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## Pickering Emulsion-Enhanced Interfacial Biocatalysis: Tailored Alginate Microparticles Act as Particulate Emulsifier and Enzyme Carrier

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Xin Yang,<sup>a</sup> Yaolei Wang,<sup>a</sup> Ruixue Bai,<sup>a</sup> Hulin Ma,<sup>a</sup> Weihao Wang,<sup>a</sup> Hejia Sun,<sup>a</sup> Yuman Dong,<sup>a</sup> Fengmei Qu,<sup>a</sup> Qiming Tang,<sup>a</sup> Ting Guo,<sup>a</sup> Bernard P. Binks<sup>b,\*</sup> and Tao Meng<sup>a,\*</sup>

**A robust Pickering emulsion stabilized by lipase-immobilized alginate gel microparticles with a coating of silanized titania nanoparticles is developed for biphasic biocatalysis. The good recyclability and high stability of the proposed interfacial catalysis system have been verified, retaining about 90% of relative enzyme activity in 10 catalytic cycles with operation for 240 h. Meanwhile the Pickering emulsions remain stable during a storage time of one year. The green system can be widely applied to construct powerful platforms for enzyme or microorganism-driven interfacial catalysis.**

As the core of biocatalysis, enzymes play unique roles in the chemical industry, where they catalyze reactions under mild and sustainable conditions.<sup>1-6</sup> However, enzymes commonly exhibit activity in water, while organic substrates are often poorly soluble in aqueous media therefore presenting a central issue in biphasic biocatalysis.<sup>7</sup> To obtain sufficient mass transfer in an aqueous-organic system, instead of undesired shear mixing,<sup>8-10</sup> colloidal particle-stabilized Pickering emulsions<sup>11</sup> have proven to be promising systems for promoting biphasic biocatalysis.<sup>12</sup>

In general, there exists two approaches for biphasic enzymatic catalysis in Pickering emulsions: free enzyme located in (say) the inner aqueous phase<sup>13-18</sup> or enzyme-immobilized particles anchored around droplet interfaces.<sup>19-27</sup> The latter is a better strategy because it enables enzymes to be recycled, maximizes the contact area between internal enzymes and external substrates, reduces the diffusion distance of substrate molecules and improves the stability of

enzymes. One such enzyme immobilization method includes adsorption of enzymes into mesoporous silica particles<sup>20-21</sup> or into carbonaceous microspheres<sup>22</sup>. However, the enzymes suffer leaching and denaturation after several cycles of re-use due to the weak interactions between enzymes and carriers. Other methods include the covalent conjugation of enzymes to metal-organic frameworks,<sup>23</sup> Janus particles,<sup>24</sup> polymer,<sup>25</sup> graphene oxide nanosheets<sup>26</sup> or directly to colloidosomes.<sup>27</sup> However, there is inevitably a decrease in enzyme activity during the chemical treatments. In comparison, the physical encapsulation of enzymes into carriers is an ideal means due to the low cost and high versatility, *e.g.* Wang *et al.* have utilized enzyme encapsulated polymersomes to form Pickering emulsions as a biocatalytic system. However this still undergoes the harsh covalent crosslinking of the polymersomes to maintain their integrity.<sup>19</sup> Hence, it is still challenging to fabricate a robust Pickering emulsion system with enzymes encapsulated at the interfaces for biphasic biocatalysis in a green manner.

Alginate (Alg) is a green matrix due to its biocompatibility and ease of gelation,<sup>28</sup> which can be ionically crosslinked by the addition of divalent cations in aqueous solution. The mild gelation process permits full retention of biological activity of proteins, cells and DNA incorporated into the Alg matrix.<sup>29</sup> In practical, Alg particles are employed as widely used carriers for enzyme immobilization, where enzymes are trapped in the gel network while substrate and product molecules can freely transfer.<sup>30</sup> However, due to the intrinsic high hydrophilic nature of Alg particles, they fail to adhere at oil-water interfaces. Although several strategies<sup>31-34</sup> are currently available to reduce the hydrophilicity of Alg particles to stabilize oil-in-water (O/W) Pickering emulsions, little progress has been made in applying them to obtain water-in-oil (W/O) Pickering emulsions. In fact, most of the interfacial enzymatic catalysis such as transesterification and ester synthesis would benefit from a W/O type of Pickering emulsion, since the feedback effect of product inhibition on enzymatic reaction can be effectively alleviated by convenient diffusion of oil-soluble products from the interface to the continuous oil phase.

