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RESEARCH PAPER

Hyper-miniaturization of monodisperse alginate–TiO_2 composite particles with densely packed TiO_2 nanoparticles

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Abstract We report a novel technique to fabricate alginate–TiO_2 composite particles with densely packed TiO_2 nanoparticles. Using a microfluidic device, monodisperse sodium alginate droplets containing low-density TiO_2 nanoparticles (1 or 5 w/v%) were formed in the oil phase. The sodium alginate droplets formed in the oil phase were subsequently placed on a Ca^{2+}-loaded agarose-gel plate to induce shrinkage by water removal (from the droplets to the Ca^{2+}-loaded agarose-gel plate) and gelation by Ca^{2+} transport (from the Ca^{2+}-loaded agarose-gel plate to the droplets). Thus, the produced alginate–TiO_2 composite particles containing densely packed TiO_2 nanoparticles were significantly smaller than the microchannel. We also investigated the optimal conditions to successfully produce spherical composite particles by varying the oil phases, surfactants, calcium concentrations and gel strength of the agarose-gel plate. Moreover, our method could decrease the probability of channel clogging that often occurs when a colloidal suspension (e.g., nanoparticles) is used as the dispersed phase. This method facilitates the stable production of monodisperse alginate–inorganic composite particles for a wide range of applications.

Keywords Microfluidics · Calcium alginate gel · Osmotic pressure · Channel clogging · Biopolymer · Inorganic particle

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1 Introduction

Inorganic particles have been widely utilized in catalysis (Li et al. 2007; Gong et al. 2009), drug delivery (Cao et al. 2008), cell immobilization (Perullini et al. 2011; Callone et al. 2008) and adsorption–separation processes (Sizgek et al. 2009; Abramson et al. 2010; Kimling and Caruso 2012). These particles have been developed using the sol–gel templating method (Perullini et al. 2011; Hong et al. 2012; Sizgek et al. 2009; Abramson et al. 2010; Kimling and Caruso 2012; Callone et al. 2008), and such biopolymers as agarose (Du et al. 2009) and chitosan (El Kadib et al. 2011) have been increasingly used as sacrificial templates because they are non-toxic, biocompatible and biodegradable (Abramson et al. 2010; Kimling and Caruso 2012; Lan et al. 2010). In particular, alginate gel, a type of biopolymer, has attracted considerable attention because of its porous three-dimensional structure, ease of preparation and morphological control (Kimling and Caruso 2012; Martinsen et al. 1992; Hills et al. 2000; Liu et al. 2008; Robitzer et al. 2008). Therefore, the fabrication of inorganic particles using alginate gel as a sacrificial template has been extensively studied (Perullini et al. 2011; Callone et al. 2008; Abramson et al. 2010; Kimling and Caruso 2012).

To enhance catalytic properties and adsorption performance, many studies have focused on developing monodisperse particles (Abramson et al. 2010; Kimling and Caruso 2012; Gong et al. 2009; Hong et al. 2012; Lan et al. 2010; Eun et al. 2009) and biopolymer–inorganic hybrids, such as chitosan/titania (El Kadib et al. 2008) and chitosan/silica (Lan et al. 2010; Silva et al. 2005; Yeh et al. 2007; Cao et al. 2006; Molvinger et al. 2004). Therefore, it is essential that optimally sized monodisperse biopolymer–inorganic composite particles, which correspond to a wide

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