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Synthesis of TiO₂ nanoparticles in the PAMAM hydrogen network template

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Abstract: Intramolecular nanocavities in polyamidoamine (PAMAM) are usually used as a good template to synthesize nanoparticles. In this paper, TiO₂ nanoparticles were prepared successfully by the interspaces of the hydrogen network between PAMAM. The possible mechanism was that PAMAM could form the steady microspheres with many interspaces in ammonia aqueous solution at pH=10. The interspaces of the hydrogen network could act as the template for preparing TiO₂ nanoparticles. The results were proved by transmission electron microscopy (TEM) and X-ray diffraction (XRD).

Keywords: dendrimer; hydrogen bonds; microsphere; nanocomposites; template synthesis.

1 Introduction

Polyamidoamine (PAMAM) is a typical dendritic polymer (1–3), which has extensive applications in the template synthesis of metal and intermetallic compound nanoparticles due to its distinctive characteristics such as nanosize cavities with uniform size, functional groups with the strong polarity in the intramolecular and perfect fractal dendritic structure. Metal particles can enter into the intramolecular cavities of PAMAM molecules and be held and trapped by the effect of steric hindrance and/or coordination, then uniform nanocomposites are formed (4–7). If the PAMAM matrix evenly disperses in the solution, the size and the morphology of the nanocomposites would be similar to that

of PAMAM matrix. The terminal groups are different for the different generations of PAMAMs, which results in the different behaviors of PAMAMs in the solution. The PAMAMs of the half generations have a methoxycarbonyl terminal groups with weak polarity, which is difficult to attract the other molecule to form a large network structure. In solution, the PAMAMs of the half generations tend to separate (8), the size of the nanoparticles in the PAMAM template are easily controlled. Therefore, PAMAM of the half generations or PAMAM with the weak polar terminal groups are often chosen as templates (9–13). While PAMAMs of the whole generations with a strong polar amido group can easily form the large intermolecular network structure by hydrogen bond in solution, this caused the size of the nanoparticles produced to be inhomogeneous. Meanwhile, the hydrogen network is unstable and easily affected by external factors such as solvents, temperature, pH value (14) and so on. Hence, there are almost no reports about the nanoparticles prepared by the intermolecular hydrogen network between PAMAM.

However, there are some advantages for producing nanoparticles through the intermolecular hydrogen network structure of the PAMAM. The size of intramolecular cavities in PAMAM is on the angstrom scale, which is much smaller than the PAMAM molecule. The particles in the PAMAM cannot stay steadily alone, but only in the form of compounds. While the interspaces of the intermolecular network structure of PAMAM molecules are nanoscale, it is larger than that of PAMAM molecules, the metal particles produced in the interspaces can remain as nanoparticles rather than nanocomposites.

In this work, the hydrogen networks between G5.0-NH₂ PAMAM with the whole generations were prepared in an aqueous solution of ammonia, and then TiO₂ nanoparticles were synthesized using the interspaces of the hydrogen network between PAMAM as a template.

2 Experimental

2.1 Materials

5.0G PAMAM with amido terminal groups is synthesized by divergent method with propane diamine as core.

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Ammonia water (Beilian fine chemicals development co., LTD, Tianjin, China) is analytically pure, Barium Chloride (Chinese medicine group, Shanghai chemical reagent co., LTD, China) is analytically pure, Titanic sulfate (Chinese medicine group, Shanghai chemical reagent co., LTD, China) is analytically pure, the solvent is deionized water.

2.2 Synthesis and characterization of TiO₂/PAMAM nanocomposites

Twenty milliliters 0.02 mol/l titanic sulfate solution and 5 ml 20 g/l G5.0-NH₂ PAMAM solution were pipetted to a 50 ml volumetric flask, and the pH adjusted to 10 with ammonia water. Then, the mixed solution was diluted with deionized water to 50 ml. A hydrolysis reaction was performed at 80°C for 4 h. The crude product was filtered and washed with distilled water until SO₄²⁻ could not be measured (with 0.1 mol/l BaCl₂). Finally, TiO₂/PAMAM nanocomposites were obtained in vacuum oven at 60°C for about 24 h.

The morphology of PAMAM and nanoparticles were characterized with a JEM-2100 transmission electron microscope (JEOL, Japan). Samples were prepared by ultrasonic dispersing in solvents about 10 min, then evaporating the dilute suspensions onto copper grids.

