



Recent development in the environmental application of nano-sized MgO

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Abstract. Nano-sized MgO processes good thermal stability, nontoxicity, environmental friendliness and simple synthesis. It is more versatile to be used as an antimicrobial agent, fire retardant, pollutant adsorbent, active catalyst and catalyst support. These support its wide applications, particularly in environmental protection and restoration. While few real practical applications have been reported yet. To promote the practical application of nano-sized MgO in environmental science, this review systematically summarizes the structure–function relationship, property-derived applications, synthesis methods, and related growth mechanisms of nano-sized MgO with different sizes and morphologies. The advantages and disadvantages of different synthesis approaches were compared to promote the practical applications of nano-sized MgO. Micro-sized flower-like MgO with hierarchical micro-nanostructure was also reviewed due to its high activity of nanomaterials, multi-functionality and easy recovery of micro-materials. Composites of nano MgO-based materials were also reviewed focusing on their composition and application. In the last section of this review, the challenges and development directions of the practical application of nano-sized MgO are proposed.

Keywords. Nano-sized magnesium oxide; morphology; environmental application; preparation methods; flower-like.

1. Introduction

Due to insufficient anticipation and unfavourable prevention of the negative impacts of highly developed industries, the negative impact of industrial development on the environment exceeds the self-cleaning capacity of the environment and causes harmful results expressed by resource shortage, environmental pollution and ecological damage [1–3]. The direct damage and impact of environmental pollution on the ecosystem have led to the emergence of atmospheric environmental pollution, marine pollution, urban environment and other problems with global impact [4].

With the continuously globalized economy and trade, deeply internationalized environmental pollution and transboundary moved waste became a prominent manifestation [5]. Many minerals with nanostructures exist in nature, such as clay minerals and calcium, magnesium, iron and manganese oxide nanoparticles. Many natural nano minerals are non-toxic, inexpensive, abundant and have a large specific surface area and cation exchange capacity, and have become a hot research topic in the environmental field in recent years [6]. Synthetic nanomaterials are

materials with a certain nanostructure synthesized by physical and chemical processing methods. Compared with natural nanomaterials, synthetic nanomaterials are purer in composition, more diverse in structure and more outstanding in performance. Due to their generally large specific surface area and many surface-active sites, synthetic nanomaterials have received continuous attention in the treatment of environmental pollutants [7].

Among these, inorganic nano-sized materials have been widely applied in multidisciplinary sectors including energy, environment, medicine, material and biotechnology sciences due to their high stability [8–10]. Special concerns about their environment and health risks compel scientists to be more careful about their screening, particularly for their applications involved with human life. Magnesium oxide (MgO), which was recently found to be bio-compatible and bio-degradable [11,12], was worthy of in-depth review.

As with other nanomaterials, the removal of contaminants by MgO nanoparticles is closely related to their specific surface area. In general, a large specific surface area is beneficial for the removal of pollutants [13]. For MgO, the smaller the size, the larger the specific surface area, and

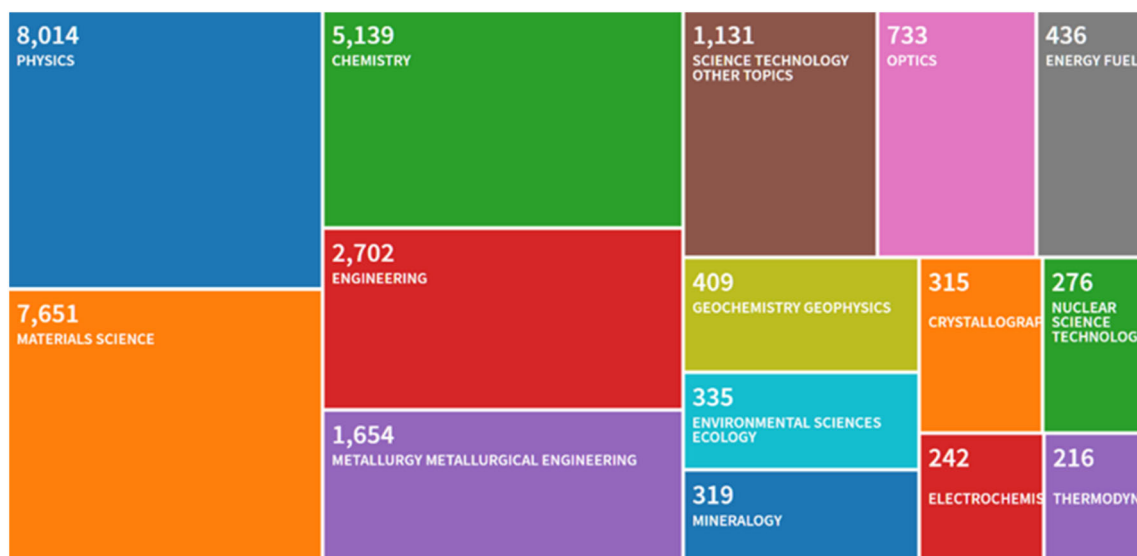


Figure 1. Research areas of published papers concerning nano-sized MgO.

the more the corresponding active sites, the more favourable the removal of pollutants. However, the smaller the size, the more difficult it is to separate and recover the precipitation after pollutant treatment. And when the particle size is larger, its specific surface area is smaller, and the removal of pollutants is not effective. In contrast, flower-like MgO with a multistage structure generally has a larger specific surface area and better pollutant removal performance, thus has a wider application prospect in the environmental field [14].

The great importance of nano-sized MgO was supported by its scientific publication numbers (figure 1): a WOS database searched on January 28, 2021, returned 29572 results for ‘nano-sized magnesium oxide’ and ‘nano-sized MgO’.

As shown in table 1, among the mainstream inorganic nanomaterials, nano-sized MgO reveals good thermal stability, nontoxicity, environmental friendliness and simple synthesis [15–17], thus can be used as antimicrobial agents [18], fire retardant [19], pollute adsorbent [20], active catalyst [21] and catalyst support [22]. These excellent properties and applications make them very broad prospects in environmental protection and restoration.

To date, methods including solid phase, liquid phase and vapor phase oxidation have been developed to synthesize nano-sized MgO with various sizes and morphologies [23]. While most of them were unable to mass-produce nano-sized MgO.

Therefore, this review systematically summarizes the structure–function relationship, property-derived applications in the environment, preparation methods, and related growth mechanisms of nano-sized MgO with different sizes and morphologies. The advantages and disadvantages of different synthesis approaches were summarized to promote the real industrial applications of nano-sized MgO.

