Metal oxide mesocrystals with tailored structures and properties for energy conversion and storage applications

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Mesocrystals (MCs) are superstructures with a crystallographically ordered alignment of nanoparticles. Owing to their organized structures, MCs posses some unique characteristics such as a high surface area, pore accessibility, and good electronic conductivity and thermal stability; thus, MCs could be beneficial for many areas of research and application. This review begins with a description of the common synthesis strategies for, and characterization and fundamental properties of metal oxide MCs. Newly developed analytical methods (that is, photoconductive atomic force microscopy and single-molecule, single-particle fluorescence microscopy) for unraveling the charge transport and photocatalytic properties of individual MCs are then introduced. Further, recent developments in the applications of various metal oxide MCs, especially in the fields of energy conversion and storage, are also reviewed. Finally, several perspectives in terms of future research on MCs are highlighted.

INTRODUCTION

The self-assembly of nanoparticle building blocks into highly ordered superstructures is one of the actively pursued research topics in materials science and technology.¹–⁴ Such hierarchical architectures have potentially tunable electronic, optical and magnetic properties, which promise various applications ranging from catalysis to optoelectronics. A mesocrystal (MC), which was first introduced by Colfen in the early years of 2000s, is defined as a superstructure consisting of nanoparticles on the scale of several hundred nanometers to micrometers.⁵–¹¹ In contrast to the classical mechanism of atom/ion-mediated growth of a single crystal, the particle-mediated growth mechanisms of MCs are termed as non-classical crystallization (Figure 1). This definition has been developed in recent years, where MCs are defined entirely according to their structures rather than their formation mechanism.¹² In this decade, a variety of MCs of metal oxides (for example, TiO₂,¹³–²³ ZnO,²⁴–³⁴ hematite (α-Fe₂O₃),³⁵–⁴⁰ maghemite (γ-Fe₂O₃),⁴¹ Co₃O₄,⁴² SnO₂,⁴³–⁴⁵ Ag₂O,⁴⁶ CuO⁴⁷–⁴⁹), metal chalcogenides (for example, SnS,⁵⁰,⁵¹ PbS,⁵² PbSe⁵³–⁵⁴), metals (for example, Au,⁵⁵ Ag₅₆,⁵⁷ Cu,⁵₈ Pt,⁵₉,⁶₀ Pd,⁶¹), organic compounds (for example, DL-alanine,⁶²,⁶₃ DL-lysine·HCl,⁶⁴ perylene derivatives⁶⁵) and biominerals (for example, sea urchin spines, egg shells)⁶⁶ have been synthesized or discovered in nature.

Among metal oxides, TiO₂ is used in many applications that deal with environmental and energy problems (for example, photodegradation of pollutants,⁶⁷ water splitting for H₂ evolution,⁶⁸ dye-sensitized solar cells⁶⁸ and lithium-ion batteries⁶⁹) owing to its chemical stability as well as its low cost and non-toxicity. When TiO₂ is illuminated with ultraviolet (UV) light, electron–hole pairs are created simultaneously. Only a small part of the photogenerated charge carriers spatially separate via diffusion and facilitate surface reactions to generate reactive species (for example, O₂⁻ and *OH) for subsequent oxidation/reduction processes on TiO₂ surfaces.⁷⁰ Thus, highly active photocatalysts require high charge separation efficiency in addition to a high specific surface area for the adsorption of reagents. Controlled crystal growth also determines the exposed facets of crystals as well as their shape and size, which have different surface physicochemical properties.⁷¹,⁷² As Yang et al.⁷³ successfully synthesized anatase TiO₂ single crystals with highly exposed reactive [001] facets, enormous efforts have been devoted to the synthesis of anatase TiO₂ crystals with different crystal planes exposed for better performance.⁷⁴ Furthermore, mesoporous TiO₂ single crystals with well-defined facets have been prepared and utilized in dye-sensitized solar cells and photocatalysis for H₂ evolution and degradation of dyes.⁷⁵,⁷⁶

It has been suggested that the dense packing of TiO₂ nanocrystals (NCs) enhances the photocatalytic activity and performance of dye-sensitized solar cells owing to the efficient interparticle electron transfer between NCs.⁷⁷–⁸³ For example, the Choi group reported that mesoporous TiO₂ consisting of compactly packed nanoparticles showed higher photocatalytic activity for H₂ evolution than that shown by colloidal and commercial TiO₂ samples in both UV and visible light (dye-sensitized) systems.⁷⁸ In addition, transient
photocurrent measurements and random walk numerical simulations have shown that the ordering of a nanocrystalline structure significantly influences charge transport and recombination, which are closely related to the performance of photovoltaic cells. Zaban and co-workers found that the highest degree of ordering in porous TiO$_2$ nanocrystalline films correlates with the highest values of effective diffusion coefficient. Indeed, MCs consisting of NCs highly oriented in the same direction are an ideal system to study this issue.

