Feature Designed Growth of 3D Flower-like SiO$_2$ Growing on Polyethyleneimine Modified CaCO$_3$ Microparticles

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We report on the ability to create complex 3D flower-like SiO$_2$ in vitro via CaCO$_3$ microparticles supported by polyethyleneimine mediated biosilicification under experimentally altered chemical influences. The morphology, structure, composition of the product have been investigated with the X-ray photoelectron spectrum, scanning electron microscope, transmission electron microscope, and energy-dispersive spectroscopy. The overall morphologies could be controlled to shift from a characteristic network of flower-like silica sphere to a sheet-like structure by adjusting physical adsorption of different amount of polyethyleneimine onto the surface of the CaCO$_3$ microparticles.

Key words: 3D flower-like SiO$_2$, Polyethyleneimine, CaCO$_3$, Biomimetic pattern

I. INTRODUCTION

Calcium carbonate (CaCO$_3$) is an important industrial filling material. Owing to their distinguished structural variety, environmental and economical advantages, they are widely applied in electronics, rubber, coating, cosmetics, and construction materials [1−3]. Generally, the morphology of CaCO$_3$ particles influences the performance in their applications. CaCO$_3$ micro/nano-structured spheres are often used in areas such as coating and cosmetics due to their good freerunning property and stability [4].

Silicon has a variety of useful properties for industrial purposes. Silica nanostructures with dimensions of a single nanometer can now be controllably fabricated in a variety of distinct topological forms (e.g., nanopores [5], nanospheres [6], and nanotubes [7]), giving rise to applications in optics [8], drug-delivery [9], microelectronics [10], and catalysis [11]. The incredible diversity of silica nanoarchitecture is also exhibited in some microorganisms [12], exhibiting distinct intricate shell details down to the 10 nm scale. Although other oxides have also been tailored on the nanoscales [13], silica is particularly interesting as a molecular building material due to its bulk stability and the ease with which its inherent structural richness can be exploited via a range of synthetic methods. A natural source of varying silica nanostructures can be found in the unicellular algae known as diatoms. Apart from their ecological significance, they are well known for the spectacular structures of their silica-based cell walls. The cell walls are structured from the nanometer to the micrometer scale, and diatom silica offers the possibility of exact reproduction of nanostructured silica in enormous numbers at minimal cost. The diatom cell wall is a composite made of silica and an incompletely characterized organic material, composed of glycoproteins and carbohydrates [14].

In order to fully exploit biological processing of silica, it would be valuable to understand the nature of the specific molecular interactions. Silica-based cell walls of diatoms are ideal experimental systems because they naturally process large amounts of silicon, they are unicellular and hence relatively simple, they can be cultured in such a way as to facilitate examination of silicon metabolism, and are amenable to the application of the powerful tools of modern molecular biology and biochemistry [15−20]. For the biomineralization of silica-based shell, also simple polyamines as polypropyleneimine derivatives play an important role [21]. Sumper has developed a model to explain the pattern formation of silica-based shells by phase separation occurring in silica solutions of these polyamines [22]. The polyethyleneimine (PEI), which is not charged in the non-dissolve state, was used in the silicification. PEI does not have side chains but contains nitrogen in the backbone of the polymer. As reported by Patwardhan et al. [23], PEI also precipitated silica particles, which were nearly spherical in shape with quite a few particles fused together. Even these particles were observed in two distinct sizes (220 and 800 nm). As it was found that, when this polymer was deposited onto the hard surface of the CaCO$_3$ microparticles by a sequential layer-by-layer (LbL) polymer adsorption method, the new unite acting as the template/catalysis/scaffold can also precipitate silica in similar mild system (room tem-
perature, pH=7 phosphate buffer, atmosphere pressure etc.) and the most exciting resulting morphology of product can be controlled from a flower-like silica network to a sheet-like structure by adjusting the amount of PEI on the new unite. In this work, we explore a method to synthesize a novel 3-dimension flower-like silica nanostructures using a biomimetic silicification (LbL) route.

II. EXPERIMENTS

A. Preparation of spherical microparticles of PSS/CaCO$_3$

In a typical experiment, 0.1 mol/mL Na$_2$CO$_3$ solution was rapidly poured into an equal volume of 0.1 mol/mL solution of CaCl$_2$ which had already solved 1.66 g poly(sodium-4-styrenesulfonate) (PSS) surfactant as stabilizing agent at room temperature, and after intense agitation on a magnetic stirrer the precipitate was filter off, thoroughly washed with pure water, and dried in air.

B. Preparation of PSS/CaCO$_3$/PEI pattern

Two approaches were used for capture of PEI by microparticles. One method, direct adsorption of macro-molecular from solution onto preformed PSS/CaCO$_3$ micro spheres (physical adsorption, layer-by-layer). Three volumes of PEI solutions of increased concentration (11, 33, and 99 mg/mL) were added into flasks containing the weighed quantity of dry PSS/CaCO$_3$ microparticles (500 mg), and the suspensions were thoroughly stirred for 2 h at room temperature. Each adsorption cycle was completed with three centrifugation steps (6000g, 5 min) followed by suspension in water for 5 min. The other method, PEI capture by PSS/CaCO$_3$ micro spheres in the process of their formation (coprecipitation). 0.1 mol/mL Na$_2$CO$_3$ solutions was rapidly added into an equal volume of 0.1 mol/mL solution of CaCl$_2$ which contained 1.66 g PSS surfactant as stabilizing agent, then different concentrations of PEI polymer solution (11, 33, and 99 mg/mL) were added at room temperature, after intense agitation on a magnetic stirrer the precipitate was filter off, thoroughly washed with pure water, and dried in air.