One other point worth emphasizing is that the flower-like micro-sized MgO with a hierarchical micro-nanostructure shows excellent flame retardancy due to its unique multi-layer structure [24,25]. This unique morphology also showed high potency for the application as a high-capacity CO₂ adsorbent [26,27]. Therefore, the current development in the synthesis of flower-like MgO was also reviewed. In the last section of this review, the challenges and development directions of the industrial application of nano-sized MgO are proposed.

Table 1. Comparison of mainstream nano powder materials.

Nano metal oxide	Flame retardant	Catalyst	Antimicrobial	UV resistant	Insulating property	Chemical stability	Thermostability	Ageing resistance	Absorbability
MgO	✓	✓	✓	✓	✓	✓	✓	✓	✓
ZnO		✓	✓	✓					
SiO ₂		✓	✓	✓		✓			✓
TiO ₂		✓	✓	✓		✓	✓	✓	
CaCO ₃						✓	✓		

2. Property and environmental application

Generally, MgO is widely accepted as a stable metal oxide due to strong ionic bonds by coordinating one Mg^{2+} with six O^- , which resembles NaCl [28,29]. While MgO with the size down to dozens to hundreds of nanometres offers large numbers of catalytically active sites due to defects formed on the lower coordinated surface, edges and corners [30]. This makes the nano-sized MgO a good candidate for a heterogeneous catalyst. Apart from this, a large specific surface area endows the nano-sized MgO with excellent adsorption properties. That is to say, the high reactivity of nano-sized MgO is determined by both its defect numbers and specific surface area.

2.1 Adsorbent for pollutants

The printing and dyeing industry, paint industry, dye manufacturing industry, mining industry and transportation industry will produce a large amount of wastewater from various related processes [31]. The exact amount of wastewater discharged into the environment by various industries cannot be calculated, but it can be said that this amount is quite large, which is a major environmental problem. Nano magnesia can be used as an efficient dissociation adsorbent to adsorb toxic chemicals and has excellent removal ability for dyes, heavy metal ions and bacteria in water.

2.1a Adsorbent for textile dyes: The discharge of large quantities of dye wastewater from the textile industry has caused irreparable damage to the environment. Among the various traditional physical and chemical methods for dye removal, the adsorption method stands out for its simplicity and efficiency [32].

The general synthesis method of nano-sized MgO is by dropwise adding the alkali solution into excess Mg^{2+} solution. Therefore, a surface of positively charged MgO is formed. This kind of nano-sized MgO is particularly suitable for the adsorption of anionic dyes due to its surface-anchored $-\text{OH}$ and hydrogen bond.

Dalvand *et al* [33] used a MgO nano-sheet with a thickness of 26 nm to dislodge anionic dye pollutants (reactive orange and reactive yellow). Interestingly, the maximum adsorption capacity against reactive orange is more than 30 times higher than reactive yellow. Different from conventional cognition, the author claimed that hydrogen bonds formed between $-\text{NH}_2$ (in dye molecular) and $-\text{OH}$ (on the MgO surface) instead of the electrostatic interaction between the anionic dyes and the MgO surface, which contribute mainly to the adsorption performance of nano-sized MgO. This significant adsorption difference was explained by the different orientations between reactive orange and reactive yellow with MgO. The author deemed the former was normal to the surface of nano-sized MgO,

while the latter lay on the surface of nano-sized MgO. Also, the used MgO adsorbent can be easily regenerated after being calcined in a furnace.

A sol-gel combustion method was used to obtain nano-sized MgO with different crystallite sizes from urea, oxalic acid and citric acid [34]. The smallest crystallite size (12 nm) was found in the nano-sized MgO using oxalic acid as fuel. The nano-sized MgO generated from the oxalic acid fuel showed the highest adsorption capacities (207.0 and 21.5 mg g^{-1} for Reactive Red 195 (RR195) and Orange G (OG) dyes, respectively). Here, the electrostatic interaction dominated the adsorption procedure and thus around 10 times the adsorption capacity against RR195 than that against OG. While 2.5 times SO_3^- groups per molecule in RR195 than that in OG contributed mainly to this boosted adsorption capacity.

As mentioned above, the adsorption capacity of nano-sized MgO against anionic dyes adopted a sequence of Reactive Red 195 > Reactive Orange > Reactive yellow. The charge type on the surface of resulted nano-sized MgO depended mainly on the synthesis method. The generally reported pH of zero-point charge (pH_{zpc}) of MgO is 12.4, which means a positively charged nano-sized MgO [26]. This is because the general synthesis method of nano-sized MgO is dropwise adding the alkali solution into excess Mg^{2+} solution. In another word, a negatively charged nano-sized MgO will form by inversely dropwise adding Mg^{2+} solution into excess alkali solution. By doing this, a nano-sized MgO which applies to cationic dyes could be obtained.

2.1b Adsorbents for heavy metal: Various heavy metals, such as Cr^{3+} , Cd^{2+} , Cr^{6+} , Pb^{2+} , Hg^{2+} , etc., are discharged into various water systems through industrial wastewater and lay a huge health hazard for humans [35]. The adsorption method is widely used to remove heavy metal ions. In the adsorption process, the adsorbent with a high specific surface area firmly captures the heavy metal ions on its surface by physical or chemical means, to achieve the purpose of separation from the solution. Nano-sized MgO of different morphologies, such as nanorods, nanosphere and fishbone fractal nanostructures, were widely used for the adsorption of heavy metal ions [36] due to their surface-anchored affluent defects and abundant coordinated sites.

While the hard recovery of nano-sized MgO from treated water may result in secondary pollution. Ge *et al* [37] synthesized a magnetic Fe@MgO nanocomposite in a precipitation-calcination way. The Fe@MgO core-shell nanocomposite revealed a large specific surface area with mesoporous structure and high magnetic saturation value, which favours magnetic separation. Fe@MgO nanocomposite revealed maximum adsorption capacities of 1476.4 mg g^{-1} for Pb^{2+} and 6947.9 mg g^{-1} for methyl orange, respectively.

A relatively simple and economic combustion synthesis technique was used by Madzokere and Karthigeyan [38] to

synthesize nano-sized MgO with crystalline size ranging from 12 to 17 nm. A quantity of 0.20 g of nano-sized MgO could remove 96% of Cu^{2+} from a 10 ppm CuCl_2 solution, which far exceeded the removal efficiency of 15% by a commercial-grade nano-sized MgO.

