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Hierarchically structured magnesium based oxides: synthesis strategies and applications in organic pollutant remediation

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Hierarchically structured materials have emerged as promising alternatives in the field of adsorption and separation technology owing to their fascinating physicochemical properties such as extraordinarily high surface area, ultrahigh porosity, well-defined morphologies, facile transportation, and easy recovery. Recently, a lot of encouraging research has been conducted on rational design and synthesis strategies of hierarchical MgO and other magnesium-based mixed oxides architectures, and their applications, especially in the field of adsorption and remediation of organic contaminants. To promote and highlight the progress in the development and applications of unique MgO based hierarchical structures, a thorough summary is essential. In this review, we recapitulate advances on synthesis strategies for hierarchically ordered MgO and MgO-based mixed oxides as adsorbents and provide an outline for their applications in toxic organic pollutant remediation from waste-water systems by analyzing selected examples. Finally, we will outline the issues and challenges for developing materials to increase their efficiency for remediation of organic effluents.

1. Introduction

The presence of toxic organic effluents in industrial, agricultural, and anthropogenic discharges accounts for heavy pollution of water sources.[1] Hazardous organic pollutants like dyes, pesticides, and aromatic compounds account for various health hazards among the living as well as disrupt the delicate cycles of nature.[2] Therefore, pre-discharge treatment of waste waters is a crucial step. In this regard, adsorption is a suitable choice due to its ease of operation and cost-effectivity.[3,4] Conventional materials like activated charcoal/carbon suffer from practical problems like high cost, tedious separation processes, and ineffectiveness after regeneration, to name a few.[5,6] Hence, there appears an urgent need for the development of new materials that show high adsorption capacity along with good regeneration capabilities, while taking care of the overall synthesis and processing costs.

Development of hierarchical materials is an emerging and rapidly evolving field of current interest. Hierarchical materials are defined as organized structures which consist of state-of-the-art assemblies having a definite arrangement. These materials are finding applications in various fields like adsorption, catalysis, ion-exchange, energy conversion, and storage, sensing, biomedical applications, *etc.*[7] The major benefit of these materials, specifically in adsorption and catalysis, is due to their synergy-effect driven calculated designing *via* formation of sub-divisional inter-porous channels.[8] The presence of these hierarchical subdivisions results in fast and efficient distribution of matter along the porous architecture of the material, resulting in better diffusion and transport of matter. This is a crucial factor for a surface phenomenon like adsorption, and therefore the potential of hierarchical materials in this field is promising. Particularly, three-dimensional ordered porous structured materials, often accompanied by a hierarchical structure, are now attracting much attention, not only for their fascinating structures, but also for their promising applications in various fields such as gas sensors, catalysers, energy transformation, *etc.*[9]

Metal oxide nanoparticles are remarkable in their approach for removing toxic organic pollutants from aqueous systems due to their O-vacancy sites, Lewis acid–base sites, non-toxic properties, kinks and defects present on the surfaces, among others.[10] However, working with nanoparticles is cumbersome due to losses incurred, especially during regeneration and recovery, as their size is very small. Ideal water treatment-based adsorbents should have some basic characteristic features like (i) ease of synthesis, (ii) low cost, (iii) being environmentally benign, (iv) robustness for continuous use, and (v) regeneration for reducing waste.[11] Hierarchically structured metal oxides are promising candidates for this role owing to presence of all these desired features. Self-assembly of nano-structures to form an overall micro-sized structure

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allows greater mechanical strength and good regeneration capabilities with the hierarchical metal oxides.[11]

Among metal oxides, MgO has been extensively studied in the fields of adsorption, decontamination and catalysis.[12,13] Its environmentally benign properties, basic nature, low-cost owing to abundance in nature, and minimum environmental impact as per the Clean Water Act basic limits makes it perfect for water remediation.[14] Moreover, magnesium is a fundamental constituent present abundantly in the earth's crust and, hence, adsorbents based on magnesium are a viable choice. Its importance can be deduced from the Scopus database which returns 295 859 results with the keyword "Magnesium". The presence of special Lewis acidic and basic sites, steps and kinks, defect sites, *etc.* on the surface of magnesium oxide (Fig. 1) accounts for its ability to destructively adsorb organic pollutants.[15,16]

Recently, a lot of work has been reported on MgO-based hierarchical adsorbents for remediation of dyes and other harmful organic compounds from water systems.[17–20] In this brief review, we explore progress on synthesis strategies for hierarchically ordered MgO and MgO-based composite oxides as adsorbents and their applications in toxic organic pollutant remediation from waste-water systems. Basic and advanced synthesis strategies and applications in organic pollutant removal will be covered briefly.

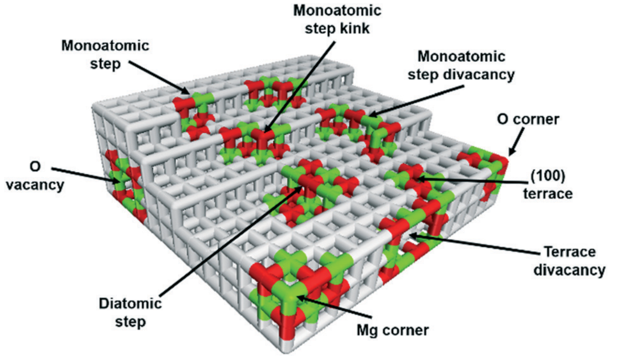


Fig. 1 A schematic representation for various MgO surface sites.

Lekha Sharma

Lekha Sharma received her B.Sc. degree in Chemistry from University of Delhi in 2011. After obtaining her M.Sc. degree in Physical Chemistry from University of Delhi in 2013, she started her Ph.D. under the guidance of Prof. Rita Kakkar in the Department of Chemistry, University of Delhi. Her research interest is focused on the synthesis of hierarchical metal oxides for environmental applications by combining theory and experiments.