<sup>a</sup> School of Life Sciences and Engineering  
Southwest Jiaotong University  
Chengdu, Sichuan, 610031, PR China  
E-mail: taomeng@swjtu.edu.cn (T. Meng)

<sup>b</sup> Department of Chemistry and Biochemistry  
University of Hull  
Hull HU6 7RX, UK  
E-mail: b.p.binks@hull.ac.uk (B.P. Binks)

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Herein, surface-active Alg microparticles were developed to act as both particulate stabilizers to stabilize W/O Pickering emulsions for the first time and enzyme carriers anchoring at droplet interfaces to enhance interfacial biocatalysis (Scheme 1). Initially, two sets of W/O emulsions co-stabilized by silane-grafted titania nanoparticles ( $s\text{-TiO}_2$ ) and Span 80 surfactant molecules were prepared, one containing calcium chloride and the other containing Na-Alg and enzymes in the water phase (Scheme S1). After gentle mechanical mixing of the two emulsions, the two sets of droplets coalesced to trigger the gelation of calcium Alg yielding enzyme-immobilized Alg with  $s\text{-TiO}_2$  coating (E@Alg@ $s\text{-TiO}_2$ ) microparticles (Scheme 1a).  $\text{TiO}_2$ -based materials usually involve improved pH stability, thermal resistance and mechanical strength.<sup>35</sup> By changing the chain length of the grafted silane, the wettability of E@Alg@ $s\text{-TiO}_2$  microparticles can be fine tuned such that they form stable W/O Pickering emulsions (Scheme 1b). Lipase, a versatile enzyme widely used even on an industrial scale, is chosen as a model enzyme to assess the catalytic performance in the esterification of hexanoic acid and 1-hexanol in water-in-hexane Pickering emulsions (Scheme 1c).

Figure 1a-c and Figure S1 show the morphologies/EDS of both Alg@ $s\text{-TiO}_2$  microparticles in which the silane coupling agent contains 6 carbon atoms (Alg@C6- $\text{TiO}_2$ ) and pure Alg microparticles respectively. As shown in Figure 1a and Figure S1a, almost all the Alg microparticles are spherical with diameters of 2-5  $\mu\text{m}$ . In contrast to Figure S1b, the surface morphology of Alg@C6- $\text{TiO}_2$  microparticles (Figure 1b) is rougher and more uneven than pure Alg microparticles due to the coating of the aggregates of C6- $\text{TiO}_2$  nanoparticles with diameters of approximately 150 nm. Compared with Figure S1c, the EDS results in Figure 1c show the presence of titanium atoms on the surface of Alg@C6- $\text{TiO}_2$  microparticles. In the process of emulsion gelation, the negatively-charged Ca-Alg microspheres can be coated with positively-charged C6- $\text{TiO}_2$

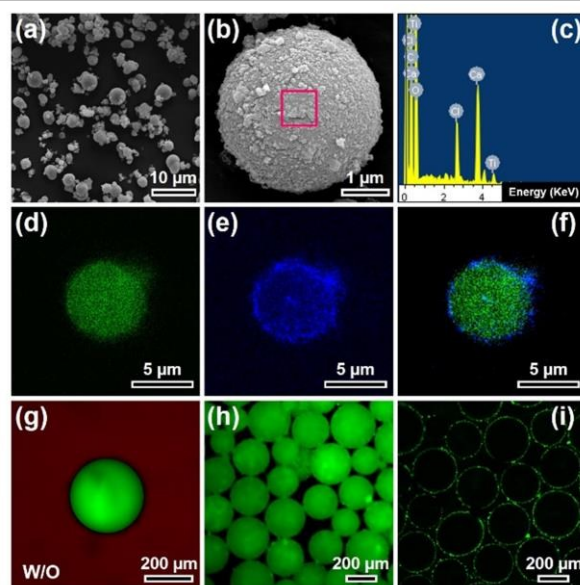
nanoparticles *via* electrostatic attraction at pH 7.4 (pH value of dispersed water phase). These above experimental results confirm the C6- $\text{TiO}_2$  nanoparticles are successfully coated on the surface of Alg microparticles. Results of the investigation of the chemical characterization and size of the C6- $\text{TiO}_2$  nanoparticles are given in Figures S2 and S3. Movie S1 shows that the pure hydrophilic Alg microparticles sink to bottom of the water phase whilst Alg@C6- $\text{TiO}_2$  microparticles are located at the interface of hexane and water. It suggests that surface-active Alg@C6- $\text{TiO}_2$  microparticles may be promising as a Pickering emulsifier.