C. 3D flower-like SiO$_2$ micropaticles preparation

A typical reaction mixture contained 800 µL of the buffer, 20 mg dried composite template microparticles, 5 µL of the tetramethoxysilane (TMOS) without any treatment before. The reactions were carried out at room temperature, atmosphere pressure and neutral pH. All the reactants were measured and added to micro sample polypropylene test tubes using an adjusting volume pipette. At this point, the reaction time was noted as zero. The tubes were then closed and shaken well to thoroughly mix the reactants in each case. After 5 min, the samples were centrifuged at 6000g for 5 min. The liquid was removed and deionized-ultra filtrated (DIUF) water was then added to the tubes. This washing of sample was repeated three times to remove the free polymer.

III. RESULTS AND DISCUSSION

The synthesis of PSS stabilized CaCO$_3$ microparticles was based on Ref.[24] with minor modification. Figure 1 shows the scanning electron microscope (SEM) images of unloaded CaCO$_3$, stabilized CaCO$_3$ with PSS, and the CaCO$_3$/PSS treated by PEI. The unloaded CaCO$_3$ particles (Fig.1(d)) appear to be irregular cubic shaped with fairly smooth surface. The morphology of the CaCO$_3$/PSS composite particles (Fig.1(a), labeled as PSS/CaCO$_3$) shows a core-shell structure, the average diameters of the core-shell particles are about 2–5 µm. It is interesting that the shape of CaCO$_3$ looks inclined to being round, which is similar to that reported by Yu et al. [25, 26]. The morphology CaCO$_3$/PSS treated by PEI are shown in Fig.1 (b) and (c). The surface of these particles appears some dots, which is attributed to the deposition of PEI. The coprecipitation method was expected to result in a higher level of PEI captured by CaCO$_3$ microparticles formed through colloidal aggregation. With a highly developed adsorption surface, the PEI polymer solution was captured by growing CaCO$_3$ microparticles.

When it comes to the preparation of 3D flower-like SiO$_2$ micropaticles, we chose TMOS as the silica precursor and sodium phosphate buffer as a solvent. We have also kept the temperature, pressure and pH be constant, so that the effect of the other parameters is clear. Figure 2(a) shows the SEM images of a typical sample PSS/CaCO$_3$/PEI with a lower PEI deposition (PEI...
polymer in mother solution of 11 mg/mL) as template to precipitate the silica, a uniform, flower-like architectures approximately 10 µm in diameter. More shapes were produced by integrating three or more particles altogether. Surprisingly, a beautiful flower-like crystal appeared when one of the single spheroids in Fig.1(a) was further magnified. The highly branched architecture was completely made up of uniform micro petals that connected to each other through the center to form 3D flower-like structures (Fig.2(b)). The spherical 3D morphology of the inorganic flower indicated the radial growth at a similar rate in all directions. With the amount of PEI solution in mother liquid increasing to 33 mg/mL, the result silica presented another morphology, some flower-like silica transferred to a sheet-like architectures appearance (Fig.2(c)). Compared with the morphology of silica obtained from another higher concentration of PEI (99 mg/mL) on the surface of the PSS/CaCO$_3$ microparticles may accelerate the TMOS hydrolyzation, a fast nucleation of amorphous primary particles followed by a slow aggregation and crystallization of primary particles happened alone the surface of the template, CaCO$_3$ acted as a “hard reaction platform”, and PEI polymer accomplished a “membrane” player. Without the CaCO$_3$ “hard reaction platform”, only silica nanoparticles were precipitated from the aqueous system (Fig.2(g)) using coprecipitation method, PSS/CaCO$_3$/PEI scaffold, broken flower petal like silica were observed (Fig.2(h)). It seems homogeneous adsorption of PEI onto the hard template determined the last morphology of silica.

Elemental composition of these products was confirmed by energy-dispersive spectroscopy (EDS), indicating that the specimen shown in Fig.3 consisted of only silicon and oxygen, because the CaCO$_3$ was covered by PEI and 3D flower-like SiO$_2$.

IV. CONCLUSION

The ability to manufacture inexpensive, abundant, and versatile nanostructured silica has potential benefits in a wide range of applications. Although man-
made processing has the power of rational design, but biological processing of silica is highly reproducible, and three-dimensional. We use a chemical procedure to prepare complex 3D flower-like SiO$_2$. These structures differ from the nearly spherical-like silica network of particles obtained in vitro by only polycationic peptide-mediated biomimetic route. Under chemical influences, overall morphologies shift from a characteristic network of flower-like silica sphere to a sheet-like structure by adjusting physical adsorption of different amount of PEI which covered onto the surface of the CaCO$_3$ microparticles. These findings will helpful for the future development of bioinspired complex 3D silica micro- and nano-devices.

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FIG. 3 (a) Transmission electron microscope and (b) EDS images of 3D flower-like SiO$_2$ precipitated by PSS/CaCO$_3$ microparticles supported PEI by physical adsorption.

FIG. 4 XPS spectrum of 3D flower-like silica precipitated by PSS/CaCO$_3$ microparticles supported PEI by physical adsorption.