TOPICAL REVIEW

Oxide-based inorganic/organic and nanoporous spherical particles: synthesis and functional properties

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Abstract

This paper reviews the recent progress in the preparation of oxide-based and heteroatom-doped particles. Surfactant-templated oxide particles, e.g. silica and titania, are possible candidates for various potential applications such as adsorbents, photocatalysts, and optoelectronic and biological materials. We highlight nanoporous oxides of one element, such as silicon or titanium, and those containing multiple elements, which exhibit properties that are not achieved with individual components. Although the multicomponent nanoporous oxides possess a number of attractive functions, the origin of their properties is hard to determine due to compositional/structural complexity. Particles with a well-defined size and shape are keys for a quantitative and detailed discussion on the unique complex properties of the particles. From this viewpoint, we review the synthesis techniques of the oxide particles, which are functionalized with organic molecules or doped with heteroatoms, the physicochemical properties of the particles and the possibilities for their photofunctional applications as complex systems.

Keywords: nanoparticles, sol–gel process, titania, silica, nanoporous materials

1. Introduction

Inorganic–organic hybrid materials fill the gaps between inorganic chemistry, polymer chemistry, organic chemistry and biology. This field of research, which originated in the sol–gel community, is presently thriving with the appearance of a new class of mesoscopic hybrid structures engineered on the nanometer scale to satisfy the requirements of a variety of applications [1]. The inorganic–organic hybrid materials can be formed via the co-condensation of functionalized oligomers or polymers with metal alkoxides in which chemical bonding is established between the inorganic and
organic phases [2]. The hybrid materials are expected to exhibit specific properties that are not achieved by the individual components. The enhanced properties have been achieved by the preparation, characterization and design of various hybrid combination techniques and their complementary functions. As mesoscopically mixed hybrid materials, inorganic–surfactant hybrids have been extensively studied since the mesophases with characteristic shapes, sizes and interconnections have been immobilized on inorganic solids to be utilized as precursors of porous solids with controllable and well-defined structures. Silica–surfactant hybrids have been converted to nanoporous silicas with a narrow pore size distribution in the range of several nanometers to tens of nanometers, and various types of nanostructures (e.g. folded sheet material (FSM), Mobil crystalline material (MCM), Santa Barbara amorphous-type material (SBA), categorized depending on the size of pores, the shape of nanostructures, etc) have been reported, resulting in numerous potential applications [4–8].

The compositional variation in particles with or without nanopores is one topic of active research. Besides silicas, doped silicas, organically functionalized silicas, other metal oxides, chalcogenides, carbons, metals and polymers are available as mesostructured materials. Among them, the incorporation of heteroatoms into a silica framework, either during or after synthesis, has received much attention. The incorporation of aluminum [9, 10], titanium [11, 12] and vanadium [13] was followed by a large number of studies on the surface grafting or doping methods of the metal ions [14, 15]. Lanthanum doping improved the thermal stability [16], whereas cerium doping is beneficial for catalytic applications [17–19]. Host–guest and guest–guest interactions using nanoporous silicas have been widely investigated [20–24], and the possible applications for bio-imaging and drug delivery based on silica that incorporates luminescent species have been reported [25–32]. For such applications, the efficient synthesis and design of heteroelements doped into the silica frameworks are important.

The shape and size-controlled synthesis of nanoporous silicas has attracted much attention not only to improve their performance, but also to develop new applications. The first report on nanoporous silica with well-defined morphology and nanostructure was published in 1994 as a nanoporous silica thin film, and various possible applications have been proposed [33, 34]. Nanoporous silica with spherical shape and narrow size distribution of particles can be used as a building block of photonic crystals, chromatographic stationary phases, etc. Therefore, the control of the size distribution has been widely conducted, and monodisperse nanoporous silica particles with a size range from several hundred nanometers to several micrometers have been prepared by the sol–gel reaction, conducted in an aqueous ammonia/alcohol solution first developed by Stöber et al [35], combined with a surfactant templating approach [36–40]. Nanoporous spherical particles composed of other oxides have also been prepared by the sol–gel-based approach. However, metal alkoxides are more likely to be hydrolyzed in the presence of water due to their lower electronegativity; thus nucleation and growth simultaneously proceed during the synthesis. If synthesis conditions are precisely optimized, various kinds of nanoporous spherical particles can be made available for a wide range of applications. Thus, the development of synthesis techniques of particles with uniform size and well-defined shape has been extensively conducted [41–44].

In this review, we focus on the preparation of nanoporous spherical particles of silica and titania with a narrow size distribution, as well as on heteroatom-doped structures. The preparation of monodisperse particles under specific conditions has attracted much attention because an increasing number of materials, which could not be produced in a conventional batch synthesis, can now be prepared using flow reactors [45–47]. Accordingly, by controlling the parameters in the techniques, one should be able to design the composition and structure of the hybrids as well as the monodispersity. The properties of these hybrids with complex composition are topics of interest in materials chemistry and various applications.