As is shown in Figure 1d-f, the morphologies of E@Alg@C6- $\text{TiO}_2$  microparticles are directly visualized by confocal laser scanning microscopy (CLSM). Evidence is provided that lipase is immobilized inside Alg microparticles (Figure 1d, green fluorescence from FITC-labelled lipase) and the C6- $\text{TiO}_2$  nanoparticles coat their surface (Figure 1e, blue fluorescence from C6- $\text{TiO}_2$  nanoparticles). Figure 1f is the merged CLSM image of Figure 1d and 1e.

Figures 1g-i show CLSM images of the Pickering emulsion stabilized by E@Alg@C6- $\text{TiO}_2$  microparticles. To clearly distinguish the emulsion type, water and hexane are stained by FITC and Nile red respectively. Figure 1g is the merged CLSM image of Figure S4a and S4b. As shown in Figure 1g, the Pickering emulsion droplet is spherical with green fluorescence (FITC) in the droplet and red fluorescence (Nile red) outside of the droplet, thus a water-in-hexane Pickering emulsion is confirmed. The overview CLSM snapshot of Pickering emulsion droplets with green fluorescence from FITC stained inner water phase shows that the mean droplet diameter is 250  $\mu\text{m}$  (Figure 1h). To confirm that E@Alg@C6- $\text{TiO}_2$  microparticles are anchored at the oil-water interface, the Alg@C6-



**Scheme 1.** Schematic representation of enzyme-immobilized surface-active Alg microparticles stabilizing W/O Pickering emulsions for interfacial biocatalysis: (a) Preparation of E@Alg@s- $\text{TiO}_2$  microparticles through Alg gelation *via* coalescence of water-in-paraffin oil emulsions, (b) wettability adjustment of E@Alg@s- $\text{TiO}_2$  microparticles at the water-hexane interface by chain length of grafted silane, (c) enzymatic catalysis at the interface of water-in-hexane Pickering emulsion. Substrate S, product P.

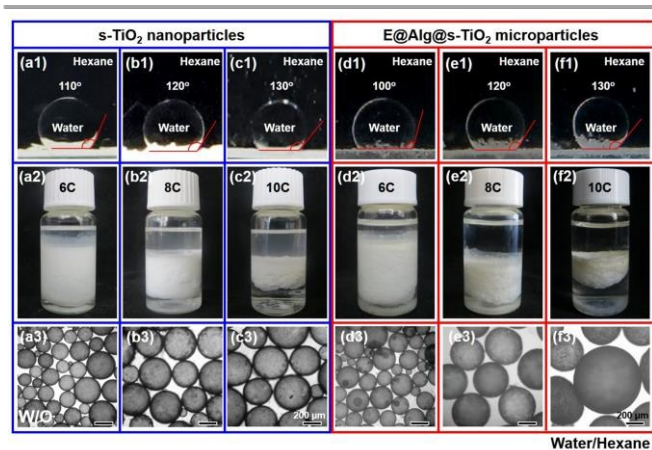


**Figure 1.** For Alg@C6- $\text{TiO}_2$  microparticles: (a) SEM image, (b) magnified SEM image, (c) EDS elemental mapping. (d-f) CLSM images of a E@Alg@C6- $\text{TiO}_2$  microparticle. Green and blue indicate FITC-labelled lipase and C6- $\text{TiO}_2$  nanoparticles, respectively. (g, h) Type of water-in-hexane Pickering emulsion stabilized by E@Alg@C6- $\text{TiO}_2$  microparticles (2 wt.%) is confirmed by CLSM. Green and red indicate FITC-labelled water and Nile red-labelled hexane respectively. (i) CLSM image of W/O Pickering emulsion showing the location of green fluorescence of FITC-labelled lipase at the interfaces.

TiO<sub>2</sub> microparticles containing FITC-labelled lipase are used to stabilize the W/O Pickering emulsion (Figure 1i). The green fluorescence from FITC-labelled lipase reveals that the emulsions droplets are thoroughly surrounded by E@Alg@C6-TiO<sub>2</sub> microparticles.