Nano-sized MgO with mesoporous structure exhibited outstanding performance in the removal of contaminants from water. While the agglomeration of nano-sized MgO adsorbents suppressed their adsorption capability. Xu *et al* [39] used citrate acid and propionate acid as template-free precursors to fabricate the electropunk mesoporous MgO ceramic fibres. The MgO ceramic fibre showed high adsorption capacities of 2983.4 and 1824.0 mg g^{-1} for Pb^{2+} and Cd^{2+} , respectively. The high capacity of mesoporous MgO ceramic fibre was ascribed to its hydroxyl-rich surface by releasing sufficient OH^- with good movability in water.

Nano-sized MgO is hard to be recovered from water, which may result in potential danger to human health. Even magnetic recovery could not guarantee 100% recovery efficiency. Immobilizing the nano-sized MgO onto the ceramic fabric is very favourable for both its full recycling and easy regeneration.

In the above literature, some special morphologies of MgO nanoparticles, especially mesoporous magnesium dioxide nanoparticles, have a higher adsorption capacity, since they possess a higher specific surface area than other morphologies such as ordinary spherical- and rod-shaped particles. And these mesoporous MgO nanoparticles have the merits of good solution mobility and easy separation from solution, which is beneficial to saving energy and reducing operating costs in practice. Besides, nano-sized MgO is not efficient in adsorbing all heavy metal ions. For example, their efficiency in adsorbing Cd^{2+} is much lower than that of adsorbing Pb^{2+} . More efforts are needed in the future to make nano-sized MgO capable of adsorbing a wide range of heavy metal ions.

2.2 Adsorbent for CO_2 at intermediate temperature

The massive emissions of CO_2 account mainly for the growing greenhouse effect and rising global temperatures, as well as rising sea levels [40]. Artificial capture of CO_2 is one of the effective solutions. MgO is one promising CO_2 adsorbent due to the widely available Mg-contained minerals in nature that can be transferred to MgO at scale economically. MgO exposed to air is easy to absorb water and carbon dioxide and gradually becomes alkaline magnesium carbonate, lighter products than heavy products, and water is combined more quickly, under certain conditions to generate magnesium hydroxide, which is slightly alkaline and more easily adsorbed acidic carbon dioxide. While generally, the CO_2 adsorption capacity of pure MgO is only ~ 2 wt%. Nano-sized MgO with both high specific surface area and basic sites is more suitable for the adsorption of CO_2 at medium temperatures due to its low regeneration

temperature, thermodynamic feasibility, easy tuning of the basicity and overall low energy consumption [41–43].

Hiremath *et al* [44] synthesized mesoporous MgO nanoparticles via the simple complexation-combustion method by using glycine (G) and urea (U) as fuels. Mesoporous MgO nanoparticles showed the highest sorption capacity of 1.34 mmol g^{-1} at 200°C. Compared with solid nano-sized MgO, mesoporous nano-sized MgO is a much better fit for CO_2 storage due to its higher specific surface area, enhanced basicity of oxygen sites due to vast defects and increased mass transfer derived from porous structure.

Guo *et al* [45] investigated the promoted effect of rice husk ash on the CO_2 sorption performance of nano-sized MgO. The rice husk ash-supported MgO (20 wt% MgO) featured the highest CO_2 adsorption capacity of 4.56 $\text{mmol CO}_2 \text{ g}^{-1}$ due to the textural structure, nano-crystallized MgO particles, uniformly dispersed active components and enhanced surface basicity. The adsorb capacity only dropped down to 7.68% after 10 repeated adsorption cycles.

Composites of MgO nanoparticles with other alkaline metal salts or oxides often show stronger CO_2 capture capacity than single materials. NaNO_2/MgO prepared by Wang *et al* [46] showed significantly higher capture capacity than pure MgO nanoparticles in multiple cycles of adsorption. In particular, the NaNO_2 -promoted MgO exhibited shorter induction time, faster adsorption rate, higher uptake capacity and better stability over a wider temperature range. This is due to the rough surface created during the conversion of nitrite to nitrate, which slows down the decrease in specific surface area due to the increase in the volume of MgO as a result of multiple cycles.

As reported, to ensure a largely kinetically controlled carbonation profile, the ideal grain/particle size of nano-sized MgO should be <100 nm [47]. Hence, porous flower-like MgO spherical microstructure composed of nanostructured sheets, which will be discussed in detail in section 4, would be a favourable morphology for high-performance CO_2 sorbents.

2.3 Catalyst for the degradation of organic pollute

Industrial emissions of organic pollutants pose a serious threat to public health and ecosystems due to their toxicity and internal accumulation properties [48]. To date, various biological, physical and chemical methods have been developed to treat organic pollutants. Biological methods are environmentally friendly, but the associated technologies are expensive.

Traditional physical techniques, such as adsorption, have shown excellent performance in removing organic pollutants from aqueous solutions, but they require additional cumbersome treatment. The degradation of organic pollutants in industrial wastewater by chemical degradation has received great attention due to its enormous potential [49].

Among the developed methods, photocatalytic degradation by UV/solar light is one of the most promising technologies due to its simple steps and low cost [50]. Recent studies revealed that nano-sized MgO bears a photocatalytic effect and can be used as a photocatalyst for the degradation of organic dyes in aqueous solutions due to their moderate basicity and high specific surface area.

MgO can activate O_3 to form more hydroxyl radicals, thereby catalysing the ozonation reaction for the degradation of organic pollutants. Also, MgO has shown good catalytic performance in the degradation of a wide range of organic pollutants due to its high activity, environmental friendliness and low toxicity. Mashayekh-Salehi *et al* [51] prepared MgO nanoparticles by thermal/sol-gel method and the products showed high catalytic degradation activity against phenol acetate with 71.5% degradation. In the MgO/ O_3 system, complete degradation of phenol acetate could be achieved in 15 min. Zhu *et al* [52] degraded the quinolone by homogeneous precipitation obtained by nano-sized MgO. The addition of nano-sized MgO significantly boosted the degradation efficiency for quinolone by ozone from ~40 to 90%.

The large number of structural defects induced by -OH present on the surface of nano-sized MgO play a key role in its usage as a catalyst for the degradation of organic pollutants.

2.4 Catalyst for the biodiesel production from recycled cooking oil

Waste cooking oil is a difficult household waste to treat. It can be converted into biodiesel using catalytic transesterification. Transesterification is a key technology for biodiesel production, which takes place between the ester group of the waste oil and an additional alcohol hydroxyl group in the presence of a non-homogeneous or homogeneous catalyst. Homogeneous catalysts suffer from corrosive effects, high cost, high intercalation with the liquid phase of the system, and toxic by-products. Heterogeneous catalysts are widely used in biodiesel manufacturing as they avoid most of these drawbacks [53].

