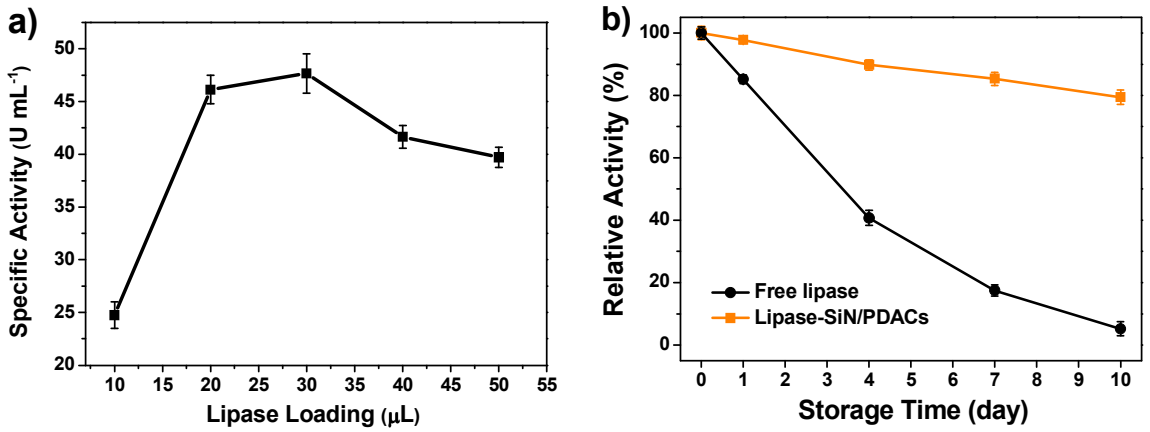

Figure S12. a) The effect of lipase loading on the specific activity of the lipase-SiN/PDACs. b) The change in specific activity of the free lipase and lipase-SiN/PDACs during the storage at 4 ^{o}C. Relative activity (%) represents the ratio of the residual activity to the initial activity of each sample measured at 37 °C for 1 h.