Rita Kakkar

After obtaining a PhD degree in Physical Chemistry from the University of Delhi, Professor Rita Kakkar undertook research on various topics. She has been teaching physical chemistry at the University of Delhi for the past 33 years. She has authored a textbook on Spectroscopy published by Cambridge University Press. Her main research interests are in Computational Chemistry and related fields. She heads a large research group, which is carrying out computational and experimental studies on catalysis by nanomaterials and by enzymes. The focus of the research on nanomaterials is to understand the growth, morphologies and stabilities of nanocrystalline forms of metals and metal oxides, their reactivities, and their catalytic role in various reactions, particularly those involving degradation of organic pollutants. Her research on nanoscale materials also includes theoretical and experimental studies on quantum dots and their size-dependent properties for use as semiconductor devices and sensors. The other area of research is the use of in silico techniques to understand enzyme catalysis and to design enzyme inhibitors. In addition, her research group investigates potential energy surfaces and reaction paths of important organic reactions, and studies the role of catalysts in these reactions. Professor Rita Kakkar has over 130 research publications in international journals and chapters in books. She has successfully supervised the work of 39 PhD students. She has delivered invited talks at several scientific conferences and has acted as an International Advisory Member in several of these.

2. Synthesis of hierarchically structured magnesium based oxides

Over the past decade, a wide range of synthetic techniques have been developed to prepare hierarchical materials. These techniques are mainly divided into two basic classes: template-based synthesis and template-free synthesis. The general concept of templating strategies is to employ a structure-directing agent, either a soft-template like a surfactant, block copolymer, or a rigid hard template like carbon spheres, to build a porous hierarchical material. On the other hand, template-free strategies are based on self-formation of precursors to produce highly-ordered hierarchical materials. These techniques are explained in detail in subsequent sections.

2.1 Templating strategies

Templating is one of the most essential and powerful techniques for controlled synthesis of nanostructured materials; they involve using a pre-existing guide with desired nanoscale features to direct the formation of materials into different forms that are otherwise unattainable.[21] Hence, templated synthetic strategies produce nanostructures with unique morphologies and properties. Templated strategies make use of replication *via* templates, particularly soft and hard templates (Fig. 2). Apart from that, colloidal crystal, and biomaterials used for developing ordered mesoporous materials are briefly discussed.

Soft templates are usually "structure directing" agents which manipulate the structural or morphological features of a product. In this case, structure formation is a matter of mutual interaction between single templating units and the inorganic precursor species forming the solid product. The formation mechanism is a highly cooperative process.

On the other hand, a hard template can be commonly described as a rigid but porous mold, of relevant nano or micro length scales, which is employed for the casting of materials. The material to be cast, or more commonly, the precursor, fills the pores of the template and is casted as a morphology which is reverse of the original morphology of the mold. This morphology can be explained as a "*negative replica*"[22,23] of the original template taken. The template is removed afterwards, either by calcination at high temperatures or by a chemical etching method, which involves strong acid/base. In addition, double replication is also used commonly in the case of MgO and is discussed in section 2.1.2.

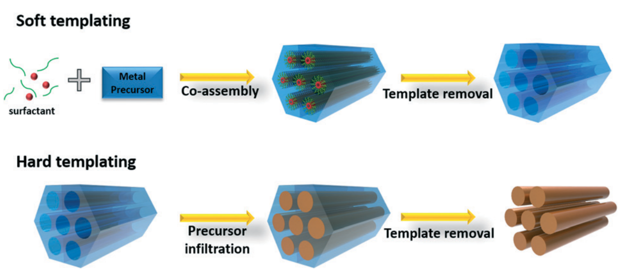


Fig. 2 Soft and hard templating methods for synthesizing MgO.

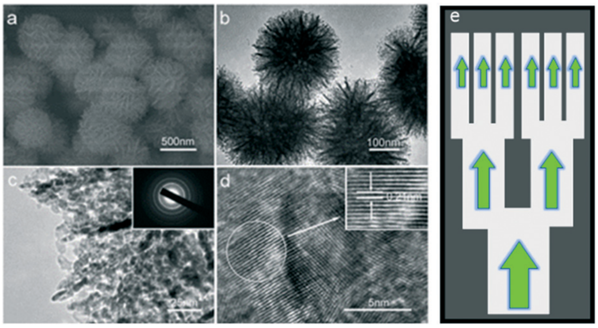


Fig. 3 (a) SEM and (b and c) TEM images and (d) HRTEM of the flowerlike magnesium oxide. The inset in c shows the selected-area electron diffraction (SAED) pattern. The inset in d shows a magnified HRTEM image. (e) Schematic representation of the tree-like hierarchical system (Fig. 3a–d reprinted from ref. 24 with permission from American Chemical Society, Copyright 2008 American Chemical Society; Fig. 3e reproduced from ref. 8 within the guidelines provided by the Royal Society of Chemistry. Copyright 2016 Royal Society of Chemistry).

2.1.1 Soft templating. Commonly employed templates are surfactants and polymers like polyvinylpyrrolidone (PVP), sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB), and polyethylene glycol (PEG).

MgO hierarchical nanostructures were prepared initially by taking PVP.[24] Magnesium oxides were synthesized by a two-step process. In the first step, magnesium glycolate with an interesting twisted flower-like hierarchical structure was

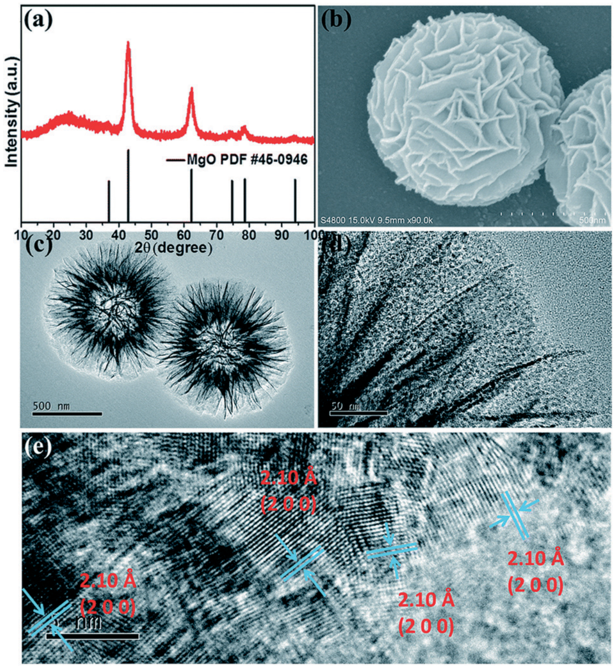


Fig. 4 (a) XRD pattern, (b) SEM and (c–e) TEM images of flowerlike MgO hollow spheres. Reproduced from ref. 13 within the guidelines provided by the Royal Society of Chemistry. Copyright 2016 Royal Society of Chemistry.