Recently, nano-sized MgO as a heterogeneous catalyst was widely applied in biodiesel production due to its high specific surface area, large porosity and affluent surface oxygen vacancy [54]. MgO's moderate surface basicity, which is significantly different from other acidic, neutral, or amphoteric carriers and adsorbents, determines that it can be a very promising catalyst or catalyst carrier for applications. The cost of biodiesel production is 1.5 times the price of petroleum diesel, limiting its further application. As an alkaline solid catalyst, nano-sized MgO has a lower reaction temperature than acid catalysts, can react at atmospheric pressure, have fewer side reactions, and has no oxidation reactions. Thus, produce biodiesel at a lower price. Starting from recycled waste cooking oil can

further reduce the cost of biodiesel and at the same time reduce the pollution of the environment.

Esmaili *et al* [55] produced biodiesel from *Moringa oleifera* seeds oil using nano-sized MgO as a catalyst using the transesterification method. The highest biodiesel efficiency of 93.69% was achieved at the temperature of 45°C, 4 h reaction time, the methanol-to-oil molar ratio of 12:1, and 1 wt% catalyst concentration.

Basyouny *et al* [56] synthesized a clinoptilolite decorated with a nano MgO (MgO/CP) hybrid structure starting from green tea extract. MgO/CP showed a specific surface area of $324.5 \text{ m}^2 \text{ g}^{-1}$, an ion exchange capacity of 141.5 meq/100 g, and total basicity of $4.34 \text{ mmol OH g}^{-1}$ which qualifies it as a basic catalyst in the transesterification reaction. The highest biodiesel yield of 94% could be obtained using 4 wt% MgO/CP, 15:1 methanol-to-oil ratio, 60°C under the 1250 rpm stirring from corn oil. A yield of 97.6% after 150 min using 4 wt% of it as catalyst load and 20:1 as the methanol-to-oil ratio at 70°C and stirring speed of 1250 rpm was achieved for palm oil. The recyclability of MgO/CP as a basic catalyst was confirmed after 5 cycles of repeated transesterification reaction.

Biodiesel prepared using MgO nanoparticles as a catalyst has an increased flash point compared to industrial diesel, making it safer during transportation and storage. Some of the products even meet the standards of fuels used in motor vehicles.

The emergence of biodiesel offers a good idea to solve the energy crisis in the future. Its raw materials are widely available and biodegradable, but its high production cost makes it difficult to achieve large-scale production and popularization. The use of nano-sized MgO as a heterogeneous catalyst can reduce its production cost and allow for its large-scale promotion. In addition, the transesterification reaction of waste cooking oil using a MgO nanocatalyst can effectively solve its pollution problem.

2.5 Structure-function relationship of nano-sized MgO

The function of nano-sized MgO was strongly dependent on both its physical and chemical structures. To clarify the structure-function relationship of nano-sized MgO, see details summarized in table 2.

3. Synthesis method of nano-sized MgO

The application of nano-sized MgO depends heavily on its morphology, size and surface-anchored functional groups. Different synthesis methods will result in nano-sized MgO with various characters as mentioned above. Generally, nano-sized MgO is produced by methods including solid-phase synthesis, liquid-phase synthesis and vapor-phase synthesis [59,60].

Table 2. Structure–function relationship of nano-sized MgO.

Property	Particle size/nm	Resulting morphology	Efficiency of applications	Applications
High specific surface area; large numbers of active sites; surface positive charge	~26 thickness	Nano-sheet [33]	500.00 mg g ⁻¹ for Reactive orange	Adsorbent for anionic dyes
	~500	Petal-shaped [57]	227.70 mg g ⁻¹ for Congo red	
	12~89	Hexagonal, cubic and spherical [34]	207.00 mg g ⁻¹ for Reactive Red 195	
Abundant coordinated sites; affluent surface defects	12~17 diameter	Mesoporous agglomerates [38]	96.00% for Cu ²⁺ in 1 h	Adsorbent for heavy metal ions
	~12 thickness	Nano-sheet [37]	1476.40 mg g ⁻¹ for Pb ²⁺	
	~20	Sphere [39]	2983.40 mg g ⁻¹ and 1824.00 mg g ⁻¹ for Pb ²⁺ and Cd ²⁺	
Moderate basicity; vast surface basic sites; high specific surface area	~8	Mesoporous [44]	1.34 mmol g ⁻¹	Adsorbent for CO ₂
	~8	Ellipsoid [46]	0.55 g g ⁻¹	
	4~6 thickness	Nano-sheet [45]	4.56 mmol CO ₂ g ⁻¹	
Abundant interfaces and grain boundary; abundant pores; various lattice defects	~7	Flower-like [58]	92.2% for organic dyes in 90 min	Catalyst for organic pollutants degradation
	10~16	Hemisphere [51]	71.5% in degradation and 62.8% in mineralization for acetaminophen	
	~25	Asymmetric [55]	Biodiesel yield in 93.69%	
High specific surface area; large porosity; affluent surface oxygen vacancy				Catalyst for the transesterification

Table 3. Varied size and morphology of nano-sized MgO synthesized by different methods.

Preparation method	Precursors	Reaction and calcine temperature/ ^o C	Reaction and calcine time/min	Size/nm	Morphology	Advantage	Disadvantage
Solid-phase synthesis	Mg(OH) ₂	-600	-60	50-200	Sphere [75]	Simple process. Simple synthesis; low cost; small size; narrow size distribution; mass production	Difficult control in particle shape
	Magnesite	-1000	-30	5-200 thickness	Nano-sheet [76]		Heavy environmental pollution
	MgCl ₂ ·2H ₂ O and NaOH	25/-	10/-	~ 70	Semi-sphere [77]	Water-free; high yield; simple process; easy control	Difficult control in particle shape
Liquid-phase synthesis	NH ₃ ·H ₂ O and MgCl ₂	25/450	Immediately/120	~ 10 Thickness	Nano-sheet [78]	Small particle size; high purity; low cost	Wide size distribution
	Urea and MgCl ₂	100/500	720/60	35-80	Cubic [79]		
	NaOH and Mg(NO ₃) ₂ ·6H ₂ O	130/700	840/120	~ 25	Fused and agglomerated [80]	Easy crystallite size and morphology control	High cost; high energy consumption
	Urea and Mg(CH ₃ COO) ₂ ·4H ₂ O	180/500	300/300	6-12 Diameter	Thorn-like [81]		
	CTAB, tartaric acid, and Mg(CH ₃ COO) ₂ ·4H ₂ O,	25/600	N/A/360	<100	Sphere [82]	Narrow size distribution; high purity; easy control; less side reaction	High cost; environmental pollution; low speed
	C ₂ H ₂ O ₄ and Mg(NO ₃) ₂	25/500	720/120	6-74 Diameter	Rod-like [83]		
	NaOH and Mg(CH ₃ COO) ₂ ·H ₂ O	25/410	20/90	~ 4	Sphere [84]	High nucleate rate; good dispersity; small particle size	Complex process
	PEG, CTAB, MgCl ₂ ·6H ₂ O and Na ₂ CO ₃	180/600	30/480	~ 8 Thickness	Flower-like [72]	Narrow size distribution; good stability; easy control	Large molecular gap
Gas-phase synthesis	MgB ₂ and O ₂	700/-	—	15-20 Diameter	Nanowire [74]	Easy control; uniform size; high purity	Complex process; high energy consumption; high cost