2. Synthesis of oxide-based well-defined particles

2.1. General procedure

There are many kinds of approaches for synthesizing inorganic–organic particles. They can be classified into (i) synthesis in a closed system (i.e. conventional batch synthesis using a flask, beaker, etc) and (ii) continuous-flow synthesis. Both methods are further divided into various types such as homogeneous precipitation, emulsion-based preparation, etc. Homogeneous precipitation is one of the most general methods of preparing various types of particles including inorganic–organic hybrids [41–44]. The products can be simply obtained by mixing the starting materials within a container and ageing them for a certain time. This is a straightforward approach, although many factors including solution composition, temperature and ageing time as well as the mixing technique should be evaluated. It is important to optimize the mixing procedure of starting materials, especially in the case of rapid reaction, because it may result in heterogeneity of the products in terms of their composition, shape and size. In particular, the batch synthesis includes a templating approach in which the three-dimensional ordered macropore structures (fabricated using photonic crystals) are filled with the precursor solution. This approach leads to the formation of particles which reflect the size and morphology of the macropores. Taking advantage of this templating approach, it is possible to avoid the formation of aggregated/polydisperse particles [48, 49].

The continuous-flow synthesis can yield homogeneous products. The option of manipulating the additional reaction parameters, compared to the batch synthesis, such as the flow rate, and the ability to stop the reaction as soon as the product forms in a microliter or even nanoliter volume, offers further possibilities for product design [45]. Through the possibility of introducing time-control parameters (flow
rate and sequence of reagent addition), the reactions can be controlled at different stages, resulting in a flexible kinetic rate and reactor design. Thus, consideration of these parameters of the synthesis methods provides the mild reaction to successfully obtain the monodisperse particles.

2.2. Oxide-based inorganic–organic hybrids

2.2.1. Silica-based particles. Stöber et al [35] reported the preparation of monodisperse spherical silica particles by the sol–gel reaction of silicon alkoxides in a homogeneous aqueous alcohol solution containing ammonia (figure 1). The synthesis parameters, such as the type of silicon alkoxide and alcohol, molar ratio of water to silicon alkoxide and added amount of ammonia, were varied to find the relationship between synthesis parameters and particle size distribution.

The preparation of monodisperse spherical silica particles was improved and successfully combined with the supramolecular templating method [9, 50], which was proposed to prepare a silica–surfactant hybrid as the precursor of nanoporous silicas. The first example of spherical silica–surfactant hybrid particles was reported by Grün et al [36]. The hybrid showed an ordered pore structure as indicated by the x-ray diffraction patterns. Spherical silica-hexadecyltrimethylammonium bromide (CTAB) hybrid particles were synthesized from a solution containing tetraethoxysilane (TEOS), ethanol, water and ammonia. Surfactants can be removed from the hybrids by heat treatment or solvent extraction to obtain nanoporous silica, although it is possible to solubilize guest species into the surfactant-templated silica, and the various optical properties based on host–guest chemistry were investigated [51, 52, 127, 128]. In Grün’s report, the nanoporous silica particles obtained by calcination had a spherical morphology with a broad size distribution.

Monodisperse spherical nanoporous silica particles were synthesized by Yano et al [37, 53–55]. Tetraalkoxysilane, alkyltrimethylammonium halide (alkyl chain length $n = 10–18$, halide = chloride or bromide), methanol and sodium hydroxide were used as starting materials. The authors optimized the synthesis conditions to form monodisperse particles with a hexagonal pore structure and sizes ranging from several hundred nanometers to a micrometer, as shown in figure 2. Shimura and Ogawa [38, 39] reported the preparation of nanoporous silica spherical particles by the same approach, and clarified the effect of the ageing time as well as the composition of the starting solution on the particle size. The size was controlled in the range of several hundred nanometers to 2 µm, while the nanoporous structure was disordered. The molar water/alcohol ratio was significantly higher than in Yano’s reports, so that the formation of micelles and subsequent hexagonally packed structure was prevented, leading to a wormhole-like nanoporous structure. The approach based on the synthesis method of Stöber et al and supramolecular templating is applicable for the preparation of monodisperse nanoporous silica spherical particles with size ranging from 400 nm to 2 µm. However, polydisperse particles (coefficient of variation CV > 12%) were formed when the particles were smaller than 400 nm.

Silicon alkoxide is more stable than the other metal alkoxides owing to its high electronegativity [62–64]. The higher electronegativity, which means strong interactions between the central element of the alkoxide and surrounding alkoxy groups, results in slower hydrolysis, indicating easier separation of nucleation and growth. Si(OH)$_4$ is formed by the hydrolysis of silicon alkoxides, and the condensation of Si(OH)$_4$ generates oligomeric species (nuclei). Thus, longer hydrolysis is advantageous for obtaining only nuclei without further growth. The separation of the nucleation and growth processes is required to prepare monodisperse particles; the growth process should occur after completing the nucleation [56, 57]. When the other alkoxides composed of metals instead of silicon are used, the hydrolysis and condensation proceed more rapidly due to their lower electronegativity, which facilitates the hydrolysis of alkoxides. As a result, both the nucleation and growth processes occur simultaneously and then polydisperse products are formed. When silicon alkoxide is used, the processes can be separated, resulting in the formation of monodisperse products.