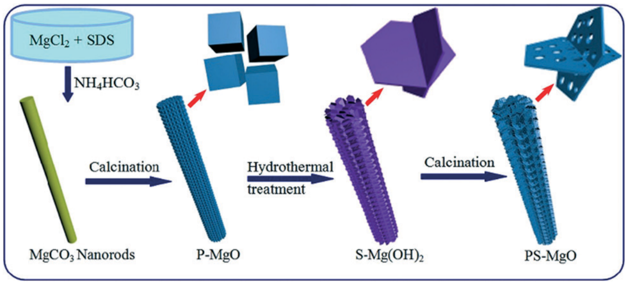


Fig. 5 Formation of PS-MgO. Reprinted from ref. 26 with permission from Elsevier.

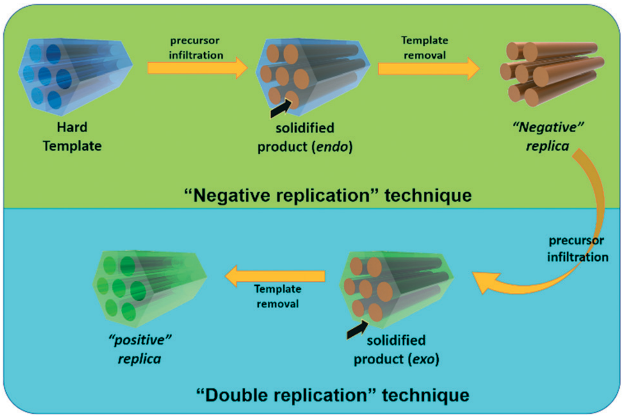


Fig. 6 A schematic representation depicting "negative replication" and "double replication" technique.

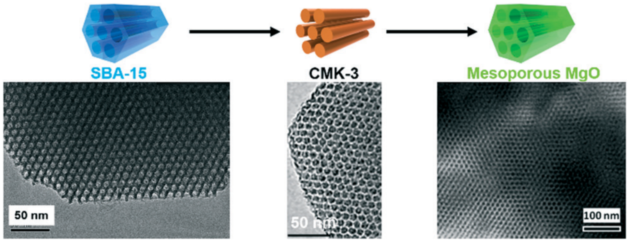


Fig. 7 Mesostructure model and corresponding TEM images of SBA-15 (reproduced from ref. 38 within the guidelines provided by the Royal Society of Chemistry. Copyright 2009 Royal Society of Chemistry), CMK-3 (reprinted from ref. 39 with permission from Nature Publishing Group. Copyright 2003 Nature Publishing Group) and mesoporous MgO (reprinted from ref. 36 with permission from American Chemical Society. Copyright 2006 American Chemical Society).

prepared by the ethylene glycol (EG) mediated process. In the next step, magnesium glycolates were calcined to afford magnesium oxides with preserved morphology. The prepared morphology, as shown in Fig. 3a–d, has a three-level hierarchical setup: the 3D-hierarchical structures consists of twisted leaf-like nanosheets interconnected to each other, which themselves are composed of nanoparticles. This structural hierarchy is referred to as a tree-like hierarchy[8] (Fig. 3e). A similar methodology, with slight modification, was employed by Yang and coworkers[13] to afford flower-like hierarchical hollow spheres (Fig. 4). In a typical experiment, ammonium hydroxide was added, in addition to the metal precursor, PVP, and EG and the so-obtained hollow magnesium glycolates were converted to oxides after calcination. The addition of ammonium hydroxide resulted in Ostwald ripening, where smaller crystallites located in the central part of the spherical aggregates dissolve and re-deposit on the outer parts, resulting in the formation of hollow spheres.

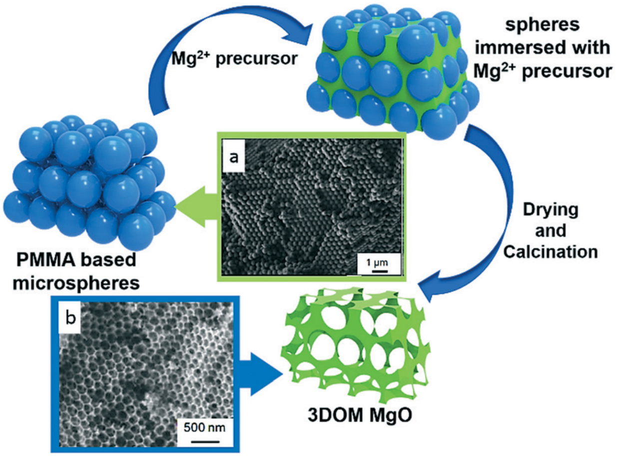


Fig. 8 Schematic description of synthesis of 3DOM materials, along with TEM images of (a) PMMA based spheres and (b) 3DOM MgO. TEM images reprinted from ref. 49 with permission from American Chemical Society, Copyright 2012 American Chemical Society.

A different surfactant was employed to obtain a tunable morphology. Dummer and group[25] used SDS in aqueous basic medium to produce plate-like hexagonal morphology using two different precipitating agents, NaOH and tetrapropylammonium hydroxide solution (TPAOH), as surface-directing agents. In the absence of SDS, while smaller $Mg(OH)_2$ crystallites were obtained by using NaOH, larger crystallites were found with TPAOH due to directed particle

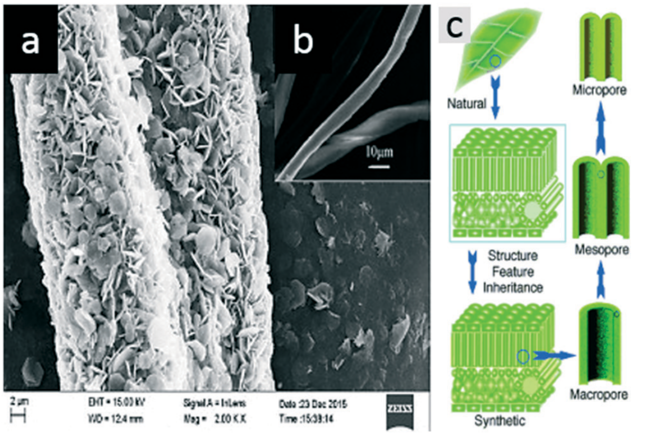


Fig. 9 SEM image of (a) biomorphic Mg-Al LDHs (b) cotton fiber and (c) the hierarchical structure feature of the leaf. (Fig. 9a and b reprinted from ref. 56 with permission from Elsevier, Copyright 2016 Elsevier; Fig. 9c reprinted from ref. 61 with permission from John Wiley & Sons. Copyright 2013 John Wiley & Sons).

