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# Arrangement of Metal Oxide Nanoparticles by DNA<sup>†</sup>

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## Abstract

*Assembly of metal oxide nanoparticles with the aid of DNA was investigated. One-dimensional arrangement of ZrO<sub>2</sub> nanoparticles using DNA as a template was shown by TEM observation. It is considered that the DNA assembly of ZrO<sub>2</sub> nanoparticles is due to the Coulomb interactions between the negatively charged DNA and positively charged ZrO<sub>2</sub> nanoparticles.*

**KEY WORDS:** (Zirconia), (Nanoparticles), (DNA), (Assembly), (Coulomb interactions)

## 1. Introduction

When used as building blocks for nanostructures, nanoparticles make further miniaturization of structures and devices possible<sup>1)</sup>. Recently, assembling nanoparticles on the nanoscale has received considerable attention<sup>2-11)</sup>, and one tool for creating these assemblies is biomaterials. Deoxyribonucleic acid (DNA) is an appropriate biopolymer template for constructing defined inorganic materials, and highly selective base-pairing interactions between complementary single-strand DNA chains have been used in nanoassemblies. Additionally, native double-helical DNA can directly interact with metal ions and their complexes. Although the role of DNA in assembling metal nanoparticles has been reported<sup>12-20)</sup>, assembling metal oxide nanoparticles remains a challenge.

Metal oxide ceramic nanoparticles have been extensively investigated due to their successful applications and potential in various fields such as electronics, catalysis, pharmaceuticals, energy storage, and medical applications, and using DNA to assemble metal oxide nanoparticles may allow novel hybrid nano-biomaterials with synergetic properties and functions to be realized. Zirconia (ZrO<sub>2</sub>) is an attractive ceramic material due to its excellent mechanical, tribological, thermal properties, and good oxygen ionic conductivity. Its nanoparticles have a broad range of applications, including thermal barrier coatings, solid-state electrolytes, solid oxide fuel cells, oxygen sensors, and heterogeneous catalysts etc<sup>21-27)</sup>. The aim of this study is to investigate the assembly of ZrO<sub>2</sub> ceramic nanoparticles with the aid of DNA. Herein, we show the first example of a one-dimensional arrangement of metal

oxide nanoparticles using DNA as a template.

## 2. Experimental

The ZrO<sub>2</sub> ceramic nanoparticles, which were synthesized by a hydrothermal reaction, were in colloidal solution. An aqueous solution of ZrOCl<sub>2</sub>·8H<sub>2</sub>O was neutralized by K<sub>2</sub>CO<sub>3</sub> solution. Then the solution was hydrothermally treated at 150 °C for 1 hour in the Teflon lined stainless steel vessel. After the reaction, undesirable K<sup>+</sup> and Cl<sup>-</sup> were removed by an ultrafiltration and 5 M HCl was added to the product for the dispersion of the nanoparticles in water.

Two types of DNA solutions were used in this study: λ-DNA and a short DNA fragment. The ZrO<sub>2</sub> 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<sub>2</sub> solution (concentration 50 μmol/L) with a HCl solution was prepared to maintain a constant pH value of 3.0. Then 900 μL ZrO<sub>2</sub> 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.

The short DNA fragment contains nine, discretely sized bands of 50, 100, 200, 300, 400, 500/525, 700, and

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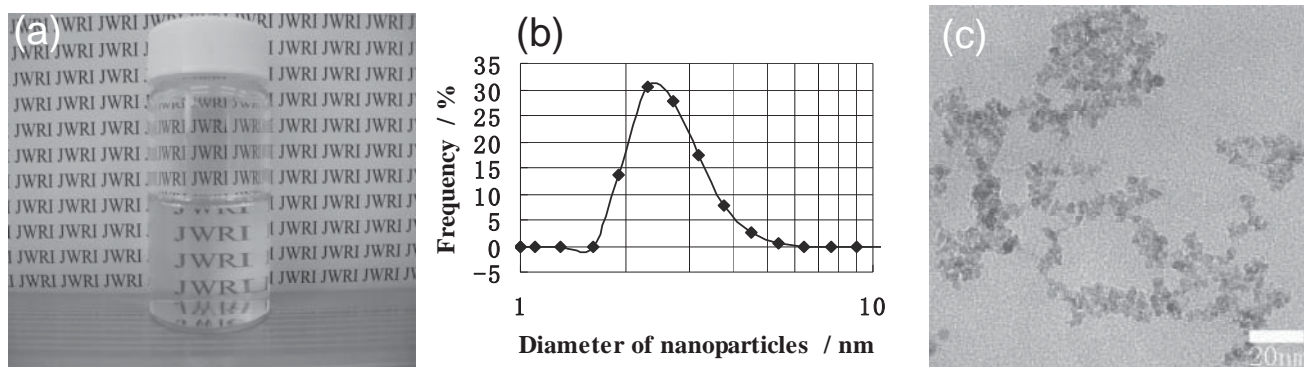
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**Fig. 1** (a) Photograph and (b) particle size distribution of the synthesized transparent zirconia nanoparticles in water. (c) TEM image of the synthesized zirconia nanoparticles.