Figure 2 shows the effect of the surface wettability of both s-TiO<sub>2</sub> nanoparticles and E@Alg@s-TiO<sub>2</sub> microparticles on the stability of W/O Pickering emulsions. As shown in Figure 2a1-f1, the three-phase contact angle of a water drop under hexane on a layer of particles is determined. The contact angle for s-TiO<sub>2</sub> nanoparticles increases progressively from 110° to 130° upon increasing the chain length of the silane reagent from 6 to 10 (Figure 2a1-c1)). Likewise, the contact angle for E@Alg@s-TiO<sub>2</sub> microparticles increases from 100° to 130° (Figure 2d1-f1)). The increased hydrophobicity of the particles with silane chain length is similar in the two cases. As seen in the photos of the vessels (Figure 2a2-f2) and the microscopy images (Figure 2a3-f3), both s-TiO<sub>2</sub> nanoparticles alone and E@Alg@s-TiO<sub>2</sub> microparticles can be used to stabilize water-in-hexane Pickering emulsions. However, less water is emulsified and the drops are larger as the chain length of the silane agent increases from 6 to 10. Relatively hydrophobic particles possessing a contact angle > 90° prefer to stabilize W/O emulsions.<sup>36</sup> The decreasing emulsion quality upon increasing the particle hydrophobicity is in line with earlier findings for silica particle-stabilized emulsions.<sup>37</sup>

Using E@Alg@C6-TiO<sub>2</sub> microparticles as emulsifier, we varied the particle concentration in water-in-hexane emulsions. Between 0.5 wt.% and 2 wt.% particles, Figures S5 and S6 show that the extent of coalescence decreases progressively and the average droplet diameter decreases to around 250 μm, yielding an emulsion

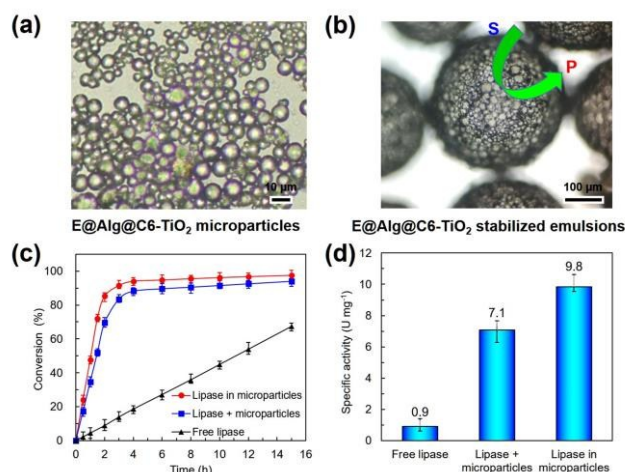


**Figure 2.** Left blue box: photos of a water drop under hexane on a layer of (a1) C6, (b1) C8 or (c1) C10-silane grafted TiO<sub>2</sub> nanoparticles; photos and optical micrographs of water-in-hexane Pickering emulsions stabilized by C6 (a2, a3), C8 (b2, b3) or C10 (c2, c3)-silane grafted TiO<sub>2</sub> nanoparticles (no Span 80). Right red box: photos of a water drop under hexane on layer of enzyme-immobilized Alg microparticles coated by C6 (d1), C8 (e1) or C10 (f1)-silane grafted TiO<sub>2</sub> nanoparticles; photos and optical micrographs of water-in-hexane Pickering emulsions stabilized by enzyme-immobilized Alg microparticles coated by C6 (d2, d3), C8 (e2, e3) or C10 (f2, f3)-silane grafted TiO<sub>2</sub> nanoparticles. All emulsions refer to 1 h since preparation at room temperature with a particle concentration of 2 wt.%.

of high water-oil interfacial area. This will be beneficial for biphasic catalysis reactions.<sup>38</sup> Therefore, the silane with chain length of 6 and 2 wt.% of particle emulsifier is used in subsequent experiments.

The obtained E@Alg@C6-TiO<sub>2</sub> microparticles at a particle concentration of 2 wt.% are used to construct an interfacial catalysis system within a water-in-hexane Pickering emulsion by hand shaking (see Movie S2). Figure 3a and b show the optical microscopy images of E@Alg@C6-TiO<sub>2</sub> microparticles and water-in-hexane Pickering emulsions stabilized by these particles respectively. The E@Alg@C6-TiO<sub>2</sub> microparticles are spherical with diameters of 2-5 μm. These microparticles become densely coated at the water-hexane interface of droplets acting as both an emulsifier and biocatalyst. As shown in Figure 1f, the CLSM image demonstrates that C6-TiO<sub>2</sub> nanoparticles and lipase are located at the surface and within the Alg microparticles respectively. The loading rate and immobilization efficiency of the lipase are 16 mg/g and 17% respectively.