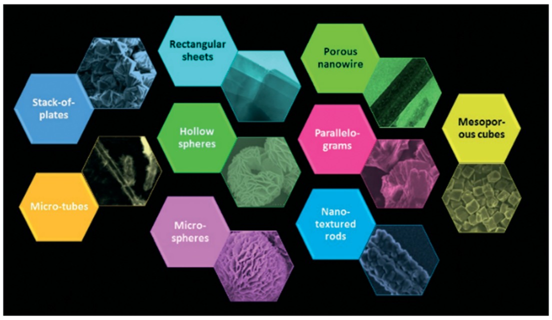


Fig. 10 Different morphologies of MgO as prepared by various precursors: stack-of-plates (reprinted from ref. 77 with permission from Elsevier. Copyright 2011 Elsevier), microtubes (reprinted from ref. 72 with permission from American Chemical Society. Copyright 2007 American Chemical Society), rectangular sheets (reprinted from ref. 78 with permission from Elsevier. Copyright 2010 Elsevier), hollow spheres (reprinted from ref. 13 with permission from Royal Society of Chemistry. Copyright 2016 Royal Society of Chemistry), microspheres (reprinted from ref. 70 with permission from American Chemical Society. Copyright 2015 American Chemical Society), porous nanowires (reprinted from ref. 67 with permission from Royal Society of Chemistry. Copyright 2013 Royal Society of Chemistry), parallelograms (reprinted from ref. 79 with permission from Royal Society of Chemistry. Copyright 2016 Royal Society of Chemistry), nano-textured rods (reprinted from ref. 80 with permission from Royal Society of Chemistry. Copyright 2016 Royal Society of Chemistry) and mesoporous cubes (reprinted from ref. 76 with permission from Royal Society of Chemistry. Copyright 2016 Royal Society of Chemistry).

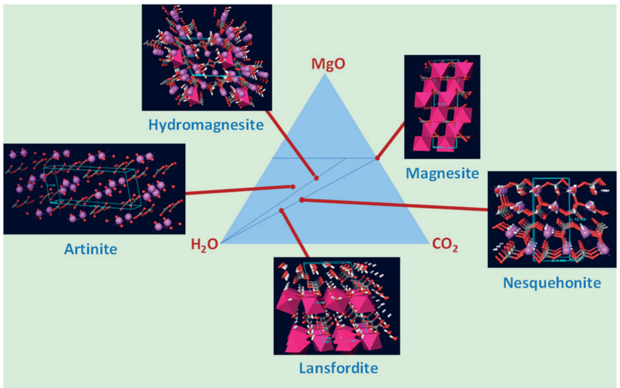
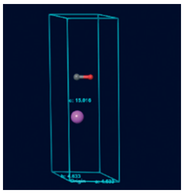
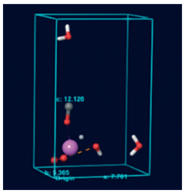
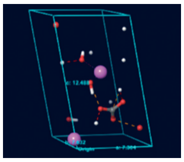
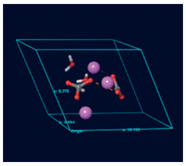
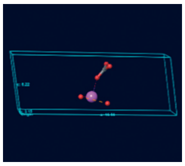


Fig. 11 Crystal structures of some basic hydrated magnesium carbonates and their respective position in the MgO–CO_2–H_2O ternary phase system (not to scale). Color codes: magnesium, purple, oxygen, red, carbon, gray, hydrogen, white. Pink polyhedra depict the MgO_6 octahedra units.

Table 1 Unit cell representation and parameters for different hydrated magnesium carbonate precursors

MgO precursors	Unit cell	Cell parameters
Magnesite		$a = b = 4.633$ Å $c = 15.016$ Å $\alpha = \beta = 90.000$ $\gamma = 120.000$
Nesquehonite		$a = 7.701$ Å $b = 5.365$ Å $c = 12.126$ Å $\alpha = \gamma = 90.000$ $\beta = 90.451$
Lansfordite		$a = 7.364$ Å $b = 7.632$ Å $c = 12.488$ Å $\alpha = \gamma = 90.000$ $\beta = 101.750$
Hydromagnesite		$a = 10.105$ Å $b = 8.954$ Å $c = 8.378$ Å $\alpha = \gamma = 90.000$ $\beta = 114.440$
Artinite		$a = 16.560$ Å $b = 3.153$ Å $c = 6.220$ Å $\alpha = \gamma = 90.000$ $\beta = 99.100$

growth by quaternary alkyl chains associated with TPAOH. The presence of SDS contributed to the tunable surface hydroxyl group density, being greater in the case of NaOH and *vice versa* for TPAOH. In another study,[26] to a precursor metal salt solution, SDS was added with further addition of NH_4HCO_3 and the contents were stirred at 40 °C for an hour. The obtained nanoparticles-assembled MgO microrods were calcined and further treated hydrothermally. At this point, the microrods consisted of hexagonally shaped nanosheets assembled in a crossed fashion. The obtained products were calcined at 500 °C with the formation of porous nanosheets assembled MgO microrods (Fig. 5). Honeycomb-like MgO spheres were prepared by a CTAB-assisted method taking sulfate as precursor and Na_2CO_3 with Na_2SO_4 as mineralizer.[27,28]