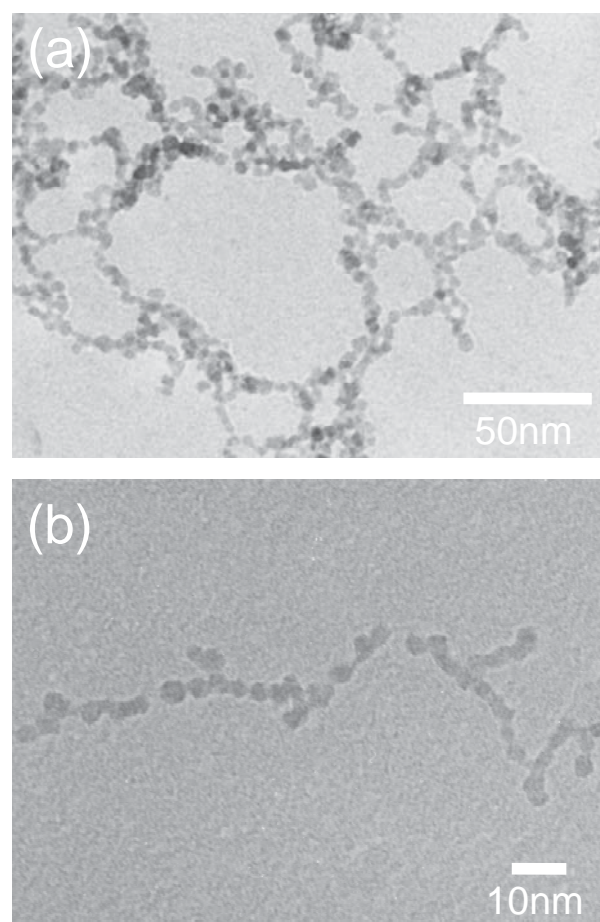
1000 bp where each band is linear and double-stranded. Each 5  $\mu\text{L}$  provided 50 ng of DNA per band, indicating each band had a short DNA fragment concentration of 10 ng/ $\mu\text{L}$ . This translated into a basepair concentration for each band of 15.38  $\mu\text{mol/L}$ ; thus, the total bp concentration for the nine bands should be 138.5  $\mu\text{mol/L}$ . To realize a pH of 3.0, the 100  $\mu\text{L}$  short DNA fragment of 138.5  $\mu\text{mol/L}$  was diluted ten-fold to a 1000  $\mu\text{L}$  solution of 13.85  $\mu\text{mol/L}$  with HCl solution (0.0025 mol/L). In the same manner, the zirconia solution (11.3 mmol/L) was diluted two thousand times with a HCl solution (0.0025 mol/L) to make a 1000  $\mu\text{L}$  solution with a zirconia concentration of 5.65  $\mu\text{mol/L}$ . Then 1000  $\mu\text{L}$  zirconia solution (5.65  $\mu\text{mol/L}$ ) was added to the 1000  $\mu\text{L}$  short DNA fragment solution (13.85  $\mu\text{mol/L}$ ) to yield a mixed solution with a pH of 2.8. The particle size distribution of the obtained  $\text{ZrO}_2$  nanoparticle colloidal solution was measured by the dynamic light scattering (DLS) method, whereas transmission electron microscopy (TEM) was used to observe the  $\text{ZrO}_2$  nanoparticles and their assembled nanostructures.

### 3. Results

**Figure 1(a)** and **(b)** shows a photograph and particle size distribution of the obtained transparent  $\text{ZrO}_2$  colloidal solution. The  $\text{ZrO}_2$  nanoparticle surface contains numerous positive charges at a pH value of 3 because the isoelectric point of  $\text{ZrO}_2$  ceramic is around 5-6, and due to the electric repulsion force in water, each  $\text{ZrO}_2$  nanoparticle is assumed to be dispersed separately. The average diameter of the  $\text{ZrO}_2$  nanoparticle is about 3 nm, and has a very narrow particle distribution (**Fig. 1(b)**). **Figure 1(c)** shows a TEM picture of the  $\text{ZrO}_2$  nanoparticles. Although the primary  $\text{ZrO}_2$  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  $\text{ZrO}_2$  nanoparticles can be dispersed perfectly in water under this low pH condition.