The XRD spectra were recorded on a D8-Advance X-ray diffractometer (Bruker, Germany) (40 kV, 40 mA)

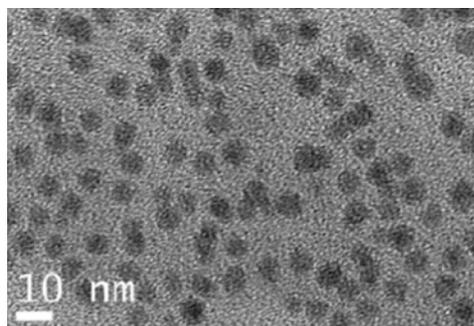


Figure 1: TEM image of G5.0-NH₂ PAMAM in the methanol solvents.

with Cu-Kα radiation ($\lambda=0.1542$ nm). The samples were burned in the muffle furnace at 650°C for 10 h.

3 Results and discussion

The transmission electron microscopy (TEM) image of G5.0-NH₂ PAMAM is shown in Figure 1. The molecular structure of PAMAM is spherical, about 6 nm in diameter (15). Meanwhile, there are many nanocavities in the molecular structure, which corresponded to the theoretical structure of the PAMAM with high generations.

The TEM image of G5.0-NH₂ PAMAM in the aqueous solutions is shown in Figure 2A. It can be seen that the PAMAM molecules aggregate into a microsize sphere and form a lot of interspaces. The high resolution TEM

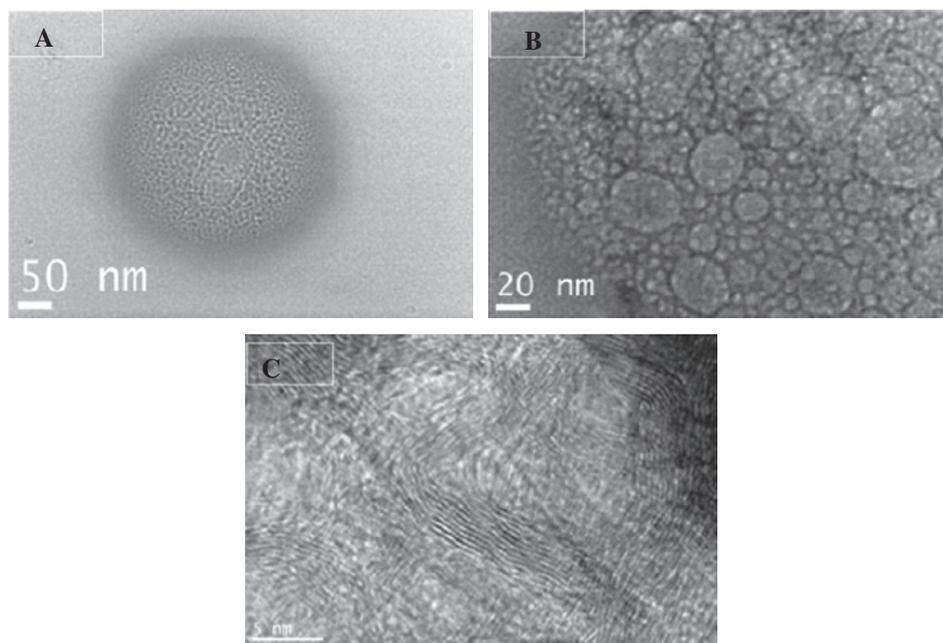


Figure 2: TEM and HRTEM images of the PAMAM microspheres [magnification: (A) 4×10^4 ; (B) 1×10^5 ; (C) 8×10^5].