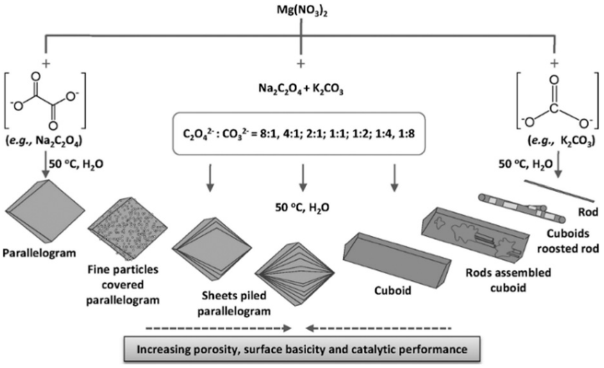


Fig. 12 Morphological evolution of MgO particles constructed from the precipitation reactions of $Mg(NO_3)_2$ in the presence of various ratios of $Na_2C_2O_4$ to K_2CO_3 followed by calcination at 550 °C. Reprinted from ref. 79 with permission from Royal Society of Chemistry. Copyright 2016 Royal Society of Chemistry.

Table 2 Adsorption capacities for hierarchically structured g based oxides for various dye pollutants

Adsorbents	Surface area/m^2 g^{-1}	Pollutants	q_m/mg g^{-1}	Ref.
Porous rod-like MgO	164.1	Congo red	3236	17
Hierarchical MgO nanostructure	147.5	Malachite green	1205	18
Hierarchical MgO nanostructure	147.5	Congo red	1051	18
Porous hierarchical MgO	148	Congo red	2409	20
Mesoporous MgO architectures	94	Congo red	689.7	76
MgO-AOT nanostructures	191.36	Congo red	588	93
Ni–MgO nanostructures	58.55	Methyl blue	367	98
PANI/MgO composites	—	Reactive orange	558.4	99
Hierarchical MgO–$MgFe_2O_4$ composites	—	Congo red	498	100
MgO@silica core–shell	567	Methylene blue	420	101

A popular class of non-ionic surfactants is polymers, widely used as soft templates for the synthesis of oxides. Triblock polymers, known as Pluronics, are composed of polyethylene oxide-*block*-polypropylene oxide-*block*-polyethylene oxide (PEOx–PPOy–PEOx). A one-pot synthesis of ordered mesoporous MgO/carbon composites utilizing the block polymer Pluronic F127 in ethanol was reported.[29] The authors reported that, as the content of MgO increases, a phase transformation from hexagonal to cubic meso-structure was observed. MgO with layer and flower-like rhombohedra morphology was mediated by hydromagnesite and magnesite using Pluronic 123.[30] Polymers like polyethylene glycol (PEG) are also reported in the literature for the synthesis of hierarchical MgO.[31] PEG is used as a structure directing template for the formation of $MgCO_3 \cdot 3H_2O$ with flower-like hierarchical morphology. Solvothermal fabrication of different morphologies of MgO was reported using PVP, PEG, CTAB, Pluronic P123, or F127 surfactants using oleic acid and dodecylamine as solvent[32] producing polycrystalline MgO.

A common challenge with a soft template methodology is that the crystallinity of the product obtained is poor. To tackle this, additives like NaCl are introduced as flux along with the surfactant favoring *in situ* crystallization and thus enhancing strength of the pore walls within the porous morphology of the MgO obtained.[33,34] However, soft-templating involves complicated sol–gel chemistry; therefore, morphology of the obtained product can be highly sensitive to physical and chemical conditions (temperature, pH, and solvent). All these parameters must be well-controlled to avoid disordered products.[35]

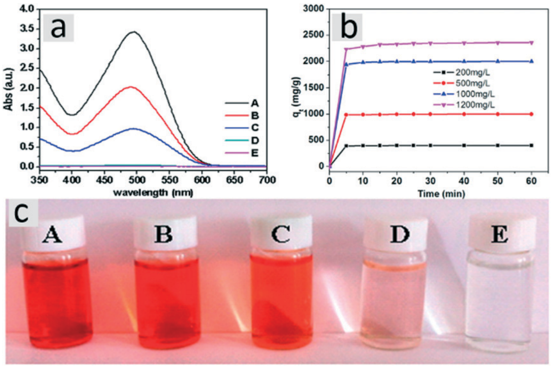


Fig. 13 (a) Photograph of initial Congo red aqueous solution treated by the MgO architectures with different dosage (A) 0 g L^{-1}, (B) 0.05 g L^{-1}, (C) 0.10 g L^{-1}, (D) 0.25 g L^{-1}, and (E) 0.50 g L^{-1}. (b) UV-vis spectra of Congo red after treatment by MgO with different dosages. (c) Time profiles of Congo red adsorption on the porous hierarchical MgO. Reprinted from ref. 20 with permission from American Chemical Society. Copyright 2013 American Chemical Society.

2.1.2 Hard templating. The first method reported on highly ordered MgO preparation was a hard templating "double replication" technique[36,37] (Fig. 6). A SBA-15 silica matrix was synthesized and utilized to develop a CMK-3 carbon matrix. MgO was synthesized by a wet impregnation technique using nitrate as precursor (Fig. 7). Although the products obtained were ordered and mesoporous, the method had its limitations such as poor wettability of CMK-3 and disordering of the ordered MgO mesoporous structure at high temperatures. The role of temperature on lattice disordering was further investigated by Li and group.[40] With each 50 degree rise in calcination temperature (373 to 403 K), the sample became disordered with larger pore size and reduced basicity. Therefore, morphology obtained with the CMK-3 template assisted method was highly governed by the temperature.