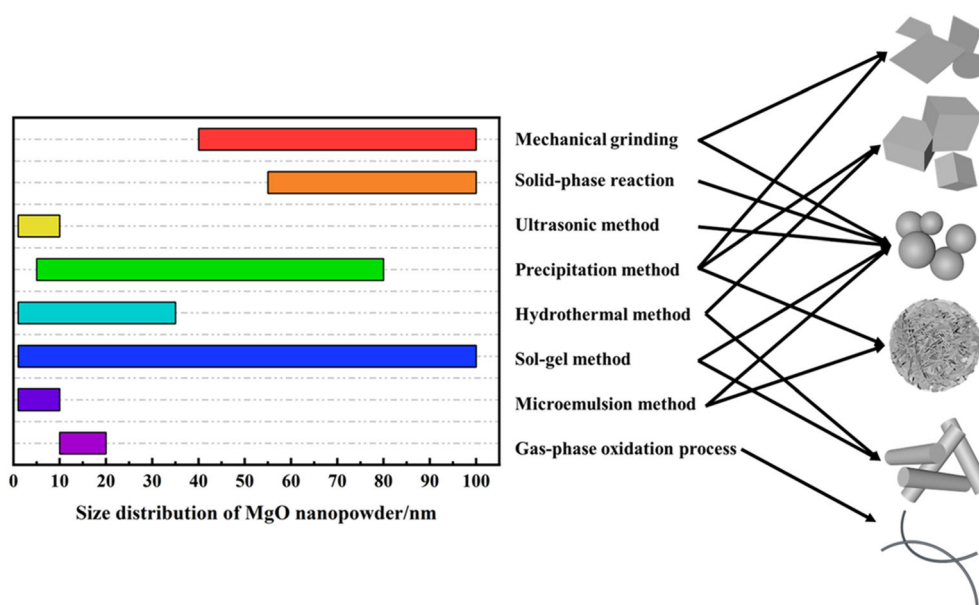


Figure 2. Size and morphology of nano-sized MgO prepared from various methods.

3.1 Solid-phase synthesis

3.1a Calcination followed by mechanical grinding: Mechanical grinding is an easy way to get nano-sized MgO from bulk MgO, in which MgO powder is further smashed under mechanical force. While the impurities are easily introduced during grinding [61]. Moreover, the morphology of the nanoparticles is difficult to be controlled.

This method has the advantages of simple synthesis, low cost, small size in nanoparticles and narrow size distribution, which is suitable for large-scale industrial production. However, the vast dust generated during this process is harmful to the environment [62].

3.1b Solid-phase reaction: In recent years, solid-phase reaction for the synthesis of nano-sized MgO has been developed. This method overcomes the agglomeration problem of the traditional wet method and bears the advantages of no solvent, high yield and easy control of reaction conditions [77].

The solid-phase method generally includes only several simple steps including mixing, grinding, washing and centrifugal separation. The low-temperature solid-phase method has become one of the main methods for preparing new nanomaterials because of its high selectivity, high yield, simple process, controllable particle size and less pollution.

3.2 Liquid-phase synthesis

3.2a Precipitation method: Mg(OH)₂ may be fabricated by precipitating one magnesium salt in a basic solution. Then Mg(OH)₂ could be calcined into nano-sized MgO

[63]. The commonly used precursor solutions are magnesium salts (e.g., MgCl₂, MgSO₄, Mg(NO₃)₂, etc.) and precipitants are strong bases (e.g., ammonia, urea, NaOH, etc.).

While the shape and size of nano-sized Mg(OH)₂ is hard to control by this method, since the very fast precipitation is in the super-saturation state. Then a homogeneous precipitation method with a uniformly increased solution pH value was proposed to easily control the size and morphology of nano-sized MgO [64]. The characteristic of homogeneous precipitation is to steadily release the precipitator into Mg²⁺ containing solution under violent agitation. In doing so, evenly dispersed supersaturated crystalline ions will form a

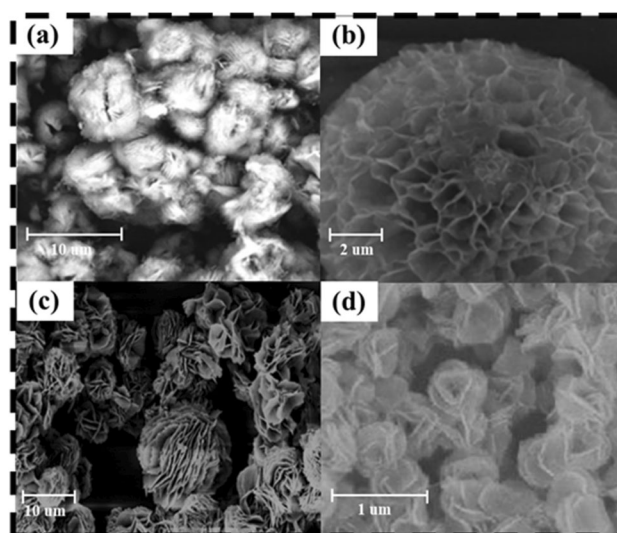


Figure 3. Different morphologies of flower-like nano/micro-sized MgO prepared by (a) Modwi *et al* [88], (b) Ahmed *et al* [90], (c) Ahmad and Mobin *et al* [91], and (d) Cui *et al* [92].

