

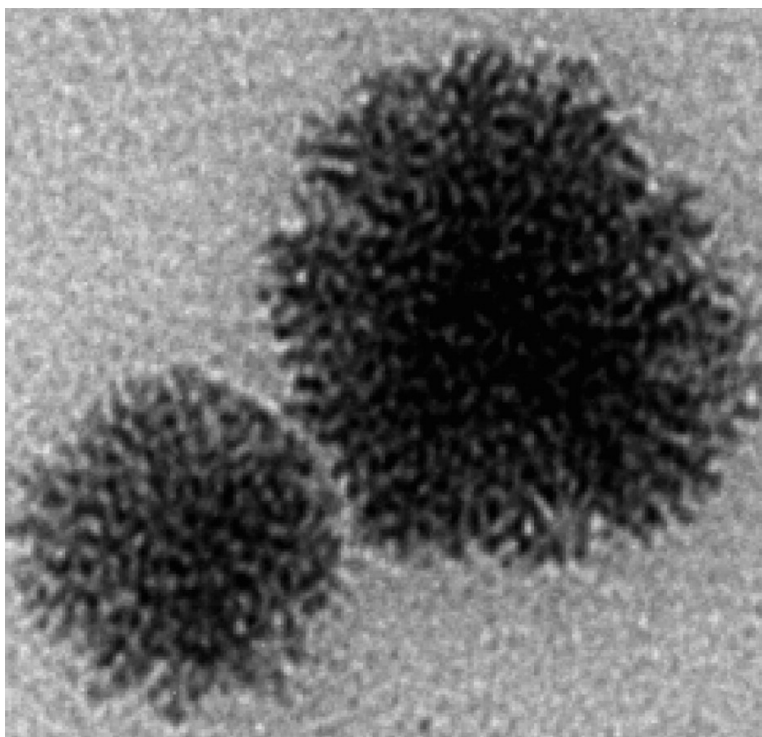
Communication

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Synthesis of Very Small TiO₂ Nanocrystals in a Room-Temperature Ionic Liquid and Their Self-Assembly toward Mesoporous Spherical Aggregates

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The realization of nanodevices with advanced functions requires the development of new and efficient approaches for the combination of the very small building blocks into desired structures.¹ Self-assembly through noncovalent interactions (e.g., hydrogen bonding interaction,² π - π interaction,³ charge-transfer interaction,⁴ acid/base proton transfer,⁵ van der Waals forces,⁶ host-guest interaction,⁷ and electrostatic forces⁸) is an effective technique that has been proven successful in forming different nanoparticle assembly motifs. The importance of understanding factors governing the creation of nanoparticle assembly stems from the desire to precisely optimize the functional properties of the nanostructures for optical, micro-electronic, magnetic, catalytic, and chemical/biological applications.⁹

Until now, most of the reports concerned with the self-assembly of nanoparticles into ordered nanostructures are focused on metallic elements (e.g., gold and silver). Few superstructures of other inorganic nanoparticles, such as metal oxides, have been fabricated.³ This is unfortunate, as metal oxides represent the most diverse class of materials, with properties covering almost all aspects of materials science and physics in areas including superconductivity, ferroelectricity, magnetism, transparent conducting materials, and gas sensors. A good example is crystalline titanium dioxide (TiO₂), the nanostructures of which are the key component of liquid solar cells,¹⁰ electroluminescent hybrid devices,¹¹ and advanced photocatalysis.¹² It is especially demanding to make crystalline TiO₂ nanostructures at ambient conditions, as the usual sol-gel chemistry performed in water-rich solvent mixtures unequivocally results in amorphous titania which does not possess the desired electronic properties and relies on a high temperature recrystallization. This, however, usually destroys the previously existing nanostructures.¹³ Just recently, first work on sol-gel reactions in nonaqueous media shows the availability of nanocrystalline titania at ambient conditions.¹⁴ To the best of our knowledge, there are few well-defined mesoporous titania with high crystallinity available.