The metal oxides were fabricated from alkoxide precursors within the pore channels of the carbon templates. Presynthesized SBA-15 mesoporous silica spheres were employed for the synthesis of hollow MgO and mixed oxide of MgO and Al_2O_3 spheres.[41] While the obtained hollow MgO spheres were highly crystalline with periclase MgO phase, the prepared porous Mg–Al mixed metal oxide hollow spheres showed poor crystallinity due to the amorphous nature of alumina.[41] Carbon spheres obtained by the hydrothermal treatment of carbohydrates like glucose are commonly employed as hard templates for the synthesis of hollow spherical metal oxides.[42,43] Miaosen and group[44] utilized carbon spheres obtained after hydrothermal treatment of glucose, as hard templates for the synthesis of hollow mixed layered double oxides Mg–Al and Mg–Fe LDO (layered double oxides) spheres. The as-prepared precursor LDH (layered double hydroxides) nanosheets possess positive charge and are therefore driven by electrostatic force towards the negatively charged carbon spheres, leading to a coating of LDH on the carbon spheres. After the removal of carbon cores by calcination, multi-metal LDOs with hollow spherical morphology

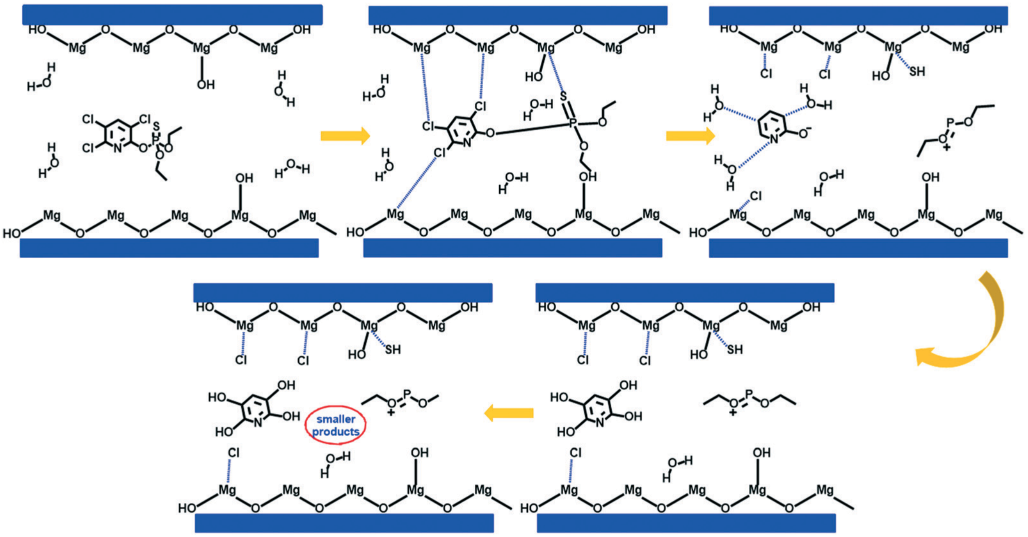


Fig. 14 Plausible reaction mechanism for degradation of chlorpyrifos on the surface of hydroxylated Hr-MgO. Reprinted from ref. 112 with permission from American Chemical Society. Copyright 2017 American Chemical Society.

were formed.[44] Carbon spheres as hard templates have also been synthesized by using a benign route to produce hollow MgO spheres.[45,46]

Hard-templating suffers from a number of drawbacks. First, the choice of a hard template is limited to only a few options. While a silica matrix is practically impossible to be employed for MgO-based materials, use of carbon templates is limited due to poor surface wetting and breakdown of the ordered structure during template removal. When modification of surface functional groups is accomplished using strong oxidizing agents like HNO_3,[37] a large amount of thermal energy is released during template removal *via* combustion, sufficient enough to harm the porous structure of the product.[47] Furthermore, hard templating is a complicated approach involving multiple steps at each stage.

2.1.3 Colloidal crystal templating. Three dimensionally ordered macroporous (3DOM) materials have porosity in the range of sub micrometers and have a close packed, face-centered array, providing a larger pore system for better transportation of matter.[48,49] They are widely designed by using colloidal crystal such as poly(methyl methacrylate) (PMMA) or polystyrene (PS) and exhibit a range of uniform close-packed and interconnected skeletons (reverse opal structure) (Fig. 8).

Generally, the formation of 3DOM metal oxides was employed by infiltering the template with metal alkoxide, which solidified *via in situ* sol–gel process. The fundamental issue with alkoxide precursors is lack of stability with respect to hydrolysis of metal ions and their cost, which limits their use for scaling up. To curb this, metal salts were used along with chelating agents like oxalic acid, citric acid, EDTA, and ammonia.[50] This had an advantage in that the template was impregnated with a metal-chelate solid complex, which was converted to oxide at high temperature. The major disadvantage of this approach was the limitation of preparing mixed metal oxides, as the chelating agent binds differently with different metal ions, resulting in unwanted metal ratios. In this regard, a facile approach was pioneered by Sadakane and group.[49] Metal salts were dissolved in ethylene glycol (EG) solution and EG mediated the formation of a metal-glycolate complex which was subsequently transformed to oxide.[49] Mesoporous ordered MgO was prepared by this approach along with various other metal oxides. To further develop a fast and efficient methodology, an epoxide-assisted sol–gel approach has been designed in recent years for fabricating various metal oxides and composites.[51] So far, only disordered MgO has been developed using PMMA. Recent approaches have been developed that utilize a dual templating method, *i.e.*, a combination of colloidal crystal templating and surfactant templating by utilizing a triblock polymer along with PMMA. The obtained products show an enhanced surface area.[52]

2.1.4 Bio-templating. To promote a "greener" synthesis of these products by using renewable sources from nature, bio-templates like rice,[53] biomass,[54] cellulose,[55] cotton[56–60] and leaves[61] are frequently used nowadays in MgO-based research, thereby reducing chemicals as well as bio-waste. Fig. 9 shows the common bio-templates used for preparing Mg-based oxides and their applications in catalysis. Bio-inspired templating employs scaffolds of the biological tissues ranging from the macroscale to nanoscale.[35] Bio-templating is generally achieved by impregnation with a precursor solution, either by "wet impregnation" or by the "incipient wetness" technique. The wet impregnation technique involves the dispersion of matrix as powder in dilute precursor solution thereby facilitating the diffusion of precursor into pores of the template. However, the incipient wetness approach uses a saturated solution of precursor, the volume of which is restricted to the total pore volume of the matrix to be filled. The incipient wetness technique usually leads to higher loading than the wet impregnation.[47] MgO-based bio-templates are extensively utilized in various fields like bacterial removal,[61] carbon dioxide capture,[54,62] catalysis,[53,59] dye adsorption,[56,61] and other several applications.[58,60]