In this review, we focus on the synthesis and structures of metal oxide MCs, mostly TiO$_2$ MCs, and their applications for energy conversion and storage. We selected examples, which showed the most marked enhancement of physical properties in applications. For instance, owing to their high specific surface area and mesoporous structures, TiO$_2$ MCs could show higher photocatalytic activity for H$_2$ evolution and organics degradation than that shown by bulk single crystals. The higher photocatalytic activity of TiO$_2$ MCs is strongly related to the facile interparticle electron transport between NCs in the MC superstructure. Finally, we summarize our contribution together with some future research directions in various aspects.

SYNTHESIS OF MCS

In this section, we briefly overview the synthesis of metal oxide MCs by several different approaches. As the details of the synthesis procedures for and formation mechanisms of MCs are beyond the scope of this article, we request interested readers to refer to the comprehensive reviews cited in Introduction section. 

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**Figure 1** Schematic illustration of classical and non-classical crystallization. (a) Classical crystallization pathway, (b) oriented attachment of primary nanoparticles forming an iso-oriented crystal upon fusing, (c) mesocrystal (MC) formation via self-assembly of primary nanoparticles covered with organics. Reprinted with permission from reference Wohlrab et al. Copyright 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

**Figure 2** (a) Schematic illustration of the formation of spindle-shaped anatase TiO$_2$ mesocrystals (MCs). (b) Scanning electron microscopy (SEM) and (c) transmission electron microscopy (TEM) images of TiO$_2$ MCs. Reprinted with permission from reference Ye et al. Copyright 2011 American Chemical Society.
The method most commonly used to synthesize MC materials is based on hydrothermal/solvothermal treatments in which a solution is maintained at a specific temperature and aged for a specific period of time. The resulting precipitates are then collected and washed to remove impurities. In some cases, the precipitates require further annealing. For example, the Qi group synthesized spindle-shaped anatase TiO$_2$ MCs by the solvothermal treatment of a solution of tetrabutyl titanate in acetic acid and subsequent calcinations. As illustrated in Figure 2a, the reaction between tetrabutyl titanate and acetic acid first forms unstable titanium acetate complexes by ligand exchange/substitution, concomitant with the release of butanol. The concomitant Ti–O–Ti condensation forms transient amorphous fiber-like precursors. Flower-like precursors are then produced at the expense of the transient precursors and release soluble titanium-containing species for the nucleation and growth of anatase NCs. These NCs undergo oriented aggregation along the [001] direction, consequently resulting in the formation of spindle-shaped anatase MCs (Figures 2b and c). The Brunauer–Emmett–Teller surface area and pore volume of the synthesized TiO$_2$ MCs were 114 m$^2$ g$^{-1}$ and 0.14 m$^3$ g$^{-1}$, respectively. Further, using the solvothermal method, Li and co-workers synthesized single crystal-like anatase TiO$_2$ MCs with a high surface area of 180 m$^2$ g$^{-1}$ and a uniform pore diameter of 3.4 nm. These TiO$_2$ MCs had either massive or granular structures in which most of the high-energy {001} surfaces were hidden in the bulk.

The O’Brien group were the first to prepare anatase TiO$_2$ MCs via the topotactic transformation of NH$_4$TiOF$_3$ crystals. The topotactic transformation is a solid-state transformation in which the final product is structurally and orientationally related to the starting material. Figure 3 illustrates the topotactic transformation of NH$_4$TiOF$_3$ to anatase TiO$_2$ MC. As the structures of NH$_4$TiOF$_3$ and anatase TiO$_2$ are very similar, the positions of Ti atoms in the [001] planes are well matched with each other. Using a similar synthesis strategy, Yu et al. synthesized layered anatase TiO$_2$ nanosheets with exposed {001} facets by a simple hydrothermal method, followed by calcination.

