CrystEngComm

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Journal Name RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Template-free synthesis of TiO_2 microspheres with tunable particle size via a non-aqueous sol-gel process

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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TiO_2 microspheres with tunable particle size were prepared in alcohols without template via a facile non-aqueous sol-gel process on the basis of ester elimination mechanism. The diameter of TiO_2 microspheres in the range of 0.4-2.9 μm was controlled by the ratio of methanol in the solvent.

TiO_2 possesses many favorable properties, e.g. non-toxicity, low cost, chemical inertness, and photostability, which results in applications such as pigments[1], water remediation[2], photocatalysts[3] and photovoltaics[4]. Recently, TiO_2 microspheres have attracted great attention for the novel properties that combine structural integrity in micro-scale and large number of active sites in nano-scale[5-7]. For example, anatase TiO_2 beads with high surface areas and controllable pore sizes can enhance the light harvesting within the electrodes without sacrificing the accessible surface for dye in dye-sensitized solar cells[8, 9]. On the other hand, chemical and physical properties of TiO_2 microspheres, such as the dispersibility, light-responsibility, adhesiveness, wettability and chemical resistance, are dependent on the particle size, which results in an increasing desire for the size control of TiO_2 microspheres.

Though various methods, such as sol-gel process[10-12], hydrothermal[13, 14] or solvothermal process[14], have been employed to prepare TiO_2 nanostructures, controlled synthesis of TiO_2 nanostructures is difficult to be achieved in a facile way due to the extremely high reactivity of titanium alkoxides. During the last decade, the non-aqueous sol–gel processes have been developed for the preparation of titania nanocrystals in a mild way[15-17]. In the non-aqueous sol–gel processes, in some case, the formation of Ti–O–Ti bridges occurs through the condensation reaction between the ligands coordinated to two different titanium centers, accompanying the elimination of organic groups[18]. Alkyl halide elimination and ester elimination are the most common routes, but alkyl halide elimination reactions produce environmentally unfavorable and volatile alkyl chlorides[19, 20]. Though great efforts have been paid to prepare TiO_2 nanostructures on the basis of ester elimination mechanism[21], there are few reports concerning to prepare well-defined TiO_2 microspheres at the sub-microscale and microscale levels.

Usually, the templates or other additives are employed to control the particle size of TiO_2 microspheres. For example, spherical TiO_2 particles of variable sizes are produced in a sol-gel synthesis with addition of a salt or a polymer solution[11, 12]. However, the post-synthetic treatments aimed to remove the templates or additives may lead to the increase of time and cost. Ideally, a facile template-free method is preferred to control the particle size of TiO_2 microspheres in a wide range.

In the present work, a facile non-aqueous sol-gel process is developed to prepare TiO_2 microspheres on the basis of ester elimination mechanism without template. The samples were prepared with titanium isopropoxide (TTIP) as Ti source, formic acid, and alcohols as solvent at 150 °C under a solvothermal condition. The solvent was pure ethanol, pure methanol, or the mixture of ethanol and methanol. Effects of various parameters, such as the concentration of formic acid, the reaction time, the reaction temperature and the amount of methanol in the solvent, on the morphology were investigated. The mechanisms for the formation of the TiO_2 microspheres and the size control were also proposed. Although the preparation of TiO_2 microspheres is not new, it is the first time, to our knowledge, that TiO_2 microspheres with tunable particle size are prepared via a template-free non-aqueous sol-gel process.

Fig. 1 shows XRD patterns of the samples prepared for various time in ethanol. The sample prepared for 1 h is amorphous. All the diffraction peaks of the samples prepared for 6 h, 12 h and 18 h are assigned to anatase (JCPDS No. 21-1272), indicating that pure anatase is synthesized. The crystallinity of the samples increases with increasing reaction time. The crystal size of the samples prepared for 6 h, 12 h and 18 h, estimated by Scherrer equation, is 4.5, 6 and 6.3 nm, respectively, indicating that the crystal size of the samples increases with increasing reaction time.