2.2 Template-free strategies

Besides the templating routes, template-free methods are also widely used in the synthesis of mesoporous hierarchical materials. While surfactant-based soft-templating methods are harmful for the environment, and also result in sample impurity and poor crystallinity of the oxides, hard templating routes usually suffer from disadvantages related to high cost and tedious synthetic procedures, which may prevent them from being used in large-scale applications.[63] Hence, developing facile, economical, and effective methods for creating controllable architectures remains an important challenge.[64] In most template-free methods, mesopores stem from the aggregation of nanoscale building blocks.[65] However, a template-free approach typically provides less architectural control than templating methods.[48]

Template-free strategies to produce morphologically-rich oxides commonly arise *via* direct precipitation, in which synthesis and self-assembly are coupled *in situ* to produce highly ordered structures. This is an ideal scenario, as it lowers synthesis costs and simplifies production processes by eliminating template assembly and template removal steps[48] plus it has various advantages, such as a single-step process, facile large-scale production, and effective avoidance of organic reagents.[17] There is a general approach of obtaining MgO directly through its precursors. These precursors are known to crystallize in different morphologies depending upon their compositions (Fig. 10). For example, hydrated basic magnesium carbonates, such as magnesite ($MgCO_3$), nesquehonite ($MgCO_3 \cdot 3H_2O$), lansfordite ($MgCO_3 \cdot 5H_2O$), artinite ($MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$), dypingite ($4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$) and hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) are known to crystallize in diverse morphologies, due to differences in their crystal structures (Fig. 11). The crystal structure of hydromagnesite, nesquehonite, lansfordite and artinite is monoclinic and that of magnesite is trigonal. The corresponding cell parameters are given in Table 1 for all common hydrated magnesium carbonates except dypingite, whose crystal structure is not known. While nesquehonite and dypingite crystallize in needle and wire shape morphology respectively, the hydromagnesite phase exists in both sheet and assembled sheet morphologies, whereas magnesite forms stable rhombohedral structures.[66] A lot of facile methods have been reported in the literature on MgO formation by pyrolysis of these basic hydrated carbonates.[67] Hydromagnesite displays fascinating morphologies, such as flower-like,[68] nanosheets,[40] microsheets,[20] rosette,[69] microspheres,[70] needle,[71] microtube[72] and house-of-cards[66] by facile synthesis methods. Ethanol-assisted synthesis of hydromagnesite microsheets was reported by digesting $Mg(HCO_3)_2$ in ethanol, which was formed by bubbling CO_2 into aqueous MgO.[20] A direct approach for obtaining hierarchical MgO microspheres was reported through a simple ageing method, taking $MgCl_2$ and Na_2CO_3 to initially form hydromagnesite and thermally decomposing it at 500 °C to form MgO.[70] Hydrothermal treatment was also utilized to synthesize a variety of morphological MgO through hydromagnesite.[40,66,68,73]

Precursors other than basic hydrated carbonates, such as acetate,[74] oxalate,[75,76] and hydroxide,[75] also exhibit very interesting morphologies. MgO with unique "stack of plates" morphology[77] (Fig. 10) was developed using oxalate precursor prepared *via* a novel route: metal chloride solution converted into magnesium oxychloride and then converting it to oxalate using ammonium oxalate. For comparison, a direct route from chloride to oxalate was also followed where an irregular cube-like morphology was obtained. Nevertheless, the mechanism of the formation of the unique "stack of plates" morphology is unclear.[77]

Other than precipitation, hydrothermal strategies have also been employed for the synthesis of unique morphologies.[68,81,82] Interestingly, by introducing a trace amount of sodium tripolyphosphate and hydromagnesite seed into the mixture of potassium carbonate and magnesium nitrate salt, novel MgO microspheres displaying excellent separation performance were obtained.[83] Henceforth, surface modifiers like sodium silicate, sodium polyphosphate, sodium phosphate, sodium tripolyphosphate, *etc.* are incorporated nowadays to modify surface texture as well as surface base properties of the MgO obtained.[17,84,85]

Tailoring surface properties of the obtained MgO by varying its calcinations temperature is an area under investigation.[86] Texturing of the surface of microrods of MgO has been achieved by processing them at higher temperatures. At elevated temperatures, the precursors undergo various stages of decomposition, recrystallization, and crystal growth as well as sintering, that can greatly alter properties related to surface, *i.e.*, adsorption, catalysis, or electrochemistry.[84,85] MgO prepared at higher temperatures displayed distinct nanotexturing of the surface, because crystallite size is a function of temperature. Processing at even higher temperatures resulted in the intergrowth of crystallites at the microrod surface.[80]

Many studies have been reported in the literature on the solvothermal synthesis of hierarchical MgO. In such types of syntheses, the solvent usually plays the role of a *quasi* structure directing agent. The solvent provides adequate solubility to the precursor species. Apart from that, interactions between precursor species are regulated by polarity of the solvent. Therefore, different solvents have been employed and their effects have been studied on the morphology and shape of MgO crystallites. To see the effects of polarity on the medium, Lian and group conducted a controlled synthesis of $Mg(OH)_2$ to generate different morphologies by altering the reaction medium using water and ethanol.[87] While an aqueous medium favored the growth of nanowires, a mixture of ethanol–water medium supported the growth of microflowers. Finally, hierarchical MgO was obtained by calcining the as-prepared precursors. A similar approach was followed by Hadia and Mohamed[88] to synthesize MgO nanowires using NaOH as base and nitrate precursor in 1 : 1 water–ethanol. The nanowires were obtained with a diameter of 16–20 nm. In contrast, by just changing metal nitrate to chloride with 1 : 1 water–ethanol solvent, the obtained products have a nano plate-like morphology with disordered mesopores, as reported by Ling and group.[89] However, pure water as solvent results in hexagonal nanoplates with bigger crystallite size. Thus, the crystal grows in pure water while the presence of ethanol controls the size of the crystallite. Similar to the above report, Liu *et al.*[90] conducted hydrothermal synthesis of MgO using nitrate precursor in pure water to form hexagonal nano-flakes, consisting of several nanoparticles.