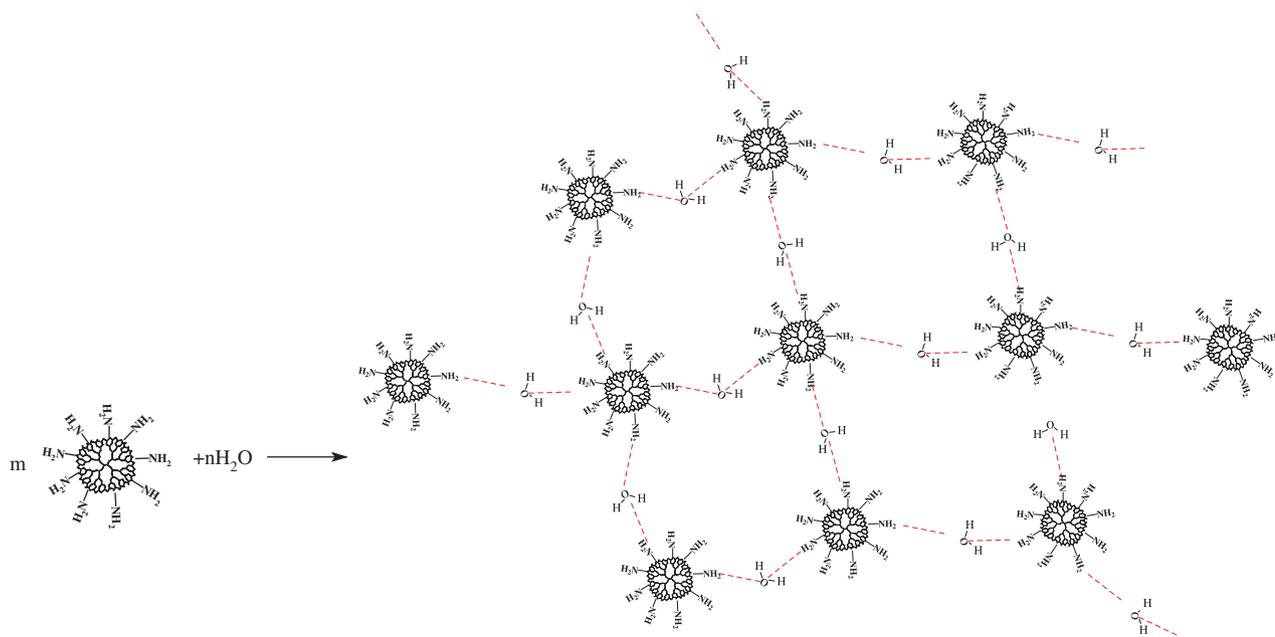


Figure 3: The possible formative route of PAMAM hydrogen network microsphere.

images (Figure 2B and C) show that the width of the black backbones is about 5–6 nm, and nanocavities also appear in the backbones in Figure 2C. It indicates that the backbones shall be the aggregations of PAMAM molecules, and the nanocavities are the intramolecular cavities. In Figure 2B it can be also seen that most of the interspaces have uniform diameter of about 8–10 nm, while some interspaces larger than G5.0-NH₂ PAMAM molecules are also seen. So the larger interspaces are not the same as the nanocavities of the intramolecular PAMAM molecules, and it should be formed by the bridging PAMAM molecules due to the intermolecular interaction.

In a word, the driving force to form the microsphere in the aqueous solutions may be the interactions of the hydrogen bonds. The possible mechanism is illustrated

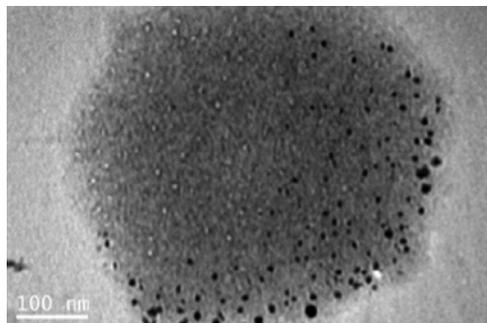


Figure 4: TEM photograph of TiO_2 nanoparticles synthesized in the PAMAM microsphere.

as Figure 3. The hydrogen bonds can be formed between the amido terminal groups of the G5.0-NH₂ PAMAM and the oxygen atoms of the water molecules. The 3-D supra-molecular network microsphere could be formed through hydrogen bonding interactions between the G5.0-NH₂ PAMAM microspheres with many amido terminal groups. The energy of the hydrogen bond is so weak that it can be easily broken by the subtle changes of external factors such as temperature, the oscillation of the solution and the irradiation of the electron beam in the TEM test. Thus some bigger cavities appeared in the hydrogen network between PAMAM.

Figure 4 shows the TiO_2 nanoparticles synthesized in the PAMAM microsphere. The light spots on the surface are the interspaces formed by the PAMAM molecules, and the black ones are the TiO_2 nanoparticles. The size of the most TiO_2 nanoparticles are 10 nm in diameter, which accords with that of the interspaces of the microsphere; some are larger because they are synthesized in the larger interspaces. It indicates that the interspaces can act as templates for preparing the TiO_2 nanoparticles.

Figure 5 shows the X-ray diffraction profiles of TiO_2 nanoparticles synthesized by the interspaces of the hydrogen network between the PAMAM. The narrow and strong diffraction peaks of TiO_2 nanocomposites appeared at 2θ of ca. 25.44°, 37.90°, 44.16°, 48.18°, 64.58° and 77.16°, respectively (16), which correspond to the anatase crystal structure of TiO_2 .

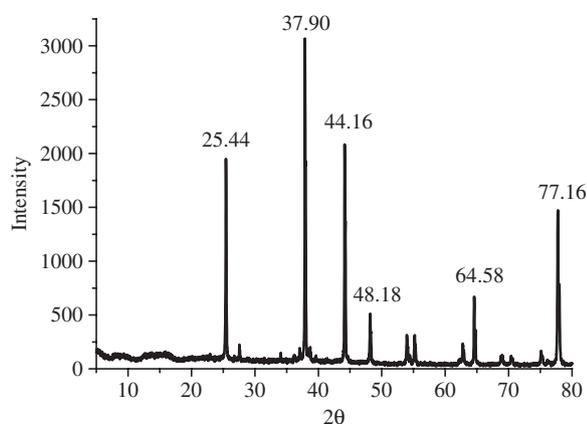


Figure 5: XRD patterns of TiO₂ nanoparticles.