Fig. 2 shows FE-SEM images of the samples prepared for various time in ethanol. Well-defined microspheres are obtained in the sample prepared for 1 h and 6 h (see Fig. 2a-b). The surfaces of the microspheres are smooth (see the insets of Fig. 2a and Fig. 2b). The average diameters of the microspheres remain to be 2.9 μm

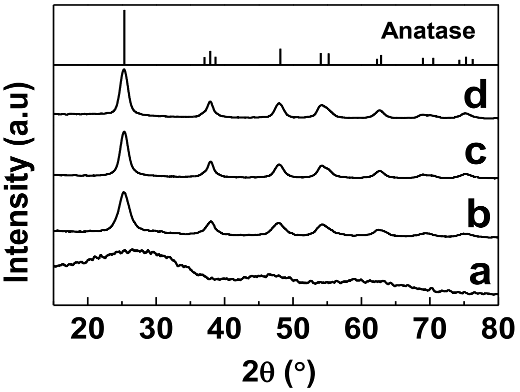

Figure 1. XRD patterns of the samples prepared for various time in ethanol: (a) 1 h, (b) 6 h, (c) 12 h, (d) 18 h.

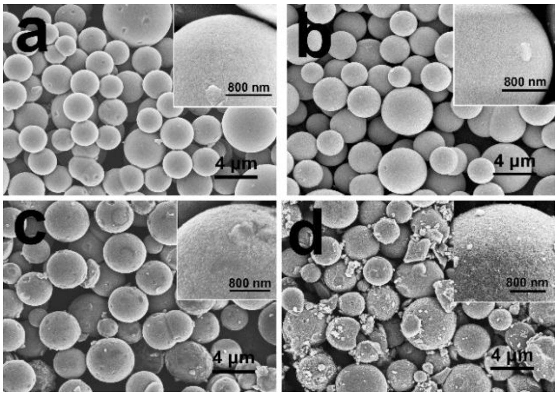

Figure 2. FE-SEM images of the samples prepared for various time in ethanol: (a) 1 h, (b) 6 h, (c) 12 h, (d) 18 h.

when the reaction time extends from 1 h to 6 h (see Fig. S1). The standard deviations of the size distributions for the samples prepared for 1 h and 6 h are 0.8 μm and 0.6 μm, respectively (see Fig. S1). When the sample is prepared for 12 h, some fragments of the microsphere appear (see Fig. 2c). When the sample is prepared for 18 h, a lot of fragments of the microspheres are observed (see Fig. 2d). The surfaces of the microspheres prepared for 12 h and 18 h are rough (see the insets of Fig. 2c and Fig. 2d). According to Fig. 1 and Fig. 2, well-defined anatase microspheres are prepared for 6 h and long reaction time is unfavorable for the formation of well-defined microspheres. Moreover, TiO_2 microspheres prepared for 6 h, 12 h and 18 h may be formed by nanocrystalline TiO_2 particles. TEM images of the samples prepared for 1 h and 6 h in ethanol show that well-defined microspheres with smooth surfaces are obtained (see Fig. S2a and Fig. S2c). The microspheres prepared for 1 h are composed of amorphous nanoparticles about 4-6 nm (see Fig. S2b), while the microspheres prepared for 6 h are composed of nanocrystalline TiO_2 particles about 4-6 nm (see Fig. S2d).

FE-SEM images of the samples prepared with various molar ratio of formic acid/Ti in ethanol indicate that well-defined TiO_2 microspheres are formed when the molar ratio of formic acid/Ti is about 2 (see Fig. S3). XRD patterns of the samples prepared with various molar ratio of formic acid/Ti in ethanol reveal that crystalline anatase is obtained and the crystal size of the samples increases as the amount of formic acid increases (see Fig. S4). FE-SEM images of the samples prepared at various temperatures in ethanol reveal that well-defined TiO_2 microspheres can be prepared at 150 °C and high temperature is unfavorable for the formation of well-defined TiO_2 microspheres (see Fig. S5). Therefore, well-defined TiO_2 microspheres can be prepared at 150 °C for 6 h when the molar ratio of formic acid/Ti is about 2.

