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

OHARA Satoshi *, SATO Kazuyoshi **, TAN Zhenquan *, UMETSU Mitsuo ***

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 (ZrO_2) nanoparticles assemble with the aid of DNA. The ZrO_2 nanocrystals are important for Bio-medical applications such as bioactive coatings on bone implants.

2. Experimental

The ZrO_2 ceramic nanoparticles, which were synthesized by a hydrothermal reaction, were in a colloidal solution. Aqueous solution of $ZrOCl_2 \cdot 8H_2O$ was neutralized by K_2CO_3 solution. Then the solution was hydrothermally treated at 150 ºC 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 ZrO_2 nanoparticle colloidal solution was measured by the dynamic light scattering (DLS) method, whereas transmission electron microscopy (TEM) was used to observe the ZrO_2 nanoparticles and their assembled nanostructures.

The ZrO_2 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 ZrO_2 solution (concentration 50 μmol/L) with a HCl solution was prepared to maintain a constant pH value of 3.0. Then 900 μL ZrO_2 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 ZrO_2 colloidal solution. The ZrO_2 nanoparticle surface contains numerous positive charges at a pH value of 3 because the isoelectric point of ZrO_2 ceramic is around 5-6, and due to the electric repulsion force in water, each ZrO_2 nanoparticle is assumed to be dispersed separately. The average diameter of the ZrO_2 nanoparticle is about 5 nm, and has a very narrow particle distribution (Fig. 1(b)). Fig. 1(c) shows a TEM picture of the ZrO_2 nanoparticles. Although the primary ZrO_2 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 ZrO_2 nanoparticles can be dispersed perfectly in water under this low pH condition.

Figure 2 shows the TEM picture of the mixed solution of ZrO_2 nanoparticles and λ-DNA, and indicates that a network is formed as the ZrO_2 nanoparticles are assembled on the DNA strands. In contrast, without DNA, the ZrO_2 nanoparticles are aggregated randomly on the TEM grid (Fig. 1(c)). However, the ZrO_2 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 ZrO_2 nanoparticles.

4. Conclusion

The study suggests the DNA plays an important role in the assembling of ZrO_2 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.

† Received on 30 September 2010
* JWRI, Osaka University, Ibaraki, Japan
** Graduate School, Gunma University, Kiryu, Japan
*** Graduate School, Tohoku University, Sendai, Japan

Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

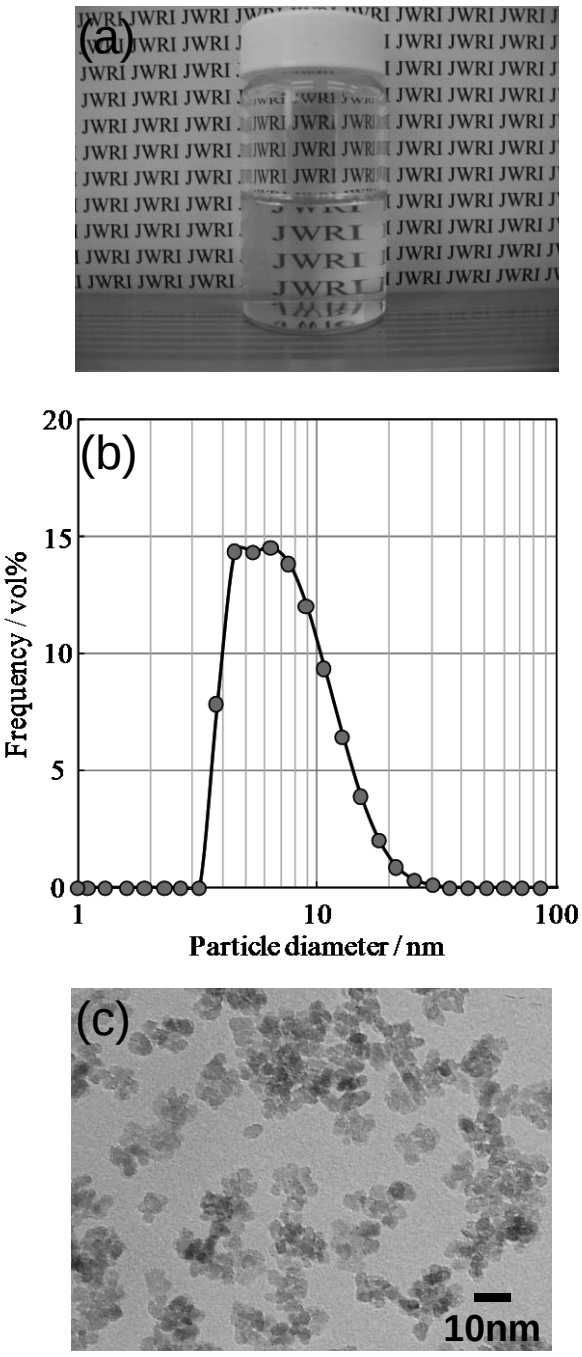

Fig. 1 (a) Optical image (b) Diameter distribution and (c) TEM image of zirconia nanoparticles.