LaMer et al theoretically proposed that the monodisperse particles can be formed by adjusting both the nucleation and growth processes [56, 57], indicating that the monodispersity in the smaller size range can be achieved by separated nucleation and growth processes. As shown in figure 3, the synthesis method by the separated process was achieved using a flow reactor that had a Y-type junction and cross-section of about 1 mm$^2$ [58]. The partial hydrolysis of TEOS occurred in the micrometer-sized channel, and subsequently the reactant solution containing the pre-hydrolyzed alkoxides, which form the nuclei, was poured into the other solution for particle growth. Figure 4 shows scanning electron microscopy (SEM) images and size distributions of the spherical particles (silica-CTA$^+$) obtained, prepared at different molar CTAC (cetyltrimethylammonium chloride)/TEOS ratios. Products with a size of 200 to 400 nm and CV values of 7–12% were obtained by separating the nucleation and growth. The silica-CTA$^+$ hybrids obtained were heat treated to eliminate CTA$^+$ and transform the hybrids into nanoporous particles.
Figure 2. (a) Argon adsorption isotherm of the monodisperse spherical nanoporous silica particles (inset: a pore size distribution calculated by the non-localized density functional theory) and (b) TEM image of a platinum-incorporated nanoporous silica particle. (Reprinted with permission from [53], The Royal Society of Chemistry © 2003.)

Figure 3. Illustration of an experimental setup using the flow reactor.

The surface area calculated by the Brunauer–Emmett–Teller (BET) method [59] increased from 500 to 1000 m$^2$ g$^{-1}$ as the CTAC/TEOS ratio in the starting solution increased, while the pore size derived by the Barrel–Joyner–Halenda (BJH) method [60] was 2 nm, irrespective of the CTAC/TEOS ratio. There are further possibilities to obtain monodisperse spherical silica particles with a controlled pore size in which another template of different alkyl chain length is used.

Urata et al [61] reported the synthesis of particles with size in the tens of nm range. The preparation was conducted in an aqueous solution containing tetramethoxysilane, CTAB and triethanolamine. As shown in figure 5, the size of the resulting nanoporous silica spherical particles was ca 20 nm. The as-synthesized particles were treated without drying for transformation into nanoporous particles by removing the templates through dialysis. A transparent aqueous suspension was obtained, suggesting that the aggregation of the nanoparticles was suppressed. It is possible to count the number of pores in individual particles and to directly examine the pore structure, enabling us to further discuss the formation mechanism of the silica–surfactant hybrids.

2.2.2. Titania-based particles. As shown in figure 6, the changes in particle size of several isolated metal alkoxides indicate how each alkoxide hydrolyzes and subsequently forms aggregates. In particular, titanium alkoxide hydrolyzes and suddenly begins to form aggregates, while silicon alkoxide seems stable for a long period. This means it is relatively difficult to separate both nucleation and growth processes, which are keys to obtaining monodisperse particles, as described in section 2.2.1. The hydrolysis and condensation reactions of the titanium alkoxides proceed rapidly [62–64], and it is more difficult to obtain the monodisperse spherical titania particles if compared to the case of silica. Ikemoto et al [65] pointed out the importance of the synthesis conditions for the formation of monodisperse...
spherical titania particles. The titania particles were prepared by the sol–gel reaction of titanium tetraethoxide (TEOT) from aqueous ethanol solutions with various pH values and molar water/TEOT ratios. When the particles were synthesized under acidic conditions, no precipitate was obtained, while the reaction solution became turbid after 40–60 s under neutral conditions and immediately under basic conditions. The monodisperse particles were obtained when the molar water/TEOT ratio was 3, whereas nucleation and growth simultaneously proceeded for the molar water/TEOT ratios of 10 and 5.26. Thus, nucleation occurred until the reaction solution became turbid and then growth started to form monodisperse particles.

One of the effective ways of suppressing the hydrolysis is to chemically modify titanium alkoxides [66–69]. Polymers, such as hydroxypropylcellulose, are utilized to prevent water from reacting with the titanium for rapid hydrolysis. Molecules that have better affinity for titanium are also utilized to control the hydrolysis reaction. Another way to control the hydrolysis of the titanium alkoxide is to add as little water as possible, e.g. the molar water/titanium alkoxide ratio of 3. Wang et al [70] prepared titania–dodecylamine (DDA) hybrid spherical particles from an aqueous 1-propanol solution containing DDA by the hydrolysis and condensation of titanium tetraisopropoxide (TTIP) without adding water. The reaction vessel was open to air and TTIP was hydrolyzed by the moisture. The resultant particles were spherical and developed a porous structure despite their polydispersity as shown in figure 7, indicating that nucleation and growth simultaneously occurred during the synthesis.

