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Joining of ceramic nanocrystals and bio-molecules towards bio-medical applications[†]

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KEY WORDS: (Zirconia) (Nanocrystals) (DNA) (Arrangement) (Coulomb interactions)

1. Introduction

Oxide nanoparticles, as the basic building blocks for nanostructure, make the further miniaturization of structures and devices possible [1]. How to assemble nanoparticles on nanoscale has generated considerable interest in recent years [2-10]. Deoxyribonucleic acid (DNA) plays an important role in assembling nanoparticles on the nanoscale because of its stable physicochemical property, linear and semi-rigid molecular structure [11]. The role of DNA in assembling metal nanoparticles has been reported [12-19], but the role of DNA in assembling oxide nanoparticles has not been reported as yet. The aim of this paper is to study how Zirconia (ZrO₂) nanoparticles assemble with the aid of DNA. The ZrO₂ nanocrystals are important for Bio-medical applications such as bioactive coatings on bone implants.

2. Experimental

The ZrO₂ ceramic nanoparticles, which were synthesized by a hydrothermal reaction, were in a colloidal solution. Aqueous solution of ZrOCl₂·8H₂O was neutralized by K₂CO₃ solution. Then the solution was hydrothermally treated at 150 °C for 1 hour in the Teflon lined stainless steel vessel. The detailed hydrothermal synthesis is described in a previously reported paper [20]. After the reaction, undesirable K⁺ and Cl⁻ were removed by an ultrafiltration and 5 M of HCl was added to the product for dispersion of the nanoparticles in water. The particle size distribution of the obtained ZrO₂ nanoparticle colloidal solution was measured by the dynamic light scattering (DLS) method, whereas transmission electron microscopy (TEM) was used to observe the ZrO₂ nanoparticles and their assembled nanostructures.

The ZrO₂ nanoparticles were assembled by λ-DNA as follows. λ-DNA, which was 48502 base-pairs (bp) long, was purchased from TaKaRa Biotechnology (Dalian) Co., Ltd. The original concentration was 0.3 μg/μL, and the equivalent base pair concentration was 450 μmol/L. The buffer was 10 mmol Tris-HCl-1mmol EDTA, pH=8.0, A260/A280=1.8-2.0. The λ-DNA solution (450 μmol/L bp concentration) was diluted to a 1 μmol/L bp concentration by adding a 0.0025 mol/L HCl solution to maintain the pH of λ-DNA near 3.0. A 900 μL ZrO₂ solution (concentration

50 μmol/L) with a HCl solution was prepared to maintain a constant pH value of 3.0. Then 900 μL ZrO₂ solution (concentration 50 μmol/L) was added to the 900 μL solution of 0.5 μmol/L bp λ-DNA to make a 1800 μL compound solution of 0.25 μmol/L bp λ-DNA.

3. Results and Discussion

Figure 1(a) and (b) shows a photograph and particle size distribution of the obtained transparent ZrO₂ colloidal solution. The ZrO₂ nanoparticle surface contains numerous positive charges at a pH value of 3 because the isoelectric point of ZrO₂ ceramic is around 5-6, and due to the electric repulsion force in water, each ZrO₂ nanoparticle is assumed to be dispersed separately. The average diameter of the ZrO₂ nanoparticle is about 5 nm, and has a very narrow particle distribution (Fig. 1(b)). Fig. 1(c) shows a TEM picture of the ZrO₂ nanoparticles. Although the primary ZrO₂ nanoparticles on the TEM grid aggregate after drying the colloidal solution, the primary nanoparticles are about 3 nm, which is consistent with that measured by DLS. Hence, it is concluded that the ZrO₂ nanoparticles can be dispersed perfectly in water under this low pH condition.

Figure 2 shows the TEM picture of the mixed solution of ZrO₂ nanoparticles and λ-DNA, and indicates that a network is formed as the ZrO₂ nanoparticles are assembled on the DNA strands. In contrast, without DNA, the ZrO₂ nanoparticles are aggregated randomly on the TEM grid (Fig. 1(c)). However, the ZrO₂ nanoparticles are arranged in the presence of λ-DNA. This arrangement is likely due to the Coulomb interactions between the negatively charged DNA and positively charged ZrO₂ nanoparticles.