In 2012, Bian et al. significantly improved the synthesis method for anatase TiO$_2$ MCs with dominant {001} facets. Their improved method is illustrated in Figure 4a; plate-like TiO$_2$ MCs are obtained by annealing a thin layer of an aqueous solution containing TiF$_4$, NH$_4$F and NH$_4$NO$_3$ (without surfactants) on a silicon wafer. In this one-step annealing process, the material undergoes changes in two stages. First, the precursors of Ti$^{4+}$, F$^-$, NH$_4^+$ and H$_2$O begin a series of combination reactions during evaporation of water at low temperatures to form NH$_4$TiOF$_3$. With further increase in annealing temperature, NH$_4$TiOF$_3$ is topotactically transformed into anatase TiO$_2$. When large amounts of N, H and F atoms are removed, the volume of nanoparticles decreases and gaps or pores are formed between nanoparticles, resulting in the formation of porous TiO$_2$.
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MCs that consist of anatase single-crystalline nanoparticles with the {001} surfaces as dominant facets. They characterized the structures of the synthesized TiO₂ MCs by scanning electron microscopy (SEM) and transmission electron microscopy. The TiO₂ MCs showed a plate-like structure several micrometers in size and 50–300 nm in thickness (Figure 4b). The MCs were composed of an ordered alignment of anatase TiO₂ NCs with an average size of approximately 40 nm. A porous structure with pore diameters of several nanometers was confirmed by high-resolution scanning electron microscopy and transmission electron microscopy images (Figures 4c and d). It is worth mentioning here that a selected-area electron diffraction pattern of the crystal (inset) corresponded to single-crystal anatase along the [001] zone axis, thus suggesting the formation of anatase TiO₂ with the {001} facet exposed. An oriented arrangement of NCs decreases the grain boundaries in a sample. The pure phase of anatase was thus retained after calcination at 800°C. The enhanced phase stability was explained by the assumption that the transformation to the rutile phase was inhibited by the elimination of interfacial nucleation sites.

To understand the formation mechanism of anatase TiO₂ MCs, they compared the scanning electron microscopy images, X-ray diffraction patterns, N₂ adsorption–desorption isotherms and pore size distribution of the samples obtained at different synthesis temperatures (Figures 4e and f). NH₄TiOF₃ growth started at 250°C with a mixture NH₄TiOF₃ and NH₄NO₃ during the evaporation of water (Figure 4e). Pure NH₄TiOF₃ with a plate-like structure was observed at 300°C, but it did not have any pore structure on the surface and its specific surface area was very low (~ 0.4 m² g⁻¹) (Figure 4f). After annealing at 400°C, the obtained product was pure anatase TiO₂ (Figure 4e) and had a porous structure with a specific surface area of 74 m² g⁻¹ and a pore size of approximately 5 nm. Furthermore, no apparent change in morphology was observed, indicating the topotactic transformation from NH₄TiOF₃ to TiO₂ by the removal of N, H and F atoms from the crystal lattice. This removal of atoms resulted in the creation of space between TiO₂ NCs, and thus, a porous structure was formed in the crystal. Upon further increasing the calcination temperature, the morphology and crystalline phase of TiO₂ remained unchanged, while the mutual fusion of NCs led to an increase in the particle size, a decrease in the specific surface area and an increase in the pore size (Figure 4f).

Another important progress is the formation of MCs via electrochemical deposition. For example, Fang et al. reported an external electric field-driven particle-mediated bottom-up approach for synthesis of Ag₂O MCs with different morphologies. Figure 5 shows the scanning electron microscopy images of the as-prepared Ag₂O MCs under different applied potentials and growth times. The morphologies of the products obtained under different conditions are remarkably different (rhombic hexahedron, cube and dodecahedron), and the rough surface of MCs reveals a nonclassical crystallization process (insets of Figure 5).