Recently, a new solvent system, room-temperature ionic liquids (RTILs), has developed to a focal point of interest in both academia and industry.¹⁵ RTILs are organic salts with low melting points. They possess a wide range of liquidus temperatures, in some cases in excess of 400 °C, and have all of the intrinsically useful characteristics of negligible vapor pressure, wide liquidus, thermal stability, high ionic conductivity, and a large electrochemical window, making them attractive novel environmentally friendly solvents for enzyme-catalyzed reactions,¹⁶ photoelectrochemical solar cells,¹⁷ and electrochemical devices.¹⁸ Most recently, the advantages of RTILs in inorganic synthetic procedures have been gradually realized and received more and more attention.¹⁹ Various metallic nanoparticles, such as palladium,^{19d} iridium,^{19e} and germanium nanoparticles,^{19f} have been formed in RTILs, displaying distinctive catalytic properties.

In this Communication, we describe the synthesis of 2–3 nm sized titania nanocrystals in a RTIL under mild conditions and their self-assembly toward mesoporous TiO₂ spheres. The resulting structures combine the convenient handling of larger spheres with a considerable high surface area and narrow pore size distribution and are expected to have potential in solar energy conversion, catalysis, and optoelectronic devices.

In a typical synthesis of TiO₂ nanoparticles, we use 1-butyl-3-methylimidazoliumtetrafluoroborate, [C₄mim]⁺ BF₄⁻ (**1**), as solvent. The chemical structure of **1** is shown schematically below.



1 : 1-butyl-3-methyl-imidazolium-tetrafluoroborate

One milliliter of titanium tetrachloride (TiCl₄) was mixed with 10 mL of **1**. After homogenization of the mixture, 2 mL of purified water was added slowly under heavy stirring at room temperature. Hydrolysis of TiCl₄ occurs immediately, as indicated by the appearance of turbidity. This turbid solution was stirred at 80 °C for another 12 h. For collection of the product, the obtained dispersion was diluted with 20 mL of water to decrease the viscosity of **1**. Afterward, the produced TiO₂ nanostructure was gathered by centrifugation. The residual of **1** in the product was removed by extracting the sample with acetonitrile, which is soluble to both the inorganic species and the RTIL, in a closed vessel at 50 °C for 8 h. The extraction process was repeated until complete removal of the RTIL from the TiO₂, as determined by a Fourier transform infrared (FT-IR) spectrum of the materials, in which the imidazolium $\nu_{(C-H)}$ stretching region (3200–3000 cm⁻¹) of **1** disappears completely.²⁰ The final product was dried in a vacuum oven at 40 °C for further characterization.

Figure 1 shows a representative TEM image of the resulting nanostructures produced in **1**. It can be seen that well-defined, discrete, and porous TiO₂ nanospheres, 70–100 nm in diameter, were formed. Each spherical aggregate is composed of hundreds of individual small nanoparticles with an average diameter of about 2–3 nm. The Scherrer equation was used to evaluate the size of the crystallite on the basis of the XRD pattern, and the calculated size fits the grain size of the TEM image well. A magnification of the image (inset) further demonstrates that the nanoparticles are linked one by one to form a scaffold, as marked with the short arrow in the inset. The stable three-dimensional spatial connectivity of the network of nanoparticles was confirmed with high-resolution SEM observations. The corresponding well-defined selected-area electron diffraction (SAED) pattern (see Supporting Information: Figure S1) of the spherical aggregates of TiO₂ nanoparticles is indicative of high nanocrystallinity of the formed product and can be assigned to the anatase phase of TiO₂. The absence of an amorphous halo, typical for amorphous titania, underlines the unusual high crystallinity for the reaction conditions and particle

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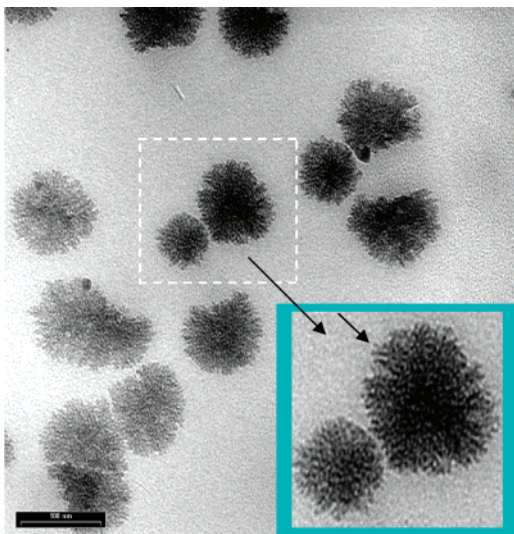