4. Conclusion

The study suggests the DNA plays an important role in the assembling of ZrO₂ nanoparticles, it provides a template for the arraying of nanoparticles. We believe that this assembly of metal oxide nanoparticles by DNA will yield novel hybrid nano-biomaterials with synergetic properties and functions.

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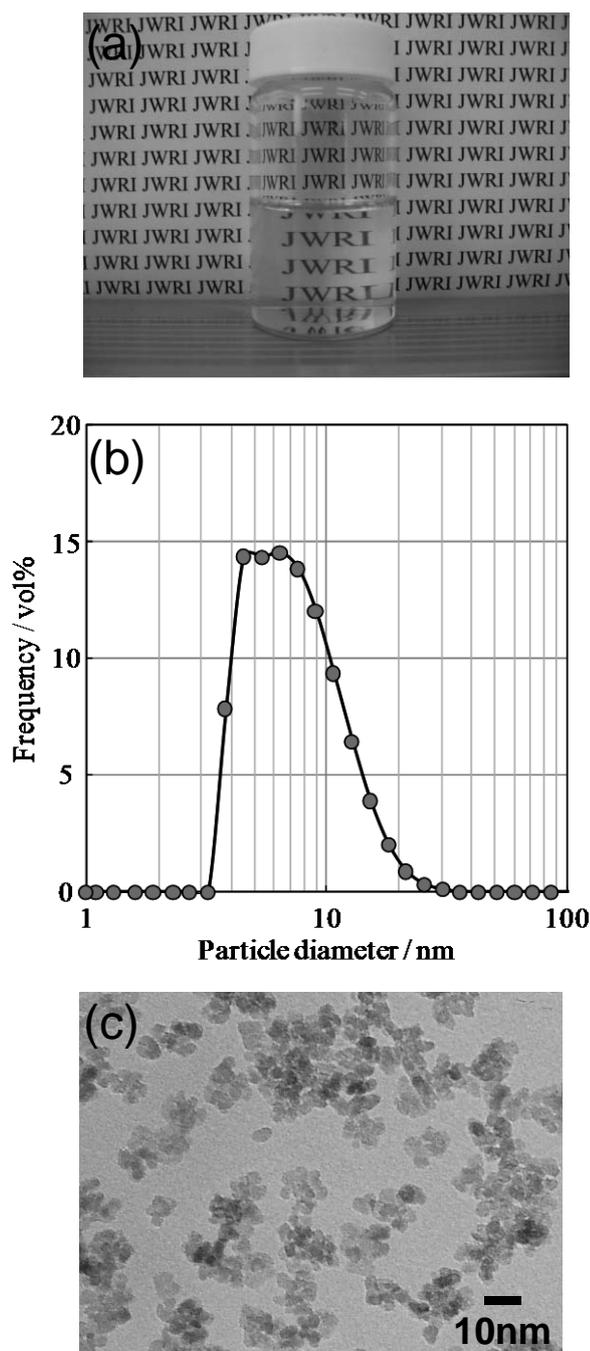


Fig. 1 (a) Optical image (b) Diameter distribution and (c) TEM image of zirconia nanoparticles.

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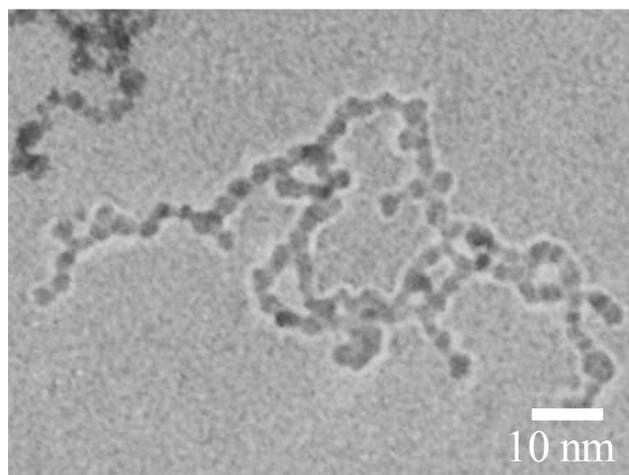


Fig. 2 TEM image of a zirconia nanoparticle assembly by λ -DNA.

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