In order to prepare monodisperse particles, the synthesis conditions have to be optimized. Well-defined titania-based hybrid spherical particles have been synthesized by various methods [71–78]. Titania–DDA [75, 76] and titania–hexadecylamine (titania–HDA) [77, 78] hybrid spherical particles with the size ranging from about 300 to
3000 nm and a narrow size distribution have been obtained by the sol–gel-based approach. The molar ratio of water to titanium alkoxide was up to about 10 (about 3 in most of these reports) and, additionally, various kinds of additives or a co-solvent were employed. Although the monodisperse particles were obtained as shown in figure 8, the reaction mechanism was complicated because of the composition of the starting solutions, and the TiO₂ yield was low due to the insufficient molar ratio for complete hydrolysis (when the molar ratio was increased to achieve higher TiO₂ yield, irregular-shaped particles were formed). Therefore, it is worth developing a method of preparing monodisperse hybrid particles with high TiO₂ yield and controlled particle size.

Titania–octadecylamine (ODA) hybrid spherical particles with a uniform submicron size were prepared by a two-step approach (reaction in the flow reactor and subsequent batch reaction) [79, 80], which was successfully used for the synthesis of monodisperse silica-based hybrids. As shown in figure 9, particles with a uniform size of about 2 nm, which may be the result of nucleation, became larger when they were added to the batch reaction solution containing water, isopropanol (IPA) and ODA. Thus, the nucleation and growth processes were effectively separated using both the flow reactor and batch reaction techniques. The optimization of the experimental conditions for the hydrolysis is one of the important factors controlling the nucleation of titania–ODA spherical particles [80]. The utilization of faster flow and smaller tube diameter resulted in the formation of uniform-sized particles (CV = 3.5%), suggesting that the size variation of the nuclei would affect particle size and distribution. Insufficient reaction time within the tube resulted in relatively polydisperse particles; thus a proper combination of the flow rate, tube length and tube diameter should be selected. The ODA was extracted from the hybrid spherical particles by washing with a hydrochloric acid–ethanol mixture (HCl–EtOH), resulting in disordered nanoporous titania spherical particles in which the BET surface area and BJH pore size were 600 m² g⁻¹ and 2.2 nm, respectively [79]. The added amount of ODA strongly relates to the surface area because ODA acts as a template for the nanoporous structure. Therefore, it is worth preparing titania–ODA particles with a variable ODA amount for large surface area titania particles. Furthermore, ODA plays a role not only in forming the spherical shape, but also in solubilizing hydrophobic dye molecules such as fluorescein. When a certain amount of fluorescein was added to the aqueous IPA solution containing ODA and mixed with the titania precursor

![Figure 7](image-url) SEM image of titania–DDA hybrid particles after DDA removal and calcination. (Reprinted with permission from [70], The Chemical Society of Japan © 2000.)

![Figure 8](image-url) SEM images of titania–HDA particles synthesized with different H₂O : Ti molar ratios: (a) 2 : 1, (b) 4 : 1, (c) 6 : 1, (d) 10 : 1, which were taken at the same magnification. (Reprinted with permission from [77], American Chemical Society © 2010.)

![Figure 9](image-url) Size distributions of titania particles after mixing two starting solutions within the flow reactor for nucleation formation (dashed line) and after mixing the reaction solution with another starting solution in an open vessel for particle growth (solid line). (Reprinted with permission from [115], The Ceramic Society of Japan © 2011.)
solution, monodisperse spherical titania–ODA particles were obtained, which had a size of about 300 nm and contained fluorescein.

2.3. Heteroelement-doped oxides with nanoporous structures

2.3.1. Titania–silica particles. The Si in the silica framework was replaced by several heteroelements (Al and Ti) to design the surface properties and impart catalytic functions [81–83]. The photocatalytic properties of the heteroelement-doped silicas have been investigated. Titanium was introduced into nanoporous silicas during or after the synthesis [12, 84–88]. Titania–silica hybrids with a wider Si/Ti ratio have also been prepared by various approaches to provide thin films [89–93] and powders [94–98].

The physicochemical properties of titania–silica hybrids were improved for applications as an efficient (photo)catalyst, adsorbent and variable refractive index material. Owing to their unique surface properties, titania–silica hybrids were utilized for a variety of acid-catalyst reactions including phenol amination, ethene hydration, butene isomerization, cumene dealkylation, 2-propanol dehydration and 1,2-dichloroethane decomposition [99]. Effective enrichment by ions of strontium and cesium was reported [100, 101], which is important for selective extraction of radioactive species. Control of the refractive index was also evaluated [102–105]. Louis et al [105] reported the temperature-dependent change of the refractive index of titania–silica hybrid films with various Si/Ti ratios. The relationship between crystal structure and refractive index
was examined in detail, and basic information was obtained for the optical uses of titania–silica hybrids.