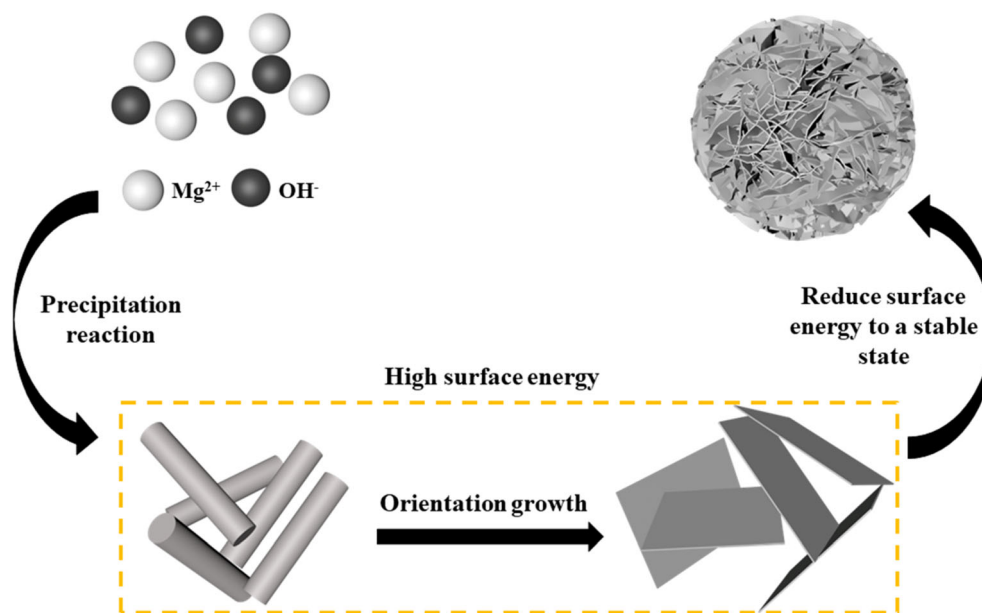


Figure 4. Growth mechanism of flower-like nano/micro-sized Mg(OH)₂.

Table 4. Relationship between composites of nano MgO-based materials and their applications.

Applications	Composite material
Adsorbent for textile dyes	TiO ₂ [96] Carbon [97]
Adsorbents for heavy metal	Fe [37]
Adsorbent for CO ₂ at intermediate temperature	Rice husk ash [45] NaNO ₂ [46]
Catalyst for the degradation of organic pollute	Biochar/Fe ₂ O ₃ [98]
Catalyst for the biodiesel production from recycled cooking oil	Clinoptilolite [56] Urea [99] CaO [100]

uniform and dense nano-sized MgO precursors with small size, narrow distribution and less agglomeration [65].

The precipitation method is easy to control the nucleation, easy to add trace components and homogeneous components, and can obtain high purity nanocomposite oxides. Its reaction process does not require harsh physical conditions, a wide source of raw materials, low cost, a small investment in equipment and high powder yield make it the preferred method for producing low-cost nanomaterials.

3.2b Hydrothermal method: The hydrothermal method is one of the most convenient ways to synthesize nano-sized MgO. Generally, the magnesium salt aqueous solution was

co-mixed with a basic aqueous solution using a varied molecular ratios of Mg²⁺/OH⁻ [66]. Then the reaction was performed in an oven at a fixed temperature. After being rinsed and calcined, the nano-sized MgO could be obtained. Variables including magnesium precursor, solvent and temperature play a critical role in the tailoring of the morphology and size of nano-sized MgO [67].

In the hydrothermal reaction, water act as a solvent, mineralizing agent, and pressure transfer medium to form inorganic products by taking part in dialysis reactions and regulating physicochemical elements [68]. The hydrothermal method can prepare both single-component tiny crystals and two-component special compound powder. It overcomes the problem of hard agglomeration, which is unavoidable by other high-temperature preparation methods. MgO nanopowders prepared by the hydrothermal method are fine, high purity, uniform dispersion, narrow distribution, easy to control the crystalline shape, and controllable shape.

3.2c Sol-gel method: The sol-gel method is realized by hydrolysing metal precursors into targeted metal hydroxide and alcohol. A three-dimensional network taking a porous gel form will form after molecules condensation and water removal. By removing the solvent by drying, a powdery metal hydroxide will be achieved. Final metal oxide could be achieved by further combustion or calcination [69].

The strong point of the sol-gel method is its simplicity, cost-effectiveness, high yield and low reaction temperature (compared with the hydrothermal method). Factors including temperature, time and pH, heavily affect the merits of

the nanoparticles. While easy agglomeration hinders the further application of nano-sized MgO. Surfactant-aided synthesis could remit the agglomeration of MgO nanoparticles.

3.2d Ultrasonic method: Starting by reducing costs, many new processes have been developed to synthesize nano-sized MgO. The ultrasonic-assisted hydrothermal method gets more attention since its narrow size distribution, high purity and high yield besides the short reaction time [70].

The ultrasonic method was proved to inhibit crystal growth and aggregation effectually. Corresponding nucleation velocity was far higher than that of the precipitant method. Nanoparticle with much smaller sizes (down to several nanometres) and uniform size distribution could be easily obtained by this method [71].

3.2e Microemulsion method: The microemulsion method has attracted extensive attention in the synthesis of nano-sized materials due to its convenience, versatility and flexibility. The micro lotion is an isotropic thermodynamic stable system usually composed of surfactants, co-surfactants (alcohols), oils (hydrocarbons) and water [72]. Interfacial-controlled grown mechanism endows this method of homogeneous precipitation and subsequent narrow particle size distribution and good stability. Besides, this method could produce very fine nano-sized MgO particles down to sub-nanometres [73].

3.3 Gas-phase oxidation process

The gas-phase method is divided into physical vapor deposition (PVD) and chemical vapor deposition (CVD). The PVD method uses an arc, high frequency, or plasma high temperature heat source to vaporize the oxide and then collected condensed nanoparticles. CVD is the use of thermal-volatile metal compounds or metal to form the required nanoparticles through a chemical reaction. According to the type of reaction, CVD can be divided into gas-phase oxidation method, gas-phase pyrolysis method, gas-phase hydrolysis method and so on [74].

The advantages of the gas phase method are the easy control of the reaction conditions, and the uniform and high purity of nanoparticles. While the whole process is complex, high energy-consuming and high cost.

3.4 Various sizes and morphology of nano-sized MgO synthesized by different methods

To distinguish the difference more clearly between various nano-sized MgO synthesized by different methods, summarized size and morphology of nano-sized MgO,

advantages and disadvantages of various synthesis methods are summarized in table 2.

In general, spherical MgO of a few nanometres can be obtained within 30 min using the liquid-phase synthesis method at less than 120°C. As the reaction time increases, the product morphology changes from spherical to rods and flakes of several tens of nanometres. The hydrothermal and sol-gel methods of reaction at above 120°C resulted in products that were easily agglomerated and larger in size. Unlike the first two methods, the growth rate is limited by the size of the micelles and the number of reactants inside the micelles for microemulsion method, although the reaction temperature is usually higher than 180°C, products of a few nanometres can still be obtained [85].