4 Conclusion

In this work, the behavior of G5.0-NH₂ PAMAM in the aqueous solutions of ammonia was studied. It was found that PAMAM molecules could form the microsphere with the interspaces about 10 nm in diameter through the intermolecular hydrogen interaction, which can be used as the good templates to synthesize TiO₂ nanoparticles.

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References

- Tomalia DJ. A new class of polymers starburst-dendritic macromolecules. *Polymer J.* 1985;17:117–32.
- Tomalia DA, Baker H, Dewald J, Hall M, Kallos G, Martin S, Roeck J, Ryder J, Smith P. Dendritic macromolecules: synthesis of starburst dendrimers. *Macromolecules.* 1986;19:2466–8.
- Newkome GR, Shreiner CD. Poly(amidoamine), polypropyleneimine, and related dendrimers and dendrons possessing different 1→2 branching motifs: an overview of the divergent procedures. *Polymer.* 2008;49:1–173.
- Balogh L, de Leuze-Jallouli A, Dvornic P, Kunugi Y, Blumstein A, Tomalia DA. Architectural copolymers of PAMAM dendrimers and ionic polyacetylenes. *Macromolecules.* 1999;32:1036–42.
- Keki S, Török J, Deák G, Daróczy L, Zsuga M. Silver nanoparticles by PAMAM-assisted photochemical reduction of Ag⁺. *J Colloid Interface Sci.* 2000;229:550–3.
- Guo-ping L, Yun-jun LO, Hou-cai X, min TH-i. Dendrimer templates for the formation of silver nanoparticles. *J Beijing Inst Tech.* 2006;352–6.
- Krot K, Denamor A, Aguilarcornejo A, Nolan K. Speciation, stability constants and structures of complexes of copper(II), nickel(II), silver(I) and mercury(II) with PAMAM dendrimer and related tetraamide ligands. *Inorg Chim Acta.* 2005;358:3497–505.
- Strydom SJ, Rose WE, Otto DP, Liebenberg W, de Villiers MM. Poly(amidoamine) dendrimer-mediated synthesis and stabilization of silver sulfonamide nanoparticles with increased antibacterial activity. *Nanomedicine.* 2013;9:85–93.
- Nepomnyashchii AB, Alpuche-Aviles MA, Pan S, Zhan D, Fan F-RF, Bard AJ. Cyclic voltammetry studies of Cd²⁺ and Zn²⁺ complexation with hydroxyl-terminated polyamidoamine generation 2 dendrimer at a mercury microelectrode. *J Electroanal Chem.* 2008;621:286–96.
- Bustos EB, Jiménez MGG, Díaz-Sánchez BR, Juaristi E, Chapman TW, Godínez LA. Glassy carbon electrodes modified with composites of starburst-PAMAM dendrimers containing metal nanoparticles for amperometric detection of dopamine in urine. *Talanta.* 2007;72:1586–92.
- Antonels NC, Meijboom R. Preparation of well-defined dendrimer encapsulated ruthenium nanoparticles and their application as catalyst and enhancement of activity when utilised as SCILL catalysts in the hydrogenation of citral. *Catal Commun.* 2014;57:148–52.
- Bai L, Wan H, Street SC. Preparation of ultrafine FePt nanoparticles by chemical reduction in PAMAM-OH template. *Colloids Surf A Physicochem Eng Asp.* 2009;349:23–8.
- Kirkpatrick GJ, Plumb JA, Sutcliffe OB, Flint DJ, Wheate NJ. Evaluation of anionic half generation 3.5–6.5 poly(amidoamine) dendrimers as delivery vehicles for the active component of the anticancer drug cisplatin. *J Inorg Biochem.* 2011;105:1115–22.
- Zanaboni G, Rossi A, Onana AMT, Tenni R. Stability and networks of hydrogen bonds of the collagen triple helical structure: influence of pH and chaotropic nature of three anions. *Matrix Biol.* 2000;19:511–20.
- Maiti PK, Cagin T, Wang GF, Goddard WA. Structure of PAMAM dendrimers: generations 1 through 11. *Macromolecules.* 2004;37:6236–54.
- Zhang Y, Wu L, Zeng Q, Zhi J. Synthesis and characterization of rutile TiO₂ nano-ellipsoid by water-soluble peroxotitanium complex precursor. *Mater Chem Phys.* 2010;121:235–40.