The hydrolytic reaction of titanium alkoxides is relatively fast and therefore requires precise control of the synthesis conditions. Sakka and Kamiya [106] pointed out that titania sometimes preferentially precipitated when a mixture of two alkoxides was used. Yoldas [107] prehydrolyzed silicon alkoxides and then added titanium alkoxides after a specific time to obtain titania–silica hybrids. Silica-rich titania–silica hybrids were obtained, but the preparation of titania-rich hybrids remains difficult. By adjusting the reactivity of titanium alkoxides, the preparation of well-defined spherical particles of titania–silica–ODA hybrids is achieved as shown in figure 10(a) [108], indicating that the particles (particle size ca 200 nm) were obtained irrespective of the Si/Ti ratio in the starting solution. The Si/Ti ratios measured by x-ray fluorescence (XRF) and by energy-dispersive x-ray spectroscopy in a transmission electron microscope (TEM-EDX, figure 10(b)) were almost the same. TEM-EDX probed individual particles whereas XRF averaged over their ensemble; therefore, the similarity of the results indicates the same composition in every particle. This conclusion is consistent with the observed homogeneity of the particle shape and size.

The photocatalytic properties of titania–silica hybrids were investigated [108]. Figure 11 shows the change in the concentration of methylene blue by UV irradiation in the presence of the particles. Methylene blue was decomposed by products with Si/Ti ratios of 0 and 0.19, while the decomposition was slow for products with Si/Ti ratios of 0.94 and 1.5. Limited decomposition was observed for products with Si/Ti ratios of 0.94 and 1.5, which can be explained by the fact that the surface of the anatase crystallites in the spherical particles was blocked by the silica domains that limited the access of the methylene blue to the active surface of the anatase.

### 2.3.2. Titania–zirconia particles.

Titania–zirconia hybrids have been prepared for dehydrogenation, decomposition of chlorofluorocarbons, partial oxidation and photocatalysis [109]. The titania–zirconia particles possessed more acid sites than titania particles [110]. The titania–zirconia hybrids have affinity to phosphopeptides so that concentration of the phosphopeptides on the surface was achieved [111]. Sizgek et al reported the preparation of millimeter-sized spherical nanoporous titania–zirconia particles with a variable Zr/Ti ratio [112–114]. The titania–zirconia hybrid particles were easy to handle owing to their large size, and the authors suggested that they can be used for adsorbing vanadium and uranium species. The monodisperse spherical titania–zirconia particles with sizes of ca 3–4 μm were synthesized and the pore size was variable from 13 to 23 nm. Because of the unique surface property of the titania–zirconia hybrids, the preparation of monodisperse spherical nanoporous titania–zirconia particles was investigated [115]. Well-defined spherical particles were synthesized as shown in figure 12(a) and the monodispersity was supported by the particle size distributions (figure 12(b)). The BET surface area derived from the nitrogen adsorption isotherm was 30 m² g⁻¹ for a Zr/Ti ratio of 0, as shown in figure 13(A), whereas the products with Zr/Ti ratios of 0.016 and 0.07 had an area of about 60 m² g⁻¹. The product with a Zr/Ti ratio of 0.07 showed a narrower pore size distribution, peaking at 4–5 nm and varying from 2 to 8 nm, compared to those of the products with Zr/Ti ratios of 0 and 0.016, in which the BJH pore size distributions ranged from 2 to 11 nm (figure 13(B)).

#### 2.3.3. Europium–silica particles.

Rare earth ions have narrow emission bands, large Stokes shifts, long luminescence lifetimes and may exhibit an up-conversion of incident light [129]; their incorporation in silica has been widely reported. Their solubility in the silica matrix is limited by clustering and ion–ion interactions. Thus, the investigation of the coordination mechanism of rare-earth ions in silica is an important research topic [130].

The europium(III) ion (Eu³⁺) is relatively non-toxic and stable to illumination. It shows narrow emission lines under visible light excitation due to shielding by the 5s and 5p orbitals, and the spectral shape depends on the electronic environment and forbidden f–f transitions [116, 117]. Thus, Eu³⁺ is a sensitive optical probe for the dopant site environment due to its luminescence properties [118]. The nanoporous silica framework is an attractive host for Eu³⁺ ions owing to the charge compensation of the non-network oxygen species in the inner surfaces. The incorporation of the complex [C₃H₅NC₂H₃][Eu(TTA)₄] into the nanopores has been investigated [119–121]. It was found that the Eu-doped yttria formed in the pores of the ordered mesoporous silica SBA-15. The synthesis of the Eu³⁺-doped nanoporous silica film for humidity sensing applications has been reported [122]. The synthesis of the Eu³⁺-containing nanoporous silica spheres

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**Figure 11.** Photocatalytic decomposition of methylene blue by the titania–silica hybrid particles with different Si/Ti atomic ratios. •: Si/Ti = 0; ○: Si/Ti = 0.19; ∆: Si/Ti = 0.94; ▲: Si/Ti = 1.5) after the removal of ODA and calcination in air at 800 °C for 1 h. (Reprinted with permission from [108], Royal Society of Chemistry © 2012.)