Fig. 3 shows FE-SEM images of the samples prepared with various volumes of methanol in the solvent, and all the samples contain well-defined TiO_2 microspheres. The surfaces of the microspheres prepared with 1 ml, 2 ml, 5 ml and 10 ml methanol are relatively smooth (see Fig. 3a-d), while the surfaces of the microspheres prepared with 20 ml and 30 ml methanol are rough (see Fig. 3e-f). The microspheres prepared with 30 ml methanol are composed of the nanoparticles (see the inset of Fig. 3f). Fig. 4 shows the particle size of the samples prepared with various volumes of methanol in the solvent. The diameter of TiO_2 microspheres dramatically decreases from 2.9 μm to 0.74 μm and the microspheres become uniform as the volume of methanol increases from 0 ml to 5 ml. The diameter of TiO_2 microspheres slightly decreases from 0.74 μm to 0.4 μm as the volume of methanol increases from 5 ml to 30 ml. TEM images of the sample prepared with 30 ml methanol show that the microspheres are composed of nanoparticles about 20-30 nm (see Fig. S6).

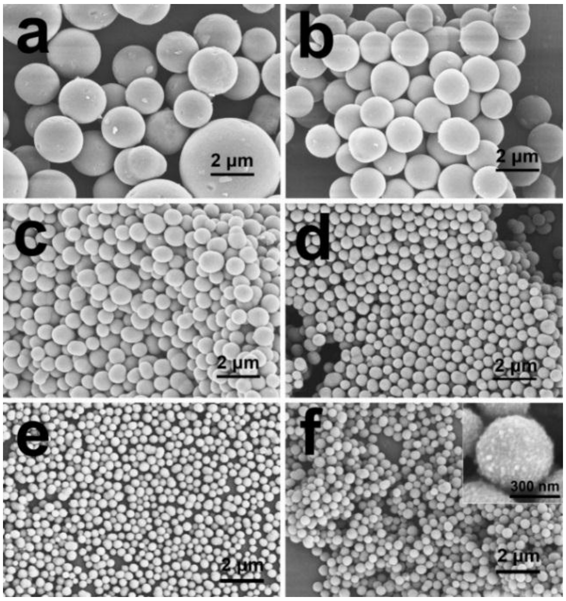

Figure 3. FE-SEM images of the samples prepared with various volumes of methanol in the solvent: (a) 1 ml, (b) 2 ml, (c) 5 ml, (d) 10 ml, (e) 20 ml, (f) 30 ml.

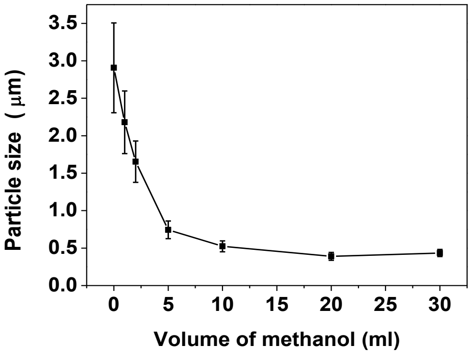

Figure 4. The particle size of the samples prepared with various volumes of methanol in the solvent.

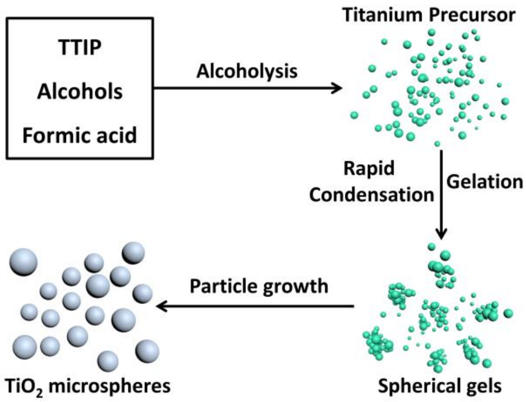

Figure 5. Schematic diagram of the formation process of TiO_2 microspheres.