In addition, the solid-phase synthesis method results in products that are mostly spherical due to the applied mechanical forces. The vapor-phase synthesis method is particularly suitable for the synthesis of MgO nanowires.

According to table 3, figure 2 reveals the corresponding size and morphology of nano-sized MgO prepared from various methods.

4. Flower-like nano/micro-sized MgO

Excepted for one size-chartered nanosphere, nanorod, nanosheet and nanoplate, hierarchical flower-like micro-sized MgO bears the merit of both high specific surface area of nanostructure and an easy retrievability of microstructure. Moreover, the hierarchical pore structure facilitates the diffusion and transport of adsorbed stuff [86]. These characteristics make flower-like micro-sized MgO promising for many applications, including catalytic degradation of pollutants, flame retardants and carbon dioxide adsorption [87].

The growing mechanism of most flower-like MgO nanoparticles is more or less the same. In the development of petal-type MgO nanoparticles, morphology control is the most important part of the research process. Therefore, the experimental details of the modulation of different morphologies of flower-like MgO nanoparticles need to be further elaborated.

Modwi *et al* [88] demonstrate a pyrolysis route for the synthesis of flower-like micro-sized MgO solely using a MgCO₃ precursor at 700°C in a tube furnace. Extended pyrolysis time results in increased sizes of target flower-like micro-sized MgO. In 1 h, pyrolysis produces the flower-like micro-sized MgO with the highest specific surface area of 27 m² g⁻¹. This sample showed an adsorption capacity of up to 158 mg g⁻¹ against Indigo Carmine dye.

Besides a pyrolysis route, the precipitation method is preferred to prepare flower-like nano/micro-sized MgO due to its less consumed energy and convenience to control the morphology. With the proceeding of the reaction, the Mg(OH)₂ reaches a super-saturation state and precipitates

nuclei driven by the crystal growth tendency. Grown nuclei develop into $\text{Mg}(\text{OH})_2$ wafers. To reach a stable state with minimum total surface energy, a large number of $\text{Mg}(\text{OH})_2$ wafers agglomerate into a flower-like morphology. After being calcined, flower-like micro-sized MgO is then obtained [89].

In addition to precursors and precipitants, the molar ratio of shielding agents for crystal surface growth, ethylene glycol, was used to regulate the morphologies of flower-like nano/micro-sized MgO [90]. The product adsorbed phosphate up to 574.71 mg g^{-1} . Ethylene glycol plays a key role in the morphology, pore structure and corresponding phosphate removal capacity of flower-like micro-sized MgO.

Another method such as the reflux method was also applied for the synthesis of flower-like nano/micro-sized MgO. Ahmad and Mobin [91] report firstly a synthesis of MgO three-dimension(3D)-flower by a simple reflux method. Prepared MgO 3D flowers showed a very high specific surface area up to $218 \text{ m}^2 \text{ g}^{-1}$.

Morphology of flower-like nano/micro-sized MgO via different methods is summarized in figure 3.

The general mechanism for the preparation of flower-like $\text{Mg}(\text{OH})_2$ by precipitation (as shown in figure 4) is that under the supersaturation condition, the nuclei are first precipitated under the driving force of crystal growth, and then continue to grow to form small wafers of $\text{Mg}(\text{OH})_2$. A large number of $\text{Mg}(\text{OH})_2$ wafers agglomerate to form flower-like $\text{Mg}(\text{OH})_2$ to reduce the surface energy and reach a stable state [93].

5. Composites of nano MgO-based materials

Nano magnesia matrix composites also have broad applications in many fields, such as sewage treatment, CO_2 capture, biodiesel conversion and so on [94,95], as shown in table 4.

6. Summary and a look to the future

Nano-sized MgO exhibits low cytotoxicity, biodegradability, biocompatibility and thermal stability due to its variable and controllable special morphology and chemical structure, which make it widely used in many fields. Nano-sized MgO has been extensively investigated to solve environmental problems in the effective removal of anionic dyes, heavy metal ions, organic pollutants, the adsorption of CO_2 and the preparation of biodiesel. Nano-sized MgO has recently been found to be biodegradable in the human body, which can reduce its potential hazards to human organisms and the environment.

Various preparation methods for nano-sized MgO have been reported. For example, the hydrothermal method requires high temperature and pressure, with high energy consumption; the gel-sol method is prone to nanoparticle agglomeration; the reaction conditions of the ultrasonic method need to be precisely regulated and are difficult to control. These problems limit their practical application in industrial production. The simplest method to control the morphology of nano-sized MgO is the homogeneous precipitation method, while the size is usually larger than a few tens of nanometres, and less than 10 nanometres of MgO is difficult to prepare. Ultrasound-assisted homogeneous precipitation has been reported to solve this problem, while the detailed mechanism is not yet clear and is difficult to apply industrially. Micro-emulsion method was used to fabricate MgO down to several nanometres fast and efficiently. While the surfactants used need to be removed in the reprocessing to avoid the altering of the surface chemical structure of obtained MgO nanoparticles.

Up to date, the practical applications of nano-sized MgO are still rare. The main obstacles are listed below.

- (1) MgO with the size down to nanometres is difficult to be recovered. Loading it on the surface of large-size carriers such as fibres, micron spheres, thin films, etc. can effectively solve this challenge.
- (2) Nano-sized MgO are prone to agglomeration, which weakens their unique functions.
- (3) The preparation of nano-sized MgO is complicated, expensive and difficult to produce industrially.

The morphology of nano-sized MgO is another important factor in determining its properties in addition to its chemical structure. Among the different morphologies, flower-like micro-sized MgO has many potential uses due to the high activity of nanomaterials, multi-functionality, and the ease of recovery of micro-materials. In particular, its multi-lamellar structure allows it to demonstrate excellent properties in terms of flame retardancy.

In future research, researchers can prepare a variety of nano-sized MgO with specific properties based on the structure-function relationship presented in this paper to meet various needs in environmental protection and restoration. Also, new economical, environmentally friendly, simple, and precise control of product morphology and mass production methods for the preparation of nano-sized MgO are worthy of further investigation.

