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A new method to synthesize super-small nanoparticles in glucose aqueous solution

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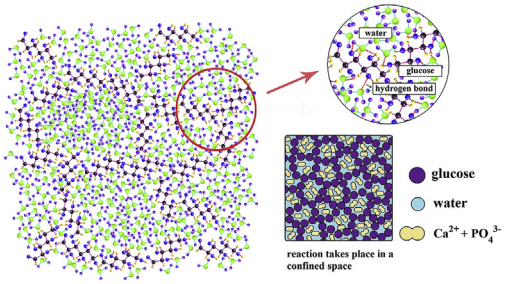
HIGHLIGHTS

- Glucose was introduced to realize green synthesis of nanomaterials.
- "Molecular cage" method was applied to synthesis on nanomaterials.
- Super-small hydroxyapatite nanoparticles with 7 nm average size were synthesized.
- Some other nanoparticles with super-small sizes were synthesized in this way.

GRAPHICAL ABSTRACT



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ABSTRACT

The chemical precipitation reaction of Ca^{2+} and phosphate aqueous solution was used to prepare super-small hydroxyapatite (HA) nanoparticles in the presence of glucose. A hypothetical "molecular cage" was built in glucose alkaline solution to limit the chemical reaction in a tiny space to control the size and morphology of HA nanoparticles. A possible reaction mechanism of HA nanoparticles confined space synthesis was proposed in this work. Compared with the previous research of the preparation of HA nanoparticles, our work in the first time successfully obtained the surper-small HA nanoparticles which had a 7 nm average size with homogeneous globular morphology. The mild and green synthetic method achieve the low-cost and controllable preparation of super-small nanoscale HA particles. In addition, $Zn(OH)_2$, $Ni(OH)_2$, Ag and SiO_2 nanoparticles (<10 nm) were also successfully synthesized by this method, indicating "molecular cage" can be appropriate for various nanoparticle synthesis and could become a universally method for the synthesis of nanoparticles.

1. Introduction

With the establishment of colloidal chemistry in 1861, nanoparticles have received more and more attention. Due to small particle size and high surface area, nano materials can be used in many fields, such as catalytic [1–3], energy storage materials [4,5], luminescent material [6], antibacterial material [7,8], heavy metal adsorption [9,10], nanoparticles drug delivery system [11,12]. Although traditional synthesis methods of nanoparticles could effectively control the particle size and morphology, the environmental pollution problems and price cost, technical restrictions still limited the mass production of nano materials. Moreover, the synthesis of nanoparticles is still lack a universally method in the present day. Using one way to synthesize diverse nanoparticles is still difficult to achieve.

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), which consists mainly of

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calcium and phosphate at a molar ratio of 1.67, is an important inorganic component of bones and teeth of the vertebrates [13]. Because of excellent bioactivity, HA is the most useful material in the inorganic phosphate family. Due to the high osteoconduction and biocompatibility [14], nanoscale HA is one of the most promising bone tissue engineering materials. In addition, the high specific surface area and strong surface adsorption abilities also lead HA materials have been successful used in drug delivery [15–18], proteins adsorption [19–21], removal of heavy mental ions [22–25] etc. However, the bioactivity of HA is always limited by the size. Traditional HA preparation methods, such as microwave-assisted [26–29], hydrothermal reaction [30–32], emulsion method [33–37] and sol-gel synthesis [38–40], usually need high temperature, high pressure or rigorous pH, which is high cost and energy use, and hardly obtained the super-small (<10 nm) HA nanoparticles.

In our work, a facile and green method has been successfully used to synthesize super-small HA nanoparticles. In the first time, the 7 nm HA nanoparticles with globular morphology have been prepared in room temperature and atmospheric pressure without catalyst and organic solvent. Glucose was used to build "molecular cage" in aqueous solution to limit the ionic reaction process in a tiny space in order to control the size of HA. In addition, the same method was also successfully used to synthesize $Zn(OH)_2$, $Ni(OH)_2$, Ag and SiO_2 nanoparticles (<10 nm), indicating the "molecular cage" is a blanket method for different inorganic nanoparticles.

2. Experiment

2.1. Chemicals

For synthesis HA nanoparticles, glucose, $CaCl_2$, $(NH_4)_2HPO_4$ and NaOH were purchased from Beijing Chemical Reagent Company (Beijing, PR China). For synthesis other nanoparticles, $Zn(NO_3)_2$, $Ni(NO_3)_2$, $AgNO_3$, sodium citrate, ethanol and ammonium hydroxide were also purchased from Beijing Chemical Reagent Company (Beijing, PR China). Ethyl orthosilicate was purchased from aladdin Reagent Co. (Shanghai, China). All chemicals were analytical grade and used without further purification. Deionized water was used throughout the experiments.