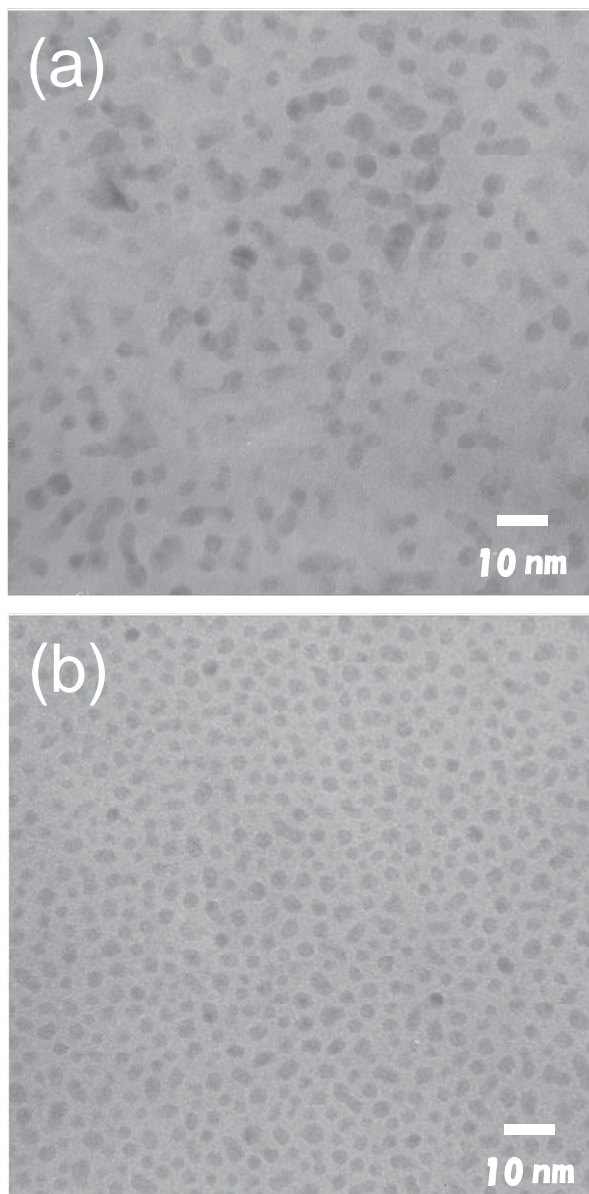
**Figure 2** shows the TEM picture of the mixed solution of  $\text{ZrO}_2$  nanoparticles and  $\lambda$ -DNA, and indicates that a network is formed as the  $\text{ZrO}_2$  nanoparticles are assembled on the DNA strands. In contrast, without DNA,

the  $\text{ZrO}_2$  nanoparticles are aggregated randomly on the TEM grid (**Fig. 1(c)**). However, the  $\text{ZrO}_2$  nanoparticles are arranged in the presence of  $\lambda$ -DNA. The  $\text{ZrO}_2$  nanoparticles are completely aligned along the DNA template, as seen in **Fig. 2(b)**, which reflects the linear morphology of the DNA. This TEM observation suggests that DNA plays an active role in the assembly process of  $\text{ZrO}_2$  nanoparticles. The 1D arrangement is likely due to the Coulomb interactions between the negatively charged DNA and positively charged  $\text{ZrO}_2$  nanoparticles.



**Fig. 2** TEM images of a zirconia nanoparticle assembly by  $\lambda$ -DNA. (a) Low and (b) high magnification images.





**Fig. 3** TEM images of the zirconia nanoparticle assembly by a short DNA fragment. Concentration of the short DNA fragment is (a) low (13.85  $\mu\text{mol/L}$ ) and (b) high (138.5  $\mu\text{mol/L}$ ). Concentration of the zirconia nanoparticles is 5.65  $\mu\text{mol/L}$ .

The  $\lambda$ -DNA molecule is very long compared to the size of  $\text{ZrO}_2$  ceramic nanoparticles. Thus, to confirm that the  $\text{ZrO}_2$  nanoparticles are arranged on DNA, a short DNA fragment with a short length was used. 50, 100, 200, 300, 400, 500/525, 700, and 1000 bp of the short DNA fragment correspond to 17, 34, 68, 102, 136, 170/178.5, 238, and 340 nm, respectively, because the length of one bp is 0.34 nm. **Figure 3(a)** shows the TEM picture of  $\text{ZrO}_2$  nanoparticles assembled on the short DNA fragment, and illustrates that several  $\text{ZrO}_2$  nanoparticles form an array on the short DNA. The number of nanoparticles on the short DNA varies with the length of DNA fragment band. Furthermore, when the concentration of the short DNA fragment increases, each  $\text{ZrO}_2$  nanoparticle is

individually observed on the TEM grid (Fig. 3(b)). Therefore, DNA may play an important role in controlling the dispersion of ceramic nanoparticles in water.

