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# Effect of stearic acid modified HAp nanoparticles in different solvents on the properties of Pickering emulsions and HAp/PLLA composites

Ming Zhang, Ai-juan Wang *, Jun-ming Li, Na Song

*School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, China*

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ABSTRACT

Stearic acid (Sa) was used to modify the surface properties of hydroxyapatite (HAp) in different solvents (water, ethanol or dichloromethane($CH_2Cl_2$)). Effect of different solvents on the properties of HAp particles (activation ratio, grafting ratio, chemical properties), emulsion properties (emulsion stability, emulsion type, droplet morphology) as well as the cured materials (morphology, average pore size) were studied. FT-IR and XPS results confirmed the interaction occurred between stearic acid and HAp particles. Stable O/W and W/O type Pickering emulsions were prepared using unmodified and Sa modified HAp nanoparticles respectively, which indicated a catastrophic inversion of the Pickering emulsion happened possibly because of the enhanced hydrophobicity of HAp particles after surface modification. Porous materials with different structures and pore sizes were obtained using Pickering emulsion as the template via in situ evaporation solvent method. The results indicated the microstructures of cured samples are different form each other when HAp was surface modified in different solvents. HAp particles fabricated using ethanol as solvent has higher activation ratio and grafting ratio. Pickering emulsion with higher stability and cured porous materials with uniform morphology were obtained compared with samples prepared using water and $CH_2Cl_2$ as solvents. In conclusion, surface modification of HAp in different solvents played a very important role for its stabilized Pickering emulsion as well as the microstructure of cured samples. It is better to use ethanol as the solvent for Sa modified HAp particles, which could increase the stability of Pickering emulsion and obtain cured samples with uniform pore size.



## 1. Introduction

Composites with nanoparticles are gaining popularity for encapsulation and release drug molecules due to their ability for targeted and controlled release [1–5]. Nanoparticles with different structure and size were used to fabricate hydrogel with pH, temperature and illumination stimulative responsibility for drug release and delivery [6]; it's application in near-infrared photodynamic therapy, with low polydispersity has also been synthesized [2]; composites with good biocompatibility have been prepared for drug release and cell culture using a Pickering emulsion method [7–8]. Besides, nano/micro particles could be used as stabilizer to fabricate Pickering emulsion, which could eliminate the side effect of surfactants and present excellent permeation property applied as the carrier of drug release, cell culture, catalytic materials, etc. [9–15].

The wettability of nano/micro particle is very important to adjust Pickering emulsion type and cured materials structure [7–8,13]. Stable O/W type Pickering emulsion could be stabilized by hydrophilic particles, and thus microspheres were prepared using them as the template; stable W/O type Pickering emulsion could be stabilized by hydrophobic particles, and thus porous materials were fabricated. So far, both the obtained microsphere and porous materials were used in many fields, such as the carriers of drug release [16–18], bone tissue engineering scaffolds [19–26].

Owing to the excellent biocompatibility, hydroxyapatite ($(Ca_{10}(PO_4)_6(OH)_2)$, HAp) has been used as stabilizer of Pickering emulsion, but mainly O/W Pickering emulsion were fabricated because of its hydrophilibity [27–29]. W/O Pickering emulsion is necessary to obtain porous materials, that is, increase the hydrophobicity of HAp. So far, surface modification is usually used to enhance the hydrophobicity of particles in order to obtain stable W/O type Pickering emulsion and porous materials [25,30–33]. Stearic acid is widely used in surface modification due to its low toxicity and high hydrophobicity [25,30–33], particle and film with enhanced hydrophobicity were fabricated by grafting stearic acid [34–37].

In this paper, HAp nanoparticles were modified by stearic acid in three solvents (water, ethanol and $CH_2Cl_2$). Activation ratio, TGA were conducted to characterize the properties of HAp particles. FT-IR and XPS were used to characterize the interaction between HAp and stearic acid molecular. Pickering emulsions were prepared using both modified and unmodified HAp nanoparticles as stabilizer with PLLA dissolved in

* Corresponding author.
*E-mail address:* ajwmxl@163.com (A. Wang).

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$CH_2Cl_2$ as oil phase and deionized water as liquid phase. Effect of modification solvents on emulsion type and emulsion stability was studied. Further HAp-PLLA microsphere and porous composites were obtained using Pickering emulsions as the template via in situ evaporation solvent method (shown in Fig. 1). SEM was conducted to characterize the morphology of cured materials.

## 2. Experimental methods

### 2.1. Materials

Deionized water, Poly-L-lactic acid (PLLA, Mw = 55,000–90,000 g/mol) are supplied by BoLi biological material Co. Ltd. of ShenZhen. Dichloromethane ($CH_2Cl_2$, 99.5%), stearic acid and ethanol are supplied by FuYu chemical Co. Ltd. of TianJin. Hydroxyapatite (HAp) is supplied by SIGMA-ALDRICH Inc.

### 2.2. Surface modification of HAp nanoparticles

Stearic acid (Sa) (10 wt%, relative to the amount of HAp powders) was dissolved in 200 ml solvent (water, ethanol or $CH_2Cl_2$, respectively) to form a Sa solution. After that, 2 g HAp powders were added to the Sa solution, and then the received solution was put into a reflux setup at 80 °C for 4 h. The modified HAp powders were collected after rinsed three times using hot ethanol alcohol to remove free Sa. Modified HAp was dried at 80 °C for 12 h. Finally, HAp powders modified in water, ethanol and $CH_2Cl_2$ were collected and marked as HAp-W, HAp-E and HAp-C, respectively.