The catalytic performance of E@Alg@C6-TiO<sub>2</sub> microparticles within the W/O Pickering emulsion is investigated using the esterification of 1-hexanol and hexanoic acid using hexane as the oil phase. Three systems are investigated. In the first, free lipase in water is used in a gently shaken biphasic water-hexane interface. In the second, free lipase is dissolved in the aqueous phase of a Pickering emulsion stabilized by Alg@C6-TiO<sub>2</sub> microparticles (no immobilized enzyme). In the third, lipase is immobilized within Alg@C6-TiO<sub>2</sub> microparticles stabilizing a Pickering emulsion. The reaction conditions of three systems were the same, such as substrate concentration, amount of lipase, oil:water ratio and shaking frequency. Figure 3c shows the extent of conversion of reactants to product as a function of time in the three cases. The conversion reaches 85-95% in the two Pickering emulsions within 4



**Figure 3.** (a) Optical microscopic image of E@Alg@C6-TiO<sub>2</sub> microparticles. (b) Microscope image of interfacial catalysis system of water-in-hexane Pickering emulsion stabilized by 2 wt.% E@Alg@C6-TiO<sub>2</sub> microparticles. (c) Plot of the conversion of 1-hexanol and hexanoic acid to ester versus reaction time for free lipase in a biphasic water-hexane system (triangles), free lipase dissolved in the water phase of a W/O Pickering emulsion (squares) and lipase immobilized in Alg@C6-TiO<sub>2</sub> microparticles anchored at droplet interfaces in W/O Pickering emulsion (circles). (d) Specific activity of lipase under the three conditions in (c). All of the measurements were repeated three times.

hours, in contrast to only 20% for the biphasic system. The significant enhancement for Pickering emulsions is attributed to the significantly increased interfacial area in the form of droplets (at least by a factor of 68) compared with the biphasic system, which increases the contact between the enzyme and substrates. It is also seen that immobilizing the enzyme as opposed to dissolving it in water slightly increases the conversion at any time.

Figure 3d shows that the specific catalytic activity of the lipase in the water phase of the Pickering emulsion ( $7.1 \text{ U mg}^{-1}$ ) is nearly 8 times higher than that of free lipase in the biphasic system ( $0.9 \text{ U mg}^{-1}$ ), demonstrating that a Pickering emulsion stabilized by Alg@C6-TiO<sub>2</sub> microparticles is effective for improving enzyme activity. Moreover, when lipase is encapsulated in Alg@C6-TiO<sub>2</sub> microparticles anchored at the droplet interfaces of a Pickering emulsion, the specific activity of the lipase ( $9.8 \text{ U mg}^{-1}$ ) is 1.4 and 11 times higher than that of lipase in the water phase of the Pickering emulsion ( $7.1 \text{ U mg}^{-1}$ ) and free lipase in the biphasic system ( $0.9 \text{ U mg}^{-1}$ ) respectively. Since all the E@Alg@C6-TiO<sub>2</sub> microparticles are distributed at the interfaces of Pickering emulsion droplets, this brings not only effective protection of the enzyme by the calcium alginate shell but also enables an increased possibility of contact between the enzyme and substrates due to a reduced diffusion distance of these molecules.<sup>39, 40</sup> Therefore, the catalytic activity of the encapsulated lipase at Pickering emulsion interfaces is higher than the other two systems.

To reveal the easy separation and recyclability of Pickering emulsions stabilized by E@Alg@C6-TiO<sub>2</sub> microparticles, the esterification of 1-hexanol and hexanoic acid in water-in-hexane Pickering emulsions is carried out repeatedly for 10 cycles. The oil phase containing the product/substrate is separated through gravitational sedimentation and Pickering emulsions stabilized by E@Alg@C6-TiO<sub>2</sub> microparticles can easily be recycled. As shown in Figure 4, there is very little deactivation of lipase immobilized in Alg@C6-TiO<sub>2</sub> microparticles during the esterification process. The specific activity of lipase is maintained at 91% even after 10 cycles with operation for 240 h. The conversion extent in the esterification remains around 90% in all cycles. The principal reason for the slight loss in activity is probably enzyme denaturation. The recycling performance of the E@Alg@C6-TiO<sub>2</sub> microparticle-stabilized Pickering emulsion is better than that of previous research such as

silica-based nanocages (35% after 5 cycles, 10 min per cycle)<sup>20</sup> and aldehyde-functionalized Janus nanoparticles (75% after 9 cycles, 40 min per cycle)<sup>24</sup>. This is attributed to the encapsulation and protection by the alginate shell with TiO<sub>2</sub> coating. Figure S7 confirms that the Pickering emulsions stabilized by E@Alg@C6-TiO<sub>2</sub> microparticles remain stable during a storage time of nearly a year. The above experimental results confirm the easy separation and impressive recyclability of Pickering emulsions stabilized by E@Alg@s-TiO<sub>2</sub> microparticles.