An external magnetic field has also been applied to induce the self-assembly of γ-Fe₂O₃ nanocubes into micrometer-sized MC structures. The thickness of the MCs is controllable by varying the concentration of the nanoparticle dispersion as well as the duration of the applied magnetic field.
OPTICAL PROPERTIES OF MCS

MCs are expected to exhibit some interesting and unique optical properties owing to their structural features. Wu et al.26 synthesized core-shell-structured ZnO MC microspheres by a hydrothermal method in the presence of a water-soluble polymer. The whole surface of these MCs was composed of densely packed ZnO nanoplatelets aligned perpendicularly to the microspheres. Interestingly, these ZnO MCs exhibited strong mechanical resonance and radiative emission at \( \sim 0.36 \) THz under 514.5-nm continuous-wave laser irradiation. This property originated from the laser-induced coherent vibration of the ZnO nanoplatelets.

Hu et al.84 demonstrated that AgIn(WO 4) 2 MCs exhibit a white emission in the visible region when excited by 460-nm light. Their photoluminescence (PL) strongly correlated with the surface nanostructures of outgrowths; a larger amount of outgrowths led to stronger emission intensities. The MCs with high surface-to-volume ratios had more surface defects, which were responsible for the radiative recombination of charge carriers. In addition, Li et al.24 found that the PL properties of hollow-type ZnO MCs are largely governed by the number and nature of defects in the ZnO lattice.

Bian et al.85 investigated the recombination of photogenerated electrons and holes in plate-like TiO 2 MCs that yields distinct PL in the visible region. Figure 6a shows a typical emission image acquired for two partially overlapping TiO 2 MCs during 380-nm photoexcitation in ambient air. Spectral measurements revealed a broad emission band at the center positions of the crystal at around 450–600 nm (Figure 6b), which originated from surface states.86,87 The average PL lifetimes of TiO 2 MCs and NCs were around 5.9 and 2.0 ns, respectively (Figure 6c). Shorter (longer) PL lifetime of the samples indicates relatively faster (slower) charge recombination. Thus, it was concluded that the MC superstructure significantly improved charge separation efficiency. They also found that the average lifetime measured at the center of the MCs (5.5 ns) was slightly shorter than that measured at their edge (6.9 ns). The location-dependent nature of PL implied that charges trapped near the edge were subjected to a different recombination probability as compared with those trapped at the center.

ELECTRON TRANSPORT IN MC

Experiments on a single assembly of NCs revealed the superior physicochemical properties of ordered superstructures that are unattainable using conventional disordered systems. To explore the intricate relationship between structure and function, Bian et al.21 investigated the photoconductivity of individual TiO 2 MCs by means of conductive atomic force microscopy, with the instrument equipped with a UV light source (Figure 7a). As shown in Figures 7b, a significant photocurrent response was observed in case of UV irradiation on a single plate-like TiO 2 MC on an indium tin oxide electrode, while there was no measurable current response without UV irradiation. From the thickness dependence of the photocurrent, the photoconductivity was calculated to be \( 2 \times 10^{-2} \Omega^{-1} \text{m}^{-1} \) in air, which was several orders greater than that of aggregated TiO 2 NCs with a similar size (\( \sim 200 \) nm) under the same conditions (Figure 7b). This result suggested that electron transport ability in TiO 2 MCs was largely improved possibly because of the intimate contact between NCs and/or between NCs and electrodes.

Single-molecule, single-particle fluorescence microscopy (spectroscopy) has emerged as a powerful tool for obtaining information about the structure and dynamics of individual objects.88,89 Bian et al.85 applied this technique to determine the location of reactive sites on plate-like TiO 2 MCs by using a redox-responsive fluorogenic probe. By accepting electrons from photoexcited TiO 2, nonfluorescent 8-(3,4-dinitrophenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (DN-BODIPY; fluorescence quantum yield \( \Phi_{fl} < 10^{-4} \) in methanol) was reduced to form highly fluorescent 4-hydroxyamino-3-nitrophenyl-BODIPY (HN-BODIPY; \( \Phi_{fl} = 0.50 \) in methanol).
The locations of the reduction sites were determined via centroid analysis of each fluorescent spot obtained for individual MCs. As shown in Figures 8b and c, most of the fluorescence spots, that is, catalytically active sites, were found to be located near the edges of the MCs. This interesting finding was consistent with the observation that Au and Pt nanoparticles were preferentially photo-deposited at the edges of TiO2 MCs with {101} facets (Figures 8e and f). In addition, the average rate of the formation of fluorescent products on the basal surfaces decreased from 5.6 to 2.3 molecules m\(^{-2}\) s\(^{-1}\) upon Au loading on TiO\(_2\) MCs, whereas the reaction rate on the lateral surfaces increased from 11 to 19 molecules m\(^{-2}\) s\(^{-1}\) (Figure 8d). These differences strongly supported the mechanism in which photogenerated electrons on the basal surfaces of TiO2 MCs can rapidly migrate to Au nanoparticles loaded on the lateral surfaces through the NC network. This anisotropic electron transport greatly improved the photocatalytic performance to be better than that of conventional disordered systems (Figures 8g and h). In fact, the metal-nanoparticle-loaded TiO2 MC composites exhibited higher photocatalytic activity than the NC-based composites. Further, the loading amounts of noble metals required to achieve 50% of the photocatalytic degradation of 4-chlorophenol were compared under the same experimental conditions. The optimum loading amounts of metals on TiO2 MCs (for example, 0.04 and 0.2 wt% for Au and Pt, respectively) were about 10 times lower than those on TiO2 NCs (for example, 0.4 and 4.0 wt% for Au and Pt, respectively). This is desirable for the practical use of TiO2 MCs as photocatalysts because of the high price of noble metals.

