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Self-assembly with varying hydrophobic centers: Synthesis of red blood cell-like basic magnesium carbonate microspheres

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ABSTRACT

Basic magnesium carbonate microspheres with a red blood cell (RBC)-like appearance and diameters of ~3 μm were synthesized by amphiphilic molecule-participated self-assembly under hydrothermal conditions. In the self-assembly, sodium dodecyl benzene sulfonate served as a template for the formation of $Mg(OH)_2$ spherical micelles and also as a reactant precursor that releases CO_2 to react with $Mg(OH)_2$. The growth of the microspheres is driven by the continuous generation of new hydrophobic centers because of the consumption of hydrophilic poles ($—SO_3{}^-$). The surfactant-directed self-assembly can be applied to the synthesis of other carbonate or metallic oxide self-assemblies, indicating that it is a universal self-assembly method for amphiphilic molecules.

Introduction

Amphiphilic surfactant molecules with both hydrophilic and hydrophobic groups tend to self-assemble into aggregates in aqueous solutions containing micelles, vesicles, lamellae or nanofibers when the surfactant concentration is higher than the critical micelle concentration (Discher & Kamien, 2004; Gu, Shi, Cheng, Lu, & Zheng, 2013; Hao & Hoffmann, 2004; Hartgerink, Beniash, & Stupp, 2001; Scanlon & Aggeli, 2008; Svenson, 2004). As a result, the microstructures, shapes, and properties of the aggregates in the aqueous surfactant solutions mainly depend on the composition and types of surfactant molecules (Liu et al., 2010; Wang et al., 2012). Therefore, amphiphilic molecules are widely used as templates for the preparation of anisotropic nanostructures (Mann, 2009). Biological tissues have been synthesized in aqueous environments under mild physiological conditions with the self- and co-assembly of biomacromolecules. These were primarily proteins, but also carbohydrates and lipids (Lakshmanan, Zhang, & Hauser, 2012; Rajagopal & Schneider, 2004; Sarikaya, Tamerler, Jen, Schulten, & Baneyx, 2003; Zhang, Marini, Hwang, & Santoso, 2002). In these processes, peptides or proteins are building blocks for the ordered assembly of materials and they are also structural templates characterized by significant surface activity (Dickinson, 1997; Liang, Patel, Matia-Merino, Ye, & Golding, 2013). The surface-active functional groups in these macromolecules may be transformed or may be removed during self- or co-assembly. This significantly affects the surface forces and the assembly process. Therefore, an investigation into a self-assembly process incorporating the transformation or removal of surface-active functional groups is of great importance.

Herein, we report a typical amphiphilic molecule-participated self-assembly process, which leads to the topological growth of RBC-like basic magnesium carbonate microspheres. In the self-assembly process, sodium dodecyl benzene sulfonate (SDBS) serves as a template for the formation of $Mg(OH)_2$ spherical micelles and also as a reactant precursor that releases CO_2, which reacts with $Mg(OH)_2$. Continuously renewed hydrophobic centers formed because of the decomposition of hydrophilic groups in SDBS, which allows the growth of RBC-like microspheres. The as-obtained microsphere structure has good structural stability and no agglomeration was observed. Its structure was retained after ultrasonic dispersion. Although several reports have dealt with the synthesis of basic magnesium carbonate microtubes (Mitsuhashi et al., 2005), petaloid-like microspheres (Ohkubo et al., 2007) and honeycomb-like microspheres (Gao & Xiang, 2010), RBC-like basic magnesium carbonate microspheres have not been reported. Olive-like copperoxide microspheres have also been successfully synthesized using the same approach, indicating that the suggested surfactant-consuming self-assembly process exists widely in nature.