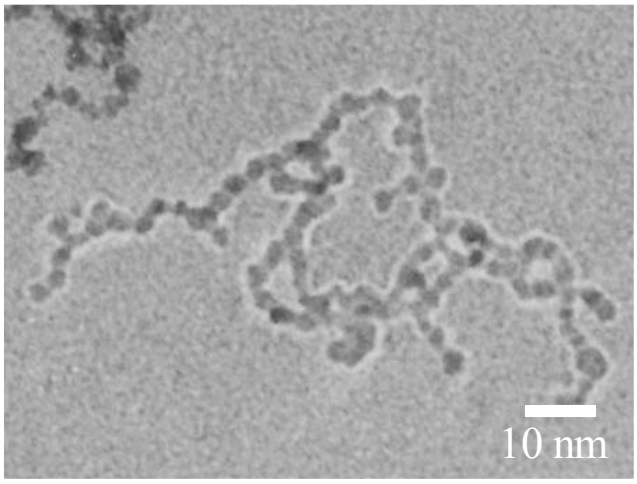

Fig. 2 TEM image of a zirconia nanoparticle assembly by λ-DNA.

References

[1] D. Velegol, K.A. Fichthorn and T. Mayer: NSF Nanoscale Science and Enigeering Grantees Conference (2004) Dec 13-15, grant CCR-0303976.

[2] A. Bae, M. Numata, T. Hasegawa, C. Li, K. Kaneko, K. Sakurai and S. Shinkai: Angew. Chem. Int. Ed., 44 (2005), pp.2030-2033.

[3]H. Nakao, H. Shiigi, Y. Yamamoto, S. Tokonami, T. Nagaoka , S. Sugiyama and T. Ohtani: Nano lett., 3 (2003), pp.1391-1394.

[4] C.A. Mirkin, R.L. Letsinger, R.C. Mucie and J.J. Storhoff: Nature, 382 (1996), pp.607-609.

[5] K. Sato, K. Hosokawa and M. Maeda: J. Am. Chem. Soc., 125 (2003), pp.8102-8103.

[6] Q. Gu, C. Cheng and D.T. Haynie: Nanotechnology, 16 (2005), pp.1358-1363.

[7] E. Braun, Y. Eichen, U. Sivan and G. Ben-Yoseph: Nature, 392 (1998), pp.775-778.

[8] A.A. Zinchenko, K. Yoshikawa and D. Baigl: Adv. Mater., 17 (2005), pp.2820-2823.

[9] A. Kumar, M. Pattarkine, M. Bhadbhade, A.B. Mandale, K.N. Ganesh, S.S. Datar, C.V. Dharmadhikari and M. Sastry: Adv. Mater., 13 (2001), pp.341-344.

[10] S. Xiao, F. Liu, A.E. Rosen, J.F. Hainfeld and N.C. Seeman: J. Nanoparticle Res., 4 (2002), pp.313-317.

[11] Lehninger Principles of biochemistry, ed. D.L. Nelson, M.M. Cox and W.H. Freeman, New York, USA, (2005).

[12] J. Richter, M. Merig and W. Pompe: Appl. Phys. Lett., 78 (2001), pp.536-538.

[13] J. Richter, R. Seidel, R. Kirsch, M. Mertig, W. Pompe, J. Plaschke and H.K. Schackert: Adv. Mater., 12 (2000), pp.507-510.

[14] W.E. Ford, O. Harnack, A. Yasuda and J.M. Wessels: Adv. Mater., 12 (2001), pp.1793-1797.

[15] M. Mertig, L.C. Ciacchi, R. Seidel and W. Pompe: Nano Lett., 2 (2002), pp.841-844.

[16] K. Keren, M. Krueger, R. Gilad, G. Ben-Yoseph, U. Sivan and E. Braun: Science, 297 (2002), pp.72-75.

[17] K. Keren, R.S. Berman and E. Braun: Nano Lett., 4 (2004), pp.323-326.

[18] C.F. Monson and A.T. Woolley: Nano Lett., 3 (2003), pp.359-363.

[19] H.A. Becerril, R.M. Stoltenberg, C.F. Monson and A.T. Woolley: J. Mater. Chem., 14 (2004), pp.611-616.

[20] K. Sato, H. Abe and S. Ohara: J. Am. Chem. Soc., 132 (2010), pp.2538-2539.