**LITHIUM STORAGE PROPERTIES OF MCS**

MCs can be used in Li-ion batteries as either anode or cathode materials. The MC structure provides not only facile electronic conduction but also fast Li ion transport between the MC electrode and electrolyte. For example, Ye et al.\(^{16}\) prepared anatase TiO2 MCs (see Figure 2) and used them as an anode material for a high-power Li-ion battery. As shown in Figure 9, the MC electrode exhibited better rate capability than a TiO2 nanoparticle electrode at high current rates. The uniformly porous structure of MCs facilitated their contact with the electrolyte and hence was also advantageous for fast Li-ion transport. The TiO2 MCs delivered specific discharge capacities of 164.9 and 151.7 mA h g\(^{-1}\) at 1 and 2 C, respectively; these values were larger than those reported for TiO2 hollow spheres and were comparable with those reported for mesoporous spheres.

Duan et al.\(^{40}\) prepared high-stability \(\alpha\)-Fe\(_2\)O\(_3\) MCs by a facile solvothermal method without polymer additives, and evaluated the discharge cycling performance of an electrode fabricated using \(\alpha\)-Fe\(_2\)O\(_3\) MCs with different morphologies. Rhombic \(\alpha\)-Fe\(_2\)O\(_3\) MCs showed the best cycling stability owing to closed and intracrystalline porosity.

**PHOTOCATALYTIC PERFORMANCE OF MCS**

The design and preparation of mesoporous TiO2 photocatalysts have attracted increasing interest in recent years owing to their exceptional properties and widespread potential applications. Tartz\(^{18}\) synthesized anatase TiO2 MCs that exhibited good photocatalytic activity for organics degradation under UV light irradiation owing to their high crystallinity. Owing to their unique structural features, TiO2 MCs...
large effective surface area of the TiO\textsubscript{2} MCs that resulted in easier hydrothermal method. The TiO\textsubscript{2} MCs are composed of rutile modification of these TiO\textsubscript{2} MCs led to a 50% improvement in removal under UV or simulated solar light irradiation. Au MCs showed good photocatalytic activity and stability for NO nanowires with an average aspect ratio of approximately 270. These the rutile TiO\textsubscript{2} nanowires that allowed fast charge transport; (ii) a photocatalytic ability to the following factors: (i) a high aspect ratio of their photocatalytic performance. The researchers ascribed the high into the photocatalyst because of open pores.

Figure 8 (a) Single-molecule fluorescence observation of photocatalytically generated fluorescent 4-hydroxyamino-3-nitrophenyl-BODIPY (HN-BODIPY) from nonfluorescent 8-(3,4-dinitrophenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (DN-BODIPY) under ultraviolet (UV) light irradiation by total internal reflection fluorescence microscopy. (b) Fluorescence image of a 0.04 wt% Au/TiO\textsubscript{2} mesocrystal (MC) particle immobilized on a cover glass in Ar-saturated DN-BODIPY solution (0.5 \textmu m in methanol) under 488-nm laser (0.1 kW cm\textsuperscript{-2}) and UV light irradiation (30 mW cm\textsuperscript{-2}). The arrows denote the locations of fluorescence spots. Optical transmission images of (c) TiO\textsubscript{2} MC and (d) 0.04 wt% Au/TiO\textsubscript{2} MC immobilized on a cover glass. The blue and red dots indicate the location of fluorescence bursts on the basal and lateral surfaces of the crystal, observed during 15 s of irradiation. Transmission electron microscopy (TEM) images of a representative crystal of (e) 0.04 wt% Au/TiO\textsubscript{2} MC and (f) 1.0 wt% Pt/TiO\textsubscript{2} MC. Schematic illustration of electron transport processes in (g) structurally ordered MC and (h) disordered nanocrystal (NC) aggregation. The symbols e\textsuperscript{-} and h\textsuperscript{+} indicate photogenerated electrons and holes, respectively. Reprinted with permission from reference Bian et al.\textsuperscript{85} Copyright 2012 American Chemical Society.