### 2.3. Preparation of Pickering emulsions and cured materials

Emulsions were prepared using different HAp particles as stabilizer with PLLA concentration of 5 w/v%, pH value of 7, HAp concentration of 0.08 wt%, oil-water ratio of 1:1, emulsification rates of 17,000 rpm for 60s (listed in Table 1). It is noted that unmodified HAp particles were dispersed in water phase and Sa modified HAp particles were dispersed in oil phase to prepare the Pickering emulsions owing to its different wettability. Cured materials were obtained via in situ evaporation of $CH_2Cl_2$ and water from the emulsion at 25 °C.

### 2.4. Characterization

#### 2.4.1. HAp particles

Activation ratio (%) is used to characterize the Sa modification effect of HAp. The method is briefly described as follows [25,34–35]. A given amount ($m_0$) of different HAp powers are dispersed in the water with ultrasonic for 15 min and then shaken for 5 min in order to well disperse the HAp nanoparticles. The sediments on the bottom are dried and weighted ($m_1$) after placement for 1 h to get obvious precipitation. Then the activation ratio (X) is calculated as Eq. (1).

$$X = \left(1 - \frac{m1}{m0}\right) \times 100\% \quad (1)$$

Besides, FT-IR (IRPrestige-21) and XPS (AXIS ULTRA) were conducted to characterize the surface chemical properties of modified and unmodified HAp nanoparticles. Thermal Gravity Analysis was conducted using NETZSCH (STA 449 F3) instrument. The weight loss of unmodified HAp particle represented as $W_0$ and weight loss of modified HAp particle represented as Wi. By measuring the weight loss of modified and unmodified HAp particle, the grafting amounts (G) could be calculated using the following Eq. (2).

$$G = (W_0 - W_1) \times 100\ \% \quad (2)$$

#### 2.4.2. Emulsions and cured materials

Emulsion type was determined by emulsion drop test [38]. Briefly, two drops of the emulsion were added to both water and oil phase respectively. If the drop is easy to be dispersed in water phase, the emulsion is O/W type; otherwise, it is W/O type. Three-dimensional video microscope was used to characterize the morphology of emulsion droplet. A drop of diluted emulsion using the same solvent of continuous phase was placed on a microscope slide and tested using HIROX KH1300 instrument. SEM was carried out using a MERLIN Compact operating at 5 kV to determine the morphology of cured materials. Dried samples were coated with gold before characterization. Further, average porous size and Cv value were calculated according to SEM imagines.

## 3. Results and discussion

### 3.1. Properties of HAp nanoparticles

#### 3.1.1. Activation ratios

Activation ratio of Sa modified HAp nanoparticles in different solvents were shown in Fig. 2(a). The higher value of activation ratio means better effect of modification [25,34–35]. Obviously, HAp particles were modified in ethanol presenting a higher value of 96% compared with other samples modified in water and $CH_2Cl_2$. More precipitation of HAp could be seen in the HAp-C and HAp-W samples means the

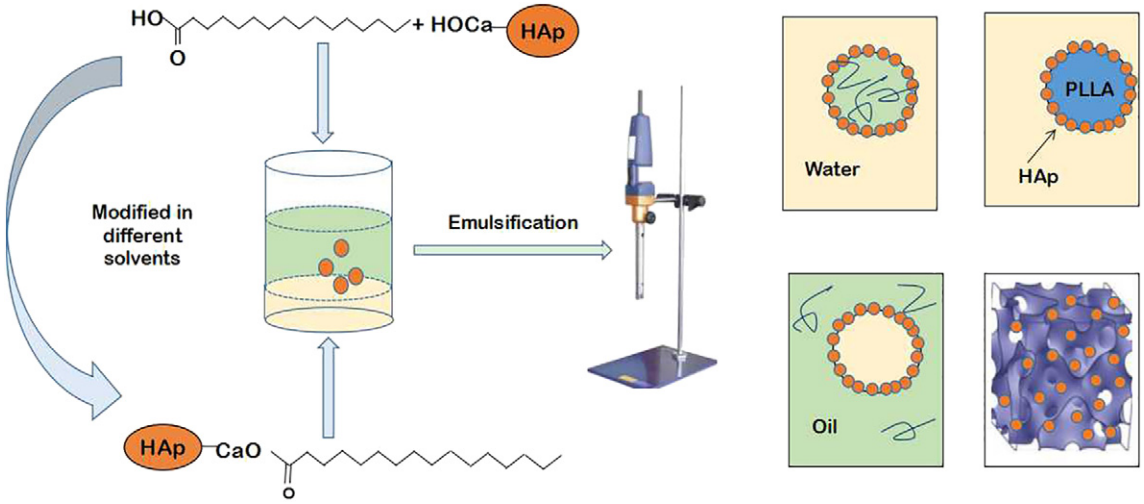


**Fig. 1.** Illustration of unmodified and Sa modified HAp nanoparticles stabilized Pickering emulsions and cured materials.