**Figure 12.** BET surface area derived from the nitrogen adsorption isotherm was 30 m² g⁻¹ for a Zr/Ti ratio of 0, as shown in figure 13(A), whereas the products with Zr/Ti ratios of 0.016 and 0.07 had an area of about 60 m² g⁻¹. The product with a Zr/Ti ratio of 0.07 showed a narrower pore size distribution, peaking at 4–5 nm and varying from 2 to 8 nm, compared to those of the products with Zr/Ti ratios of 0 and 0.016, in which the BJH pore size distributions ranged from 2 to 11 nm (figure 13(B)).
Figure 12. (a) SEM images of products with different molar zirconia/titania ratios: 1st row: as synthesized; 2nd row: after removing ODA; 3rd row: after removal of ODA and calcination at 600 °C. (b) Particle size distributions of products with different Ti/Zr ratios. Average particle size and coefficient of variation (CV) are shown in each graph. (Reprinted with permission from [115]. The Ceramic Society of Japan © 2011.)

with highly ordered nanostructures has been investigated (see figure 14) [28]. Eu³⁺-doped nanoporous silica spheres with well-defined shapes and nanometer particle sizes were synthesized, and the states of Eu³⁺ in the silica framework were investigated [123]. The highly ordered nanopores were preserved with the doping of Eu/Si up to 10 mol%, and the O—Si—O and Si—OH groups in the framework were rearranged by the interactions of the Eu³⁺ ions with the inner O atoms. Luminescence, which originated from the ⁵D₀—⁷F₁ and ⁵D₀—⁷F₂ transitions in the Eu³⁺ ions (figure 15), indicated a low symmetry of the Eu³⁺ site. Electrostatic interaction with the environmental O atoms prevented the aggregation of Eu³⁺ ions, resulting in an efficient luminescence. To fabricate bio-imaging materials, folic acid, which is used as the targeting ligand for tumor cells, was immobilized on the luminescent Eu³⁺-doped nanoporous silica spheres through mediation of 3-aminopropyltriethoxysilane (APTES), as shown in scheme 1 [29]. The immobilization of APTES and folic acid occurred on the Eu³⁺-doped nanoporous silicas. The luminescence spectra of the immobilized spheres contained the characteristic peak due to interactions between folic acid and Eu³⁺. The immobilized spheres showed high dispersion stability in phosphate buffered saline, which is useful for specific cellular imaging [131, 132].

3. Potential applications of functionalized particles

Many materials scientists have been interested in preparing oxide-based functional particles with controllable composition, nanostructure, size and size distribution, and in tailoring them for specific applications. There are several studies on the precise material design and resultant properties. Testino
et al [124] reported the synthesis of titania nanoparticles with controlled phase composition, morphology, surface area and band gap based on thermodynamic modeling. A large number of products are utilized for the photocatalytic decomposition of phenol. Interestingly, photocatalytic activity increases with increasing crystallite size, i.e. rutile nanoparticles are preferred over anatase in some cases, despite the decrease in the surface area. The authors attributed the high reactivity to the slower recombination of electron–hole pairs as compared to anatase. There has been a debate on the photocatalytic activity of titania with different crystal phases for several decades. However, there is still no consensus. A systematic investigation like Testino’s study will provide a clear conclusion.

Size-controlled particles have been utilized for bio and catalytic applications. Maurer-Jones et al [125] prepared non-porous silica and nanoporous silica with a particle size of ca 25 nm to examine nanoparticle–cell interactions. Non-porous titania with a particle size of ca 10 nm was also prepared to compare the biocompatibility of silica and titania. The effect of the nanostructure and compositional difference (silica and titania) on the nanoparticle–cell interaction...
was discussed, and it turned out that non-porous titania particles showed better biocompatibility. Despite a different size of the silica and titania particles and the broad size distribution, the work is interesting and valuable as a trial in which a material property was compared using well-defined particles with the same size/size distribution and a different composition/nanostructure. Chen et al. [126] reported the preparation of various metal nanoparticle supported oxide (titania and ceria) spheres with a uniform size. The deposition of metals onto support materials is a promising way to obtain efficient catalysts; thus numerous combinations of metals and oxides have been reported. The catalytic activity of metal-supported particles has always been an important research topic. The distribution of metal nanoparticles on oxides should be further examined to understand the origin of the high activity. This task is hindered by a limited number of available monodisperse oxides. In Chen’s report, the catalytic activity was discussed using monodisperse ceria and titania. The monodispersity enabled the authors to consider the effect of size, amount and type of metal nanoparticles as well as their size distribution.

Another possible use of monodisperse particles is to prepare artificial opal, a photonic crystal. Opal is a natural gem. It usually consists of an ordered close-packed array of submicron silica spherical particles [133, 134] and reflects light in a specific wavelength region (stop band). This range is determined by Bragg’s law; it depends on the size of the silica particles and the viewing angle, which results in iridescent structural color. Recently, the preparation and applications of nanoporous silica-based photonic crystals have been reported [135–139]. Yamada et al. discussed the use of nanoporous silica-based photonic crystals as sensing devices [137, 140, 141]. When the nanoporous silica particles adsorb molecules, the refractive index of silica dynamically changes, resulting in the structural color depending on the type of molecules. Further work is expected to realize sensing devices that would allow visual detection of various molecules.