2.2. Synthesis of HA nanoparticles

A chemical precipitation method was used to prepare the HA nanoparticles. In a typical procedure, 100 mL of $CaCl_2$ (0.01 mol/L) and 100 mL of $(NH_4)_2HPO_4$ (0.006 mol/L) solutions were mixed together and adjusted to weak acidity with HCl solution (0.1 M). A certain amount of glucose (0 g, 5 g, 10 g, 20 g or 40 g) and 1.5 g of NaOH were dissolved with 100 mL of deionized water. Then the mixed solution of $CaCl_2$ and $(NH_4)_2HPO_4$ was added drop by drop into glucose alkaline solution and the HA nanoparticles were formed immediately. The products are noted as 0GHA, 5GHA, 10GHA, 20GHA and 40GHA, respectively.

2.3. Synthesis of $Zn(OH)_2$, $Ni(OH)_2$, Ag and SiO_2 nanoparticles

Similar to the above steps, 20 g of glucose and 1.5 g of NaOH were dissolved with 100 mL of deionized water. Then 100 mL of nitrate ($Zn(NO_3)_2$ or $Ni(NO_3)_2$, 0.01 mol/L) was added drop by drop into glucose alkaline solution to prepare $Zn(OH)_2$ and $Ni(OH)_2$ nanoparticles. In order to obtain Ag nanoparticles, 20 g of glucose was added into 100 mL of sodium citrate aqueous solution (0.01 mol/L). Then 100 mL of $AgNO_3$ (0.01 mol/L) was added drop by drop into the above glucose sodium citrate solution under 94 °C thermostatic waterbath to prepare Ag nanoparticles. Ethyl orthosilicate was used to synthesize nano SiO_2 by following the steps: 20% glucose aqueous solution and ethanol were mixed together by volume ratio of 1:6, then a small amount of ammonium hydroxide was added as catalyst. Ethyl orthosilicate was added drop by drop into the above solution. The SiO_2 nanoparticles were received after 4 h later.

2.4. Sample characterizations

Nicolet 8700 Fourier transform infrared spectrometer (FTIR, Thermo Electron, USA) was used to characterize the functional groups of the samples. Crystallinities of the samples were investigated by X-ray diffraction (XRD, Bruker D8 Advance, Germany). The changes of ultraviolet absorption of HA samples were obtained by Shimadzu UV-3600 ultraviolet and visible spectrophotometer (UV–vis, Shimadzu, Japan). S-4700 field emission scanning electron microscope (SEM, Hitachi, Japan) and J-3010 high resolution transmission electron microscopy (HRTEM, Hitachi J-3010, Japan) were used to observe the morphology and size of the synthesized nanoparticles.

3. Results and discussion

3.1. Synthesis and characterizations of HA nanoparticles

In 2000, Nauta et al. [41] proved that several water molecules could be bonded by hydrogen bonds to form tiny clusters in liquid helium droplets (Fig. 1A). The extraneous water molecules could enter into the established clusters, which involved in numerous rearrangements of hydrogen bonds. Cheng et al. [42] pointed out that the distribution of ethanol and water molecules were not randomly in the ethanol/water system. Most water molecules existed in tiny aggregate form so that there was no isolated water molecule (Fig. 1B). The above thoughts offer a line of thinking to synthesize super-small nanoparticles. If the reaction to form the target compound can be finished in the limited molecular cage area that was formed by oxy-compounds, the super-small nanoparticles will be synthesized.

In this paper, ethanol was used as limited domain reagents to synthesize super-small HA nanoparticles in the first. SEM image (shown in Fig. S1, in supporting information) indicates that most of the products are nanoparticles with diameter about 6–7 nm, however some nano rod products (length is about 100 nm) were also found when the ethanol (concentration is about 50%) was used as reagent to form the molecular cage. The reason on the formation of nano rod products possibly come from the lesser hydrogen bonds between water and ethanol for only one hydroxyl in each ethanol molecule, which leads some cages were not tight junction when the reaction ions diffused into the clusters formed between the water

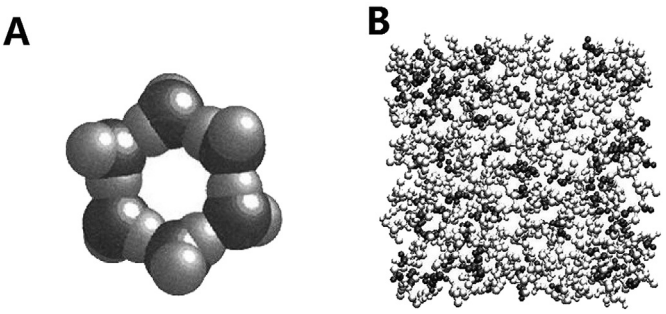

Fig. 1. The structure of water molecules in liquid helium droplets [41] (A) and the model of ethanol/water system [42] (B).