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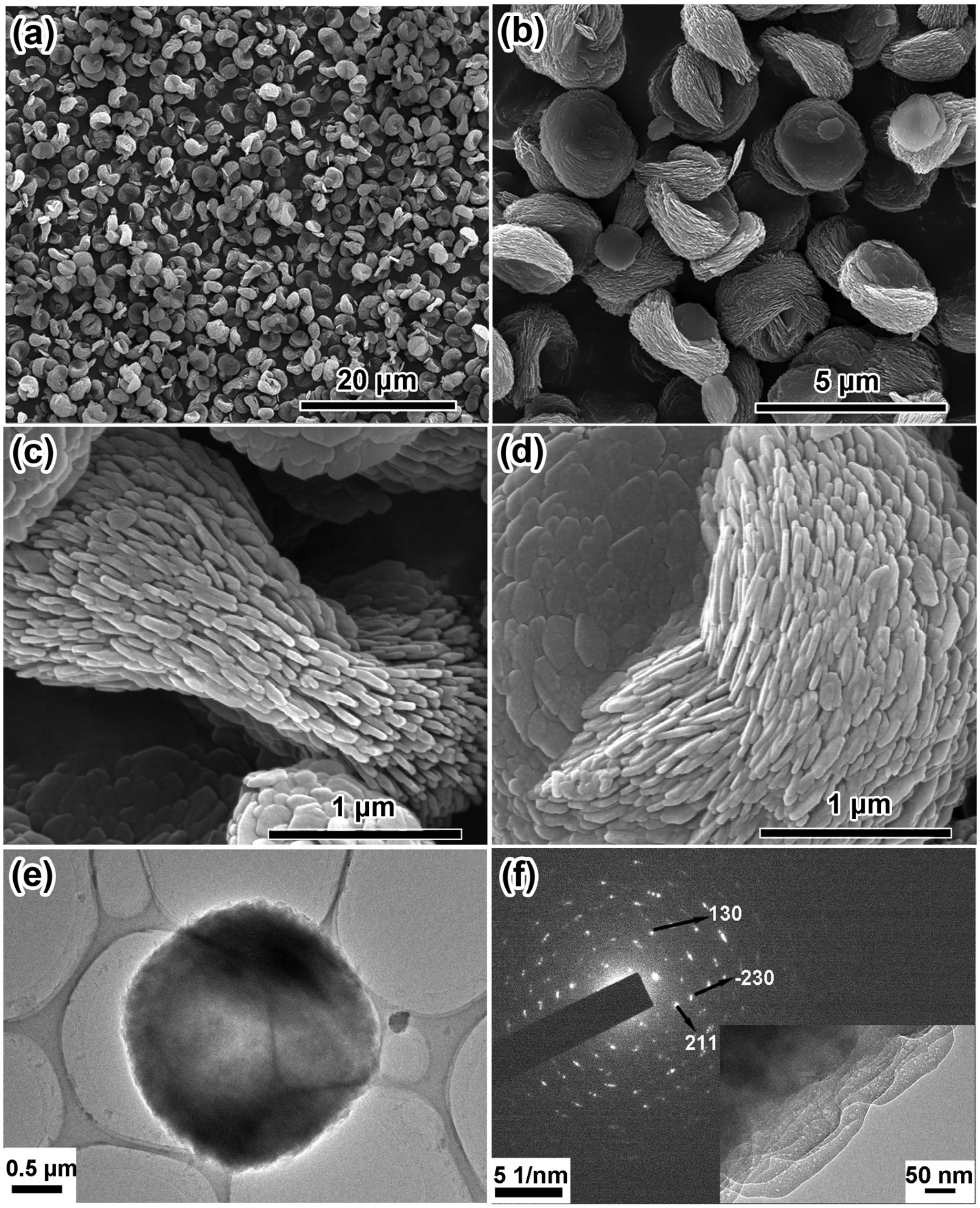

Fig. 1. (a)–(d) SEM images, (e) TEM image, and (f) SAED pattern of the RBC-like microspheres. The inset of (f) shows a TEM image of the edge of a RBC-like magnesium carbonate microsphere.

Experimental

Synthesis of RBC-like basic magnesium carbonate microspheres

Commercial $NH_3 \cdot H_2O$ (Sinopharm Chemical Reagent Beijing Co. Ltd., China), $MgSO_4 \cdot 7H_2O$ and SDBS (Tianjin Fuchen Chemical Reagents Factory, China) of analytic purity were used to synthesize the RBC-like basic magnesium carbonate microspheres. The alkyl chain in SDBS is a straight-chain. The alkyl chain is present at the para-position of $-SO_3Na$. In a typical synthesis, SDBS was added to 50 mL of a $MgSO_4$ aqueous solution (3.0 mol/L) at a mole ratio of $SDBS/MgSO_4 = 0.12$. Then, 20 mL $NH_3 \cdot H_2O$ solution (5.0 mol/L) was added to the prepared solution in a drop by drop manner with agitation. The obtained slurry was sealed in a Teflon autoclave and heated in an oven equipped with a rotary arm. Hydrothermal treatment at 150 °C for 10 h was carried out at a rotation rate of 30 rpm. After cooling to room temperature the products were filtered, rinsed with deionized water and dried in a vacuum oven at 100 °C for 24 h.

Characterization

The as-prepared RBC-like basic magnesium carbonate microspheres were characterized by scanning electron microscopy (SEM, Quanta 200F, FEI, Holand), transmission electron microscopy (TEM, JEM 2010, JEOL, Japan), X-ray diffraction (XRD, D8 Advance, Bruker, Germany), and thermogravimetric analysis (TGA, STA409PC, Netzsch, Germany) on a Q500 under nitrogen flow at a temperature ramp rate of 10 °C/min. SDBS before and after calcination was characterized by Fourier transform infrared spectroscopy (FT-IR,