Figure 9 Rate capability of TiO\textsubscript{2} mesocrystals (MCs) and nanoparticles from C/20 to 2C (1C = 170 mA g\textsuperscript{-1}) for five cycles. Reprinted with permission from reference Ye et al.\textsuperscript{16} Copyright 2011 American Chemical Society.

The above-mentioned plate-like TiO\textsubscript{2} MCs exhibited decent performance for the photocatalytic oxidation of 4-chlorophenol and rhodamine B as well as for the photocatalytic reduction of \textit{C}\textsubscript{6}H\textsubscript{4}\textsuperscript{+} in water.\textsuperscript{21} The photocatalytic activities of these TiO\textsubscript{2} MCs exhibited a 100–300% enhancement relative to that of anatase TiO\textsubscript{2} NCs with dominant [001] facets and a similar specific surface area; the observed marked enhancement in activity could not be attributed to the specific surface area of the NCs. The photocatalytic performance of the TiO\textsubscript{2} MCs was nearly similar to that of benchmark P25 TiO\textsubscript{2} (Figures 10a–c). Time-resolved diffuse reflectance spectroscopy was used to directly measure the lifetime of a charge-separated state; this measure is a criterion for evaluating the efficiency of photocatalytic reactions.\textsuperscript{70} As shown in Figure 10d, the TiO\textsubscript{2} MCs exhibited a broad transient absorption band in the visible to near-infrared range upon 355-nm laser excitation, which represented the overlapping of trapped holes (mainly 440–600 nm) and trapped electrons (mainly 660–900 nm).\textsuperscript{70} 4-(Methylthio)phenyl methanol (MTPM) was then selected as the probe molecule to estimate the lifetime of the charge-separated state.\textsuperscript{70} As can be clearly seen in Figure 10e, the 550-nm absorption band of the MTPM radical cation (MTPM\textsuperscript{+}) was indicative of one-electron oxidation of adsorbed MTPM by photogenerated holes. The half-lives of MTPM\textsuperscript{+} were determined to be \(\sim 2\ \mu\text{s}\) for the TiO\textsubscript{2} MC systems, which was much longer than that of TiO\textsubscript{2} NC (\(\sim 0.5\ \mu\text{s}\)). Hence, TiO\textsubscript{2} MCs could exhibit greatly increased photocatalytic activity owing to their superstructure that enhances charge separation.

Another interesting example is that of anatase TiO\textsubscript{2} MCs with different proportion of [001] and [101] facets synthesized by Chen et al.\textsuperscript{22} The proportion of [101] facets was tuned by adjusting the solvothermal periods. As shown in Figure 11, the TiO\textsubscript{2} MCs with a high proportion of [101] facets possessed higher photooxidation/ reduction activity than those with a lower proportion. This result was explained in terms of the synergistic effect of Ti\textsuperscript{3+} and the proportion of [101] facets. In addition, the normalized photocatalytic activity of
TiO₂ MCs was higher than that of TiO₂ nanopolycrystals when the proportion of {101} facets was equal; this indicated that the structural integrity of the crystals had a key role in determining the photocatalytic activity. Liu and co-workers synthesized hollow-type anatase TiO₂ MCs with dominant {101} facets via a new route by using PO₄³⁻/CO/F⁻ as morphology-controlling agents. The hollow MCs were more active in H₂ evolution from water splitting and CH₄ generation from photoreduction of CO₂, but were less active in O₂ evolution from water splitting than hollow single crystals. Interestingly, this reaction preference could be attributed to the fact that the hollow MCs had higher conduction and valence band edges than the hollow single crystals.