In conclusion, we describe the construction of enzyme-loaded alginate microparticles stabilizing W/O Pickering emulsions for application in biphasic enzymatic catalysis. Highly hydrophilic alginate microparticles can be fine-tuned easily to possess appropriate wettability to stabilize the target water-in-hexane Pickering emulsions by adjusting the carbon chain length of silane-grafted TiO<sub>2</sub> nanoparticles as a coating. The enzymes are encapsulated within the microparticles in a green and versatile manner. The results of a model esterification show that the proposed system with encapsulated lipase residing at droplet interfaces possesses significantly higher activity compared with the system in which the lipase is dissolved within emulsion droplets or the conventional biphasic system. The high catalytic activity and stability is due to the mild encapsulated conditions and biocompatible microenvironment, the protection of the alginate particle shell with TiO<sub>2</sub> coating, the large oil-water interfacial area and the short diffusion distances created in this Pickering emulsion. Moreover, the organic phase containing products/substrates can be easily separated through gravitational sedimentation such that the Pickering emulsions can be recovered and re-used for many cycles. We believe that such a high-performance Pickering emulsion system can provide a green platform for various interfacial biocatalytic processes of industrial interest.

## Conflicts of interest

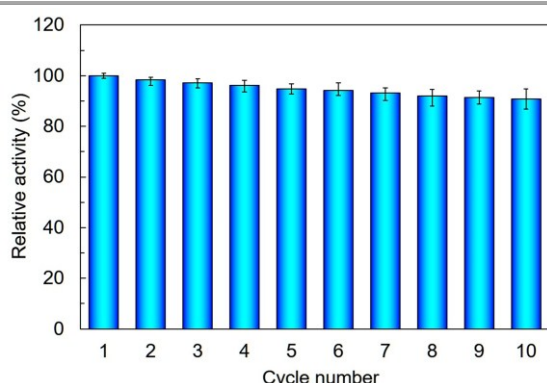
The authors declare no conflicts of interest.

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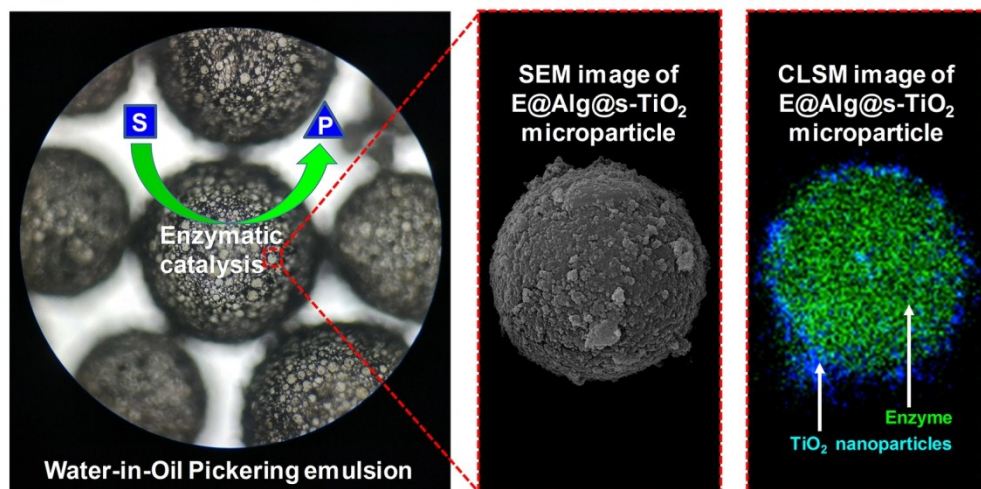
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**Figure 4.** Relative activity (ratio of residual enzymatic activity to activity in first cycle) of lipase immobilized in Alg@C6-TiO<sub>2</sub> microparticles anchored at droplet interfaces in W/O Pickering emulsions over 10 cycles (24 h per cycle).

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Tao Meng and co-workers construct alginate microparticle-stabilized water-in-oil Pickering emulsions for application in biphasic enzymatic catalysis. The alginate microparticles with a coating of titania nanoparticles encapsulate an enzyme and act as a robust Pickering emulsion interfacial biocatalyst. The green system will be widely applied in two-phase biocatalysis.

72x36mm (600 x 600 DPI)