Oxide–surfactant hybrid particles, which are regarded as a precursor for nanoporous materials, can also be utilized for several applications. For example, various dye molecules can solubilize into silica–surfactant hybrids even if the dyes are hydrophobic and thus do not interact with the hydrophilic surface (e.g. silica) [127, 142–146]. This enables the oxide–surfactant hybrids to be utilized as a pigment, a laser emitter, etc as well as for investigating the hybrid formation mechanism. On the other hand, the inherent property of the hybrids is also a topic of interest. For example, titania–ODA hybrid particles, which we have already mentioned in section 2.2.2, exhibited different refractive indices depending on the ODA amount incorporated into their structure. The refractive index of such hybrids is determined by the contribution of all the components. The relationship between particle size, composition and refractive index of the hybrids should be required to understand the control parameters of optical properties.

4. Conclusions and outlook

This review highlights the synthesis of oxide-based inorganic–organic hybrid particles as well as oxide-based
nanoporous particles doped with heteroatoms. These particles are a new class of mesoscopic structural material engineered on the molecular or nanometer scale to satisfy the requirements of a variety of applications. Silica- and titania-based inorganic–organic hybrid spherical particles were prepared by a sol–gel reaction combined with the surfactant templated approach. As compared to the conventional batch synthesis in a closed system, the improvement of the procedure for controlling the reaction was effectively applied to the preparation of monodisperse products. In addition to controlling the size and its distribution, compositional variation was achieved; the incorporation of silicon and zirconium into titania particles and Eu\(^{3+}\) into silica particles was possible not only for conventional catalysis and adsorption, but also for photofunctional applications, such as photocatalysis, bio-imaging, etc.

It is worth developing a method to prepare monodisperse particles with a variety of shapes, sizes and compositions not only for material design purposes, but also for the quantitative understanding of hybrid material properties, which will be practically attractive and useful. The higher product yield, shorter ageing time and larger-scale synthesis are also some of the goals to be achieved, which will be possible by effectively changing the various experimental conditions. The hybrid nanocomposites offer us paramount advantages to both facilitate integration and miniaturization of the devices and afford direct connections among the inorganic, organic and biological worlds. Functional nanobuilding blocks facilitate the integrative synthesis pathways in which a synergistic assembly and morphosynthesis can be strongly coupled. Multiscale structured hybrids will open up numerous opportunities for designing new materials.