Figure 1. TEM image of the TiO₂ nanoparticles formed in **1** and their self-assembly toward spherical, spongelike superstructures. The inset is a 2× magnification of the image. The scale bar is 100 nm.

sizes given. The energy-dispersive X-ray (EDX) spectrometry clearly shows only Ti and O elements in the product with an approximate molar ratio of 1:2.

The resulting spherical TiO₂ nanoparticle scaffold exhibits a mesoporous channel system, displaying unusual high surface areas and narrow pore size distribution. Figure S2 (see Supporting Information) shows a typical N₂ gas adsorption–desorption isotherm. The isotherm displays the typical type IV curve, which is usually attributed to the predominance of mesopores. There are also practically no micropores present, which are omnipresent in amorphous silicas.²¹ The average size of the mesopore is calculated to be about 6.3 nm, as shown in the inset. The presence of a pronounced hysteresis loop in the isotherm curve is indicative for a 3D intersection network of the pores,²² which also goes well with the TEM observation. The product exhibits 554 m²/g of surface area by a nitrogen Brunauer–Emmett–Teller (BET) measurement, exceeding the typical values of usual template-formed crystalline porous titania structures.²³

The formation mechanism of the present mesoporous spherical aggregates of TiO₂ nanoparticles is intriguing. Investigation of kinetic growth of small particles to form larger regular structures or even patterns has attracted considerable attention in the past few years. As diffusion-limited aggregation (DLA) mostly leads to disordered particles with no structural porosity, thus, the present reaction is believed to proceed via reaction-limited aggregation (RLA), where only a small fraction of the collisions result in the two particles involved adhering to each other.²⁴ The TiCl₄ hydrolyzed at the beginning of the reaction quickly, presumably into an amorphous TiO₂ sol within **1**, which gradually ripens into the well-defined TiO₂ nanocrystals as the reaction time proceeds. The RTIL, **1**, as solvent, obviously favors the RLA of the TiO₂ nanocrystals via specific sides, presumably even via epitaxial recognition. As known from hydrothermal titania particle synthesis,²⁵ these specific faces of the nanoparticles can then fuse to minimize interface energy, explaining the high structural stability of the aggregates. Similar directed aggregations of nanoparticles, however, leading to nanorods, were recently observed by Qi et al.²⁶ and Tang et al.²⁷ The well-defined structural porosity of the present spherical TiO₂ aggregate would then result from the tensorial RLA probability, branching the rates and the defects involved. Further investigations have to be carried out to understand in more detail the formation mechanism, thermal stability, catalytic property of the present

spongelike TiO₂ nanostructure, and the interesting interconnectivity among the nanocrystallites.

In summary, we have demonstrated for the first time the synthesis of very fine crystalline anatase particles and their self-assembly toward novel mesoporous spherical aggregates in a room-temperature ionic liquid. The produced TiO₂ nanoparticles undergo reaction-limited aggregation under mediation of the RTIL to create the new spongelike TiO₂ nanostructure. The titania nanosponge exhibits structural mesoporosity with considerable high surface area and narrow pore size distribution, rendering the materials interesting for solar cell conversion, catalysis, and electronic devices. It is expected that the present method can be easily extended to the similar nanostructures of other oxide materials, which is currently underway.

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Supporting Information Available: Corresponding selected-area electron diffraction (SAED) pattern of the mesoporous spherical aggregates of TiO₂ nanoparticles, typical N₂ gas adsorption–desorption isotherm of the mesoporous spherical aggregates of TiO₂ nanoparticles, and the calculated corresponding size distribution of the mesopores (inset) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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