#### 4. Conclusions

In conclusion, the role of DNA in assembling metal oxide nanoparticles was investigated.  $\text{ZrO}_2$  nanoparticles are assembled on DNA by Coulomb interactions between the negatively charged DNA and positively charged  $\text{ZrO}_2$  nanoparticles. We believe that this assembly of metal oxide nanoparticles by DNA will yield novel hybrid nano-biomaterials with synergetic properties and functions.

#### References

- 1) G. Schmid (Ed.): Nanoparticles (2004) Wiley-VCH Weinheim
- 2) A.H. Bae, M. Numata, T. Hasegawa, C. Li, K. Kaneko, K. Sakurai and S. Shinkai: *Angew. Chem. Int. Ed.* 44 (2005) 2030-2033
- 3) A.H. Fu, C.M. Micheel, J. Cha, H. Chang, H. Yang and A.P. Allivisatos: *J. Am. Chem. Soc.* 126 (2004) 10832-10833
- 4) H. Nakao, H. Shiigi, Y. Yamamoto, S. Tokonami, T. Nagaoka, S. Sugiyama and T. Ohtani: *Nano lett.* 3 (2003) 1391-1394
- 5) C.A. Mirkin, R.L. Letsinger, R.C. Mucie and J.J. Storhoff: *Nature* 382 (1996) 607-609
- 6) K. Sato, K. Hosokawa and M. Maeda: *J. Am. Chem. Soc.* 125 (2003) 8102-8103
- 7) Q. Gu, C. Cheng and D.T. Haynie: *Nanotechnology* 16 (2005) 1358-1363
- 8) E. Braun, Y. Eichen, U. Sivan and G. Ben-Yoseph: *Nature* 392 (1998) 775-778
- 9) A.A. Zinchenko, K. Yoshikawa and D. Baigl: *Adv. Mater.* 17 (2005) 2820-2823
- 10) 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) 341-344
- 11) S.J. Xiao, F.R. Liu, A.E. Rosen, J.F. Hainfeld, N.C. Seeman, K. Musier-Forsyth and R.A. Kiehl: *J. Nanoparticle Research.* 4 (2002) 313-317
- 12) J. Richter, M. Merig, W. Pompe, I. Monch and H.K. Schackert: *Appl. Phys. Lett.* 78 (2001) 536-538
- 13) J. Richter, R. Seidel, R. Kirsch, M. Mertig, W. Pompe, J. Plaschke and H.K. Schackert: *Adv. Mater.* 12 (2000) 507-510
- 14) W.E. Ford, O. Harnack, A. Yasuda and J.M. Wessels: *Adv. Mater.* 12 (2001) 1793-1797
- 15) M. Mertig, L.C. Ciacchi, R. Seidel, W. Pompe and A. De Vita: *Nano Lett.* 2 (2002) 841-844
- 16) K. Keren, M. Krueger, R. Gilad, G. Ben-Yoseph, U. Sivan and E. Braun: *Science* 297 (2002) 72-75
- 17) K. Keren, R.S. Berman and E. Braun: *Nano Lett.* 4 (2004) 323-326
- 18) C.F. Monson and A.T. Woolley: *Nano Lett.* 3 (2003) 359-363
- 19) H.A. Becerril, R.M. Stoltenberg, C.F. Monson and A.T. Woolley: *J. Mater. Chem.* 14 (2004) 611-616
- 20) Y. Hatakeyama, M. Umetsu, S. Ohara, F. Kawadai, S. Takami, T. Naka and T. Adschiri: *Adv. Mater.* 20 (2008) 1122-1128
- 21) Z. Ye, M. Tan, G. Wang and J. Yuan: *J. Fluoresc.* 15 (2005) 499-505

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- 22) A.U. Limaye and J.J. Helble: J. Am. Ceram. Soc. 85 (2002) 1127-1132
- 23) T. Schmidt, M. Menning and H. Schmidt: J. Am. Ceram. Soc. 90 (2007) 1401-1405
- 24) M. Trunec and K. Maca: J. Am. Ceram. Soc. 90 (2007) 2735-2740
- 25) S.S. Shankar, H. Joshi, R. Pasricha, N.R. Pavaskar, A.B. Mandale and M. Sastry: J. Colloid. Interface Sci. 269 (2004) 126-130
- 26) K. Matsui and M. Ohgai: J. Am. Ceram. Soc. 84 (2001) 2303-2312
- 27) R.H.J. Hannink, P.M. Kelly and B.C. Muddle: J. Am. Ceram. Soc. 83 (2000) 461-487