Fig. 5 shows schematic diagram of the formation process of TiO_2 microspheres. Firstly, when the molar ratio of formic acid/Ti is 2, the modified titanium precursor may be produced by the alcoholysis reaction in room temperature. The reaction is suggested to be as follows:

$$\mathrm{Ti[(OCH(CH_3)_2)]_4 + 2\ HCOOH + m\ CH_3OH + n\ CH_3CH_2OH \rightleftharpoons Ti[OCH_3]_x[OCH_2CH_3]_y[OCH(CH_3)_2]_{(2-x-y)}[OOCH]_2 + (m-x)\ CH_3OH + (n-y)\ CH_3CH_2OH + (2+x+y)\ (CH_3)_2CHOH} \quad (1)$$

where m and n are the amounts of methanol and ethanol in the starting solution, respectively; x and y are the amounts of methanol and ethanol that are involved in the alcoholysis reaction, respectively. The formic acid does not act only as an acid catalyst, but also as a bidentate ligand and changes the alkoxide precursor at a molecular level therefore modifying the whole hydrolysis condensation process[19,20]. Secondly, during the solvothermal process, the condensation reaction of the modified titanium precursor may occur with the release of various esters. The reaction is suggested to be as follows:

$$\mathrm{Ti[OCH_3]_x[OCH_2CH_3]_y[OCH(CH_3)_2]_{(2-x-y)}[OOCH]_2 = TiO_2 + x\ HCOOCH_3 + y\ HCOOCH_2CH_3 + (2-x-y)\ HCOOCH(CH_3)_2} \quad (2)$$

Condensed TiO_2 gel with high degree of crosslinking is suggested to be formed. Thirdly, as the solvothermal reaction proceeds, the condensed gel keeps growing to certain size and spherical particles are formed (see Fig. 2a). Finally, the crystallization process occurs within the spherical particles and TiO_2 microspheres composed of nanoparticles are obtained (see Fig. 2b-d). Therefore, the formation of TiO_2 microspheres may be caused by the separation of the alcoholysis reaction and the condensation reaction. However, if the molar ratio of formic acid/Ti is much larger than 2, the condensation of the modified titanium precursor may be suppressed because the strong complexation of formic acid, leading to the formation of the irregular structures (see Fig. S3d). Therefore, on the other hand, the formation of TiO_2 microspheres may be caused by the rapid condensation rate of titanium precursor.

Due to the steric factors, the observed order of reactivity is $\mathrm{MeO > EtO > Pr^{i}O > Bu^{t}O}$[22]. Therefore, the reactivity of the titanium precursor can be further modified by the kind and amount of alcohols that are mixed. Specifically, the titanium precursor prepared with methanol has higher condensation rate than that prepared with ethanol. When the sample is prepared with methanol, more nuclei are produced during the non-aqueous sol-gel process, leading to the formation of TiO_2 microspheres with smaller size (see Fig. 3f). Furthermore, when the samples are prepared with low amount of methanol, the reactivity of the modified titanium precursor is significantly improved as the volume of methanol increases, leading to a dramatically decrease of the diameter of TiO_2 microspheres (see Fig. 3a-c). When the samples are prepared with high amount of methanol, the reactivity of the modified titanium precursor is slightly improved as the volume of methanol increases, leading to a minor decrease of the diameter of TiO_2 microspheres (see Fig. 3d-f).

In summary, TiO_2 microspheres with tunable particle size are synthesized by controlling the ratio of methanol in the solvent via a template-free non-aqueous sol-gel process on the basis of ester elimination mechanism. The microspheres prepared with pure ethanol have larger diameter than that prepared with pure methanol. The diameter of TiO_2 microspheres dramatically decreases as the volume of methanol increases when the samples are prepared with low amount of methanol. The diameter of TiO_2 microspheres is controlled in the range of 0.4-2.9 μm.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

Acknowledgments

This research is supported by the National Natural Science Foundation (Grant No. 51172201) and Key Technologies R&D Program of China (2013BAE03B00).

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