EG is a suitable solvent for the designing of morphology controlled architectures. The high-viscosity of EG may slow down the ion diffusion rate, and thus prevent the particle from growing. Besides, it also plays an important role as a weak reducing agent. Selvamani and coworkers[78] reported a facile synthesis of thin rectangular sheets of MgO by taking metal chloride and urea in pure EG and calcinating the precursors in the second step. On the other hand, Nandanwar and coworkers[91] synthesized MgO microspheres using chloride and urea in a 1 : 1 mixture of water and ethylene glycol (EG). The morphology of the as-prepared MgO is both sheet-like and micro spherical. Hollow microstructures of MgO were also obtained through a similar strategy as above.[92] It was found that the formation of hollow spheres was a time-dependent process, first observed after 5 h. The formation mechanism was based on typical Ostwald ripening.

Different mineralizers also have a direct effect on the morphology of the obtained MgO precursors. This has been excellently investigated by Zheng and group.[79] The authors took different ratios of precipitating agents $Na_2C_2O_4$ and K_2CO_3, and observed a diversity of morphologies ranging from parallelograms to rod-shapes (Fig. 12).

3. Applications in adsorption of water-based organic contaminants

MgO-based hierarchical materials have been extensively employed for removal of dyes from aqueous systems and show excellent removal capabilities against a number of them.[93–97] Owing to the basic sites present on the MgO surface, it has an added advantage to bind electrostatically or through inter hydrogen bonding to dyes.[20,98] Various morphologies of MgO have been investigated for adsorption of pollutants from aqueous systems (Table 2). Out of all the morphologies displayed by hierarchical MgO, micro-spherical or flower-like morphology exhibits maximum adsorption capacity due to high specific surface areas.[18] Tian and coworkers[20] reported excellent adsorption capacity of ~2400 mg g^{-1} of synthesized porous hierarchical MgO for Congo red (Fig. 13). The authors suggested that highly porous hierarchical structure and high surface area are the factors attributed to the high uptake capacity of the adsorbent. Contrary to this, Congo red adsorption capacity as high as 3236 mg g^{-1} was reported by Bai *et al.*[17] Surprisingly, morphology of the MgO reported was rod-like, which was previously reported to be not-so-good for adsorption in comparison with sheet-like or flower-like structures.[30] These contradictory observations were explained by the fact that dye uptake was directly related to surface base properties, crystallite structures, and components of the adsorbent, rather than the specific surface area, which is morphology-dependent. This is consistent with improved dye uptake capacity of other metal oxide composites such as TiO_2 nanoparticles decorated over BiOCl nanostructures[102] or TiO_2-carbon hybrids.[103] The mechanism of the adsorption process is based on electrostatic attraction and surface complexation between the dye molecule and surface hydroxyl groups of the MgO adsorbent. At different pH, the adsorption may vary due to the variable surface charges present on the adsorbent. Since the isoelectronic point of MgO is in the range of pH 12, therefore at pH < 12, the adsorbent will have surface positive charges ($M–OH_2^+$) and hence, uptake of anionic dyes will be maximum before pH 12.[20]

Several studies have been conducted on MgO based composites and their adsorption performance against a number of dyes.[99,104–107] $MgO–MgFe_2O_4$ magnetic composite was employed for Congo red dye removal,[100] which displayed 498 mg g^{-1} adsorption capacity, far better than most of the magnetic materials.[108,109] The presence of a porous and hierarchical structure is likely to provide more surface area resulting in better uptake capacities and rapid adsorption equilibrium. Similarly, Tian and co-workers studied the performance of hierarchical porous $MgAl_2O_4$.[110] The maximum adsorption capacity was found to be 845 mg g^{-1}. On the other hand, high surface area core–shell MgO@mesoporous silica spheres were investigated for their adsorption performance against methylene blue.[101] The composite exhibited 420 mg g^{-1} uptake capacity for methylene blue. The role of silica was to serve as a strong shell to enhance mechanical stability as well as to provide mesopores for greater adsorption of pollutants.

Other than dyes, there are various other emerging contaminants like pesticides, which display adverse health effects. Degradation of acetaminophen,[19] 2-chloroethyl ethyl sulphide[111] (2-CEES) has been studied with mesoporous MgO. The adsorption of 2-CEES was compared among MgO and its composites MgO/SiO_2 and MgO/Fe_2O_3 prepared by an aerogel method and the silica composite displayed maximum capacity. It was found that mesopores play a relevant role as reactive sorption centres for 2-CEES while micropores are more important for smaller molecules which could be the products of surface reactions/2-CEES decomposition.[111] Recently, our group studied the adsorption of chlorpyrifos on hierarchical porous MgO (Hr-MgO), derived from hydromagnesite.[112] The maximum adsorption capacity was found to be excellently high at 3970 mg g^{-1}. The mechanism was revealed by using various experimental techniques as well as using density functional studies and it was found that hydroxylation of the MgO surface is important for destructive chemisorption of chlorpyrifos. The mechanism is depicted in Fig. 14.

4. Conclusions and outlook

Ordered hierarchical MgO has received great attention in adsorption applications arising from their interconnected pores, extended pore volume, enhanced surface area, and good thermal stability. We have reviewed that by modifying surface properties like morphology and textural properties; magnesium oxide can display outstanding adsorption performance. It is displayed clearly that the presence of pores and readily accessible adsorption sites can provide efficient mass transport within the pores.

The key issues for applications of hierarchical adsorbents on a commercial scale depend on the overall cost and energy efficiency of the methods employed to produce high yield products. Furthermore, regeneration of the adsorbent is another obstacle which needs to be overcome. While employing hard templates is costly for a scale-up, soft templated methods, despite being facile and cheap, do not result in a durable morphology. Therefore, simultaneous development of hard and soft templating methods for the synthesis of materials with a variety of morphologies is the need of the hour.

With the introduction of diverse and better strategies for their development, hierarchical porous MgO adsorbents have displayed excellent adsorption and removal capacities for water-based pollutants. Their commercialization lies in the potential to achieve maximum regeneration performance. It is, therefore, of vital importance to design adsorbents with improved recyclability, taking care of the overall cost efficiency.

Conflicts of interest

There are no conflicts to declare.

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