**MC-BASED COMPOSITE MATERIALS**

The direct growth method using topotactic transformation is suitable for constructing MC assemblies or layers on a variety of support materials. In 2008, Liu and Zeng developed a mild one-pot solution approach to prepare anatase TiO₂ MCs on multiwalled carbon nanotubes (CNTs) with controllable surface coverage, surface area, crystal orientation and TiO₂/CNTs ratio. CNTs were mixed with a TiF₄ aqueous solution and held over an ultrasonic water bath for 30 min. The subsequent aging at 60°C for 20 h produced CNTs covered with closely arranged TiO₂ crystallites with sizes in the range 2–4 nm (Figures 12a and b). The as-prepared TiO₂/CNTs nanocomposites showed better performance for photocatalytic degradation of an organic dye than P25 and CNTs because of (i) the high specific surface area that provided abundant adsorption sites for reactants; (ii) the porous structure that allowed efficient transport of reactants and products; (iii) the oriented arrangement of TiO₂ NCs that minimized light reflections and allowed light transmission to deeper parts of the catalyst; and (iv) surface defect sites and conductive CNTs support
that may have served as electron reservoirs to suppress the recombi-
nation of electron–hole pairs. Yang et al.92 prepared graphene-TiO2
MC composites by a facile template-free process based on a
combination of sol–gel and solvothermal methods (Figures 12c and
d). The resulting products exhibited a uniform distribution of
nanoporous anatase TiO2 MCs on the graphene sheets. Composites
prepared in the presence of different amounts of graphene oxide
exhibited higher photocatalytic activity for photocatalytic degradation
of rhodamine B than pure TiO2 MCs and P25.

SUMMARY AND PERSPECTIVES
The focus of current researches in the field of nanoscience and
nanotechnology is shifting from the synthesis of individual NCs to the
preparation and characterization of their MC superstructures and the
realization of their applications. Although self-assembly of NCs by
utilizing nanoscale attractive forces provides a simple approach for
the fabrication of MCs, the synthesis procedures are sometimes very
complicated, and hence, their large-scale applications are limited.
A highly reproducible, facile synthesis of MCs with a controlled shape
and size is strongly desirable for fundamental research and practical
applications. One of the alternative strategies for fabricating such
MCs is top–down fabrication through topotactic transformation.

MCs are also an ideal platform for constructing multifunctional
materials that incorporate a variety of functional materials. For
instance, the development of composite MCs consisting of two or
more different types of metal oxide NCs (for example, composites of
p- and n-type semiconductors) opens up exciting new opportunities
for designing and constructing much more efficient photocatalysts
and photovoltaic devices. Such binary nanoparticle superstructures
have been well developed for several metals and chalcogenides but not
yet for semiconductor metal oxides.93–95

Experiments on a single-particle assembly have revealed that
ordered superstructures produce a high yield of photogenerated
charges and have high photoconductivity, which are difficult to
achieve using traditional disordered systems consisting of crystalline
nanoparticles owing to the inevitable occurrence of charge recombi-
nation at the internal interface. The Majima group used single-
molecule, single-particle fluorescence microscopy to show that
photogenerated electrons could reach reactive sites over a micrometer
distance and are preferentially trapped at the edge of plate-like TiO2
MCs, in which [101] facets are predominantly exposed.21,85 This
anisotropic electron transport significantly retarded the charge
recombination with holes, thereby resulting in enhanced
photocatalytic activity. The excellent charge/molecular transport
properties of MCs thus hold great promise for energy conversion
and storage applications. Further development of the synthesis
methods for MCs and understanding of their fundamental
properties will lead to the production of innovative materials with
potential applications in energy conversion and storage, catalysis and
sensing.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

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Figure 12 (a) Field emission scanning electron microscopy (FESEM) and (b) transmission electron microscopy (TEM) image of mesoporous TiO2/carbon
nanotube (CNT) nanocomposites. The examined location is indicated with a frame in the inset image. Reprinted with permission from reference Liu and
Zeng91. Copyright 2008 American Chemical Society. (c, d) TEM images of graphene (GR)-TiO2 composites. Inset in panel (d) shows a selected-area electron
diffraction (SAED) pattern of the composites. Reprinted with permission from reference Yang et al.92 Copyright 2013 Elsevier BV.
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