References

[1] Wen J and Wilkes G L 1996 Chem. Mater. 8 1667
[2] Wilkes G L, Orler B and Huang H 1985 Polym. Prepr. 26 300
[3] Sanchez C, Julian B, Belleville P and Popall M 2005 J. Mater. Chem. 15 3559
[4] Hoffmann F, Cornelius M, Morell J and Froba M 2006 Angew. Chem. Int. Edn. Engl. 45 3216
[5] Kimura T and Kuroda K 2009 Adv. Funct. Mater. 19 511
[6] Slowing I I, Trewyn B G and Lin V S Y 2010 J. Mater. Chem. 20 7924
[7] Tang F Q, Li L L and Chen D 2012 Adv. Mater. 24 1504
[8] Yang P P, Gai S L and Lin J 2012 Chem. Soc. Rev. 41 3679
[9] Beck J S et al 1992 J. Am. Chem. Soc. 114 10834
[10] Ogawa M, Kuroda K and Mori J 2000 Chem. Commun. 24 2441
[11] Corma A, Navarro M T and Pérez-Parrante J P 1994 J. Chem. Soc. Chem. Commun. 1994 147
[12] Taney P T, Chibwe M and Pinnavaia T J 1994 Nature 368 321
[13] Reddy K M, Moudrakovski I and Sayari A 1994 J. Chem. Soc. Chem. Commun. 1059–1060
[14] Sayari A 1996 Chem. Mater. 8 1840
[15] Corma A 1997 Chem. Rev. 97 2373
[16] Chen L Y, Jaenicke S and Chuah G K 1997 Micropor. Mesopor. Mater. 12 323
[17] Araujo A S and Jaroniec M 1999 J. Colloid Interface Sci. 218 462
[18] Araujo A S and Jaroniec M 2000 Stud. Surf. Sci. Catal. 129 187
[19] Araujo A S and Jaroniec M 2000 Thermochim. Acta 345 173
[20] Yoon K B 1993 Chem. Rev. 93 321
[21] Ogawa M 1998 Acc. Chem. Res. C 94 209
[22] Stein A, Melde B J and Schroden R C 2000 Adv. Mater. 12 1403
[23] Scott B J, Wirsberger G and Stucky G D 2001 Chem. Mater. 13 3140
[24] Tagaya M and Ogawa M 2008 Phys. Chem. Chem. Phys. 10 6849
[25] Slowing I I, Trewyn B G and Lin V S Y 2007 J. Am. Chem. Soc. 129 8845
[26] Zhu Y, Ikoma T, Hanagata N and Kaskel S 2010 Small 6 471
[27] Okuda M, Takeguchi M, Zhu Y, Hashimoto A, Ogawa N, Tagaya M, Chen S, Hanagata N and Ikoma T 2010 Surf. Interface Sci. 42 1548
[28] Tagaya M, Ikoma T, Yoshioka T, Minami F, Motozuka S and Tanaka J 2011 Mater. Lett. 65 2287
[29] Tagaya M, Ikoma T, Yoshioka T and Tanaka J 2011 Chem. Commun. 47 8430
[30] Pan L M, He Q J, Liu J N, Chen Y, Ma M, Zhang L L and Shi J L 2012 J. Am. Chem. Soc. 134 5722
[31] Hartono S B, Ou Y W, Kleitz F, Liu J, He L Z, Middelberg A P J, Yu C Z, Li G Q and Qiao S Z 2012 ACS Nano 6 2104
[32] Yamada H, Urata C, Aoyama Y, Osada S, Yamauchi Y and Kuroda K 2012 Chem. Mater. 24 1462
[33] Ogawa M 1994 J. Am. Chem. Soc. 116 7941
[34] Ogawa M 1996 Chem. Commun. 1996 1149
[35] Stöber W, Fink A and Bohm E 1968 J. Colloid Interface Sci. 26 62
[36] Grün M, Lauer I and Unger K K 1997 Adv. Mater. 9 254
[37] Yano K, Suzuki N, Akimoto Y and Fukushima Y 2002 Bull. Chem. Soc. Japan 75 1977
[38] Shimura N and Ogawa M 2005 Bull. Chem. Soc. Japan 78 1154
[39] Shimura N and Ogawa M 2007 J. Mater. Sci. 42 5299
[40] Lu B W, Endo A, Inagi Y, Harada A and Ohmori T 2009 J. Mater. Sci. 44 6463
[41] Matijevic E 1994 Langmuir 10 8
[42] Sugimoto T 1987 Adv. Colloid Interface Sci. 28 65
[43] Jeong U, Wang Y, Ibisate M and Xia Y 2005 Adv. Funct. Mater. 15 1907
[44] Wang Y, Price A D and Caruso F 2009 J. Mater. Chem. 19 6451
[45] Song Y, Hormes J and Kumar C S S R 2008 Small 4 698
[46] Abou-Hassan A, Sandre O and Cabuli V 2010 Angew. Chem. Inter. Edn. Engl. 49 6289
[47] Wiles C and Watts P 2011 Chem. Commun. 47 6512
[48] Yang S M, Coombs N and Ozin G A 2000 Adv. Mater. 12 1940
[49] Chen J, Hua Z, Yan Y, Zakhidov A A, Baughman R H and Xu L 2010 Chem. Commun. 46 1872
[50] Yanagisawa T, Shimizu T, Kuroda K and Cato C 1990 Bull. Chem. Soc. Japan 63 988
[51] Ogawa M 2002 J. Photochem. Photobiol. C: Photochem. Rev. 3 129
[52] Sanchez C, Lebeau B, Chapat F and Boilot J P 2003 Adv. Mater. 15 1969
[53] Yano K and Fukushima Y 2003 J. Mater. Chem. 13 2577
[54] Yano K and Fukushima Y 2004 J. Mater. Chem. 14 1579
[55] Nakamura T, Mizutani M, Nozaki H, Suzuki N and Yano K 2007 J. Phys. Chem. C 111 1093
[56] Zaiser E M and LaMev V K 1948 J. Colloid Interf. Sci. 3 571
[57] LaMev V K and Dinger R 1950 J. Am. Chem. Soc. 72 4847
[58] Shibata K, Kambara K and Ogawa M 2010 Ind. Eng. Chem. Res. 49 8180
[59] Brunauer S, Emmett P H and Teller E 1938 J. Am. Chem. Soc. 60 309
[60] Barrett E P, Joyner L G and Halenda P P 1951 J. Am. Chem. Soc. 73 373
[135] Dong A A, Wang Y J, Tang Y, Zhang Y H, Ren N and Gao Z 2002 Adv. Mater. 14 1506
[136] Chen C-N, Lin H-P, Tsai C-P and Tang C-Y 2004 Chem. Lett. 33 838
[137] Yamada Y, Nakamura T, Ishi M and Yano K 2006 Langmuir 22 2444
[138] Ogawa M, Kato K and Shimura N 2009 Bull. Chem. Soc. Japan 82 121
[139] Marlow F, Muldarisnur, Sharifi P, Brinkmann R and Mendive C 2009 Angew. Chem. Int. Edn Engl. 48 6212
[140] Yamada Y, Nakamura T and Yano K 2008 Langmuir 24 2779
[141] Nakamura T, Yamada Y and Yano K 2007 J. Mater. Chem. 17 3726
[142] Ogawa M, Igarashi T and Kuroda K 1998 Chem. Mater. 10 1382
[143] Huang M H, Dunn B S, Soyez H and Zink J I 1998 Langmuir 14 7331
[144] Zhou H S and Honma I 1998 Chem. Lett. 1998 973
[145] Hoppe R, Ortlam A, Rathousky J, Schulz-Ekloff G and Zukal A 1997 Micropor. Mater. 8 267
[146] Marlow F, McGehee M D, Zhao D, Chmelka B F and Stucky G D 1999 Adv. Mater. 11 632