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References

- [1] Li J Y and Thompson D W J 2021 *Nature* **599** 425
- [2] Tollefson J 2021 *Nature* **599** 22
- [3] Qiao B and Li S 2013 *Proceedings of 3rd international conference on energy, environment and sustainable development* (Lausanne, Switzerland) p 864
- [4] Yang J R 2014 *Proceedings of 4th international conference on intelligent system and applied material* (Taiyuan, China) p 1049
- [5] Liu J G and Diamond J 2005 *Nature* **435** 1179
- [6] Godelitsas A 2016 Presented at *international conference on computer, communication, and control technology* (Kota Kinabalu) p 5828
- [7] Ikuhara Y, Pirouz P, Yadavalli S and Flynn C P 1995 *A-Phys. Condens. Matter Struct. Defect Mech. Prop.* **72** 179
- [8] Moussavi G and Mahmoudi M 2009 *J. Hazard. Mater.* **168** 806
- [9] Nagappa B and Chandrappa G T 2007 *Microporous Mesoporous Mater.* **106** 212
- [10] Rafati A, Tahvildari K and Nozari M 2019 *Energy Sources Part A* **41** 1062
- [11] Wu S W, Wang H, Sun J, Song F, Wang Z, Yang M *et al* 2016 *IEEE Electron Device Lett.* **37** 990
- [12] Chalkidou A, Simeonidis K, Angelakeris M, Samaras T, Martinez-Boubeta C, Balcells L *et al* 2011 *J. Magn. Magn. Mater.* **323** 775
- [13] Gulkova D, Solcova O and Zdrzil M 2004 *Microporous Mesoporous Mater.* **76** 137
- [14] Karthik K, Dhanuskodi S, Kumar S P, Gobinath C and Sivaramakrishnan S 2017 *Mater. Lett.* **206** 217
- [15] Abdizadeh H, Ebrahimifard R and Baghchesara M A 2014 *Composites Part B* **56** 217
- [16] Gao L, Ren K Y, Ren Z and Yu X J 2018 *Georesour. Geotechnol.* **36** 465
- [17] Kumar M R A, Nagaswarupa H P, Ravikumar C R, Prashantha S C, Nagabhushana H and Bhatt A S 2019 *J. Phys. Chem. Solids* **127** 127
- [18] Azzam A M, Shenashen M A, Mostafa B B, Kandeel W A and El-Safty S A 2019 *Environ. Prog. Sustainable. Energy* **38** S260
- [19] Zhan Z S, Shi J S, Zhang Y, Zhang Y L, Zhang B and Liu W B 2019 *Mater. Res. Express* **6** 11
- [20] Xiong C M, Wang W, Tan F T, Luo F, Chen J G and Qiao X L 2015 *J. Hazard. Mater.* **299** 664
- [21] Ge L F, Peng Z L, Wang W, Tan F T, Wang X Y, Su B *et al* 2018 *J. Mater. Chem. A* **6** 16421
- [22] Tahvildari K, Anaraki Y N, Fazaeli R, Mirpanji S and Delrish E 2015 *J. Environ. Health Sci. Eng.* **13** 73
- [23] Kumar P P, Bhatlu M L D, Sukanya K, Karthikeyan S and Jayan N 2021 *Mater. Today's* **37** 3028
- [24] Jiang L, Li K, Yang H, Liu X, Xu W and Deng B 2019 *Cellulose* **26** 5211
- [25] Tu B, Zhou K, Zhou Q, Gong K and Hu D 2021 *RSC Adv.* **11** 9942
- [26] Han S J, Bang Y, Kwon H J, Lee H C, Hiremath V, Song I K *et al* 2014 *Chem. Eng. J.* **242** 357
- [27] Lu Y, Jiang S P, Wang S P, Zhao Y J and Ma X B 2018 *J. CO₂ Util.* **26** 123
- [28] Oganov A R, Gillan M J and Price G D 2003 *J. Chem. Phys.* **118** 10174
- [29] Malliavin M J and Coudray C 1997 *J. Chem. Phys.* **106** 2323
- [30] Spivey J, Han Y F and Dooley K 2014 *Catalysis* **26** 1
- [31] Tian G Y, Wang W B, Zong L and Wang A Q 2017 *J. Environ. Chem. Eng.* **5** 1027
- [32] Katheresan V, Kansedo J and Lau S Y 2018 *J. Environ. Chem. Eng.* **6** 4676
- [33] Dalvand R, Kianpour E, Tahzibi H and Azizian S 2020 *Surf. Interfaces* **21** 100722
- [34] Nassar M Y, Mohamed T Y, Ahmed I S and Samir I 2017 *J. Mol. Liq.* **225** 730
- [35] Joseph L, Jun B M, Flora J R V, Park C M and Yoon Y 2019 *Chemosphere* **229** 142
- [36] Mahdavi S, Jalali M and Afkhami A 2013 *Chem. Eng. Commun.* **200** 448
- [37] Ge L F, Wang W, Peng Z L, Tan F T, Wang X Y, Chen J G *et al* 2018 *Powder Technol.* **326** 393
- [38] Madzokere T C and Karthigeyan A 2017 *Mater. Today* **4** 9
- [39] Xu C H, Yu Z C, Yuan K K, Jin X T, Shi S Y, Wang X Q *et al* 2019 *Ceram. Int.* **45** 3743
- [40] Buntgen U, Krusic P J, Piermattei A, Coomes D A, Esper J, Myglan V S *et al* 2019 *Nat. Commun.* **10** 2171
- [41] Hassanzadeh A and Abbasian J 2010 *Fuel* **89** 1287
- [42] Ding Y D, Song G, Zhu X, Chen R and Liao Q 2015 *RSC Adv.* **5** 30929
- [43] Ding Y D, Song G, Liao Q, Zhu X and Chen R 2016 *Energy* **112** 101
- [44] Hiremath V, Shavi R and Seo J G 2017 *J. Colloid Interface Sci.* **498** 55
- [45] Guo Y F, Tan C, Sun J, Li W L, Zhang J B and Zhao C W 2020 *Fuel* **259** 116298
- [46] Wang K, Zhao Y W, Clough P T, Zhao P F and Anthony E J 2019 *Chem. Eng. J.* **372** 886
- [47] Armutlulu A, Naeem M A, Liu H J, Kim S M, Kierzkowska A, Fedorov A *et al* 2017 *Adv. Mater.* **29** 1702896
- [48] Alharbi O M L, Basheer A A, Khattab R A and Ali I 2018 *J. Mol. Liq.* **263** 442
- [49] Lu F and Astruc D 2020 *Coord. Chem. Rev.* **408** 213180
- [50] Matafonova G and Batoev V 2018 *Water Res.* **132** 177
- [51] Mashayekh-Salehi A, Moussavi G and Yaghmaeian K 2017 *Chem. Eng. J.* **310** 157
- [52] Zhu H, Ma W C, Han H J, Han Y X and Ma W W 2017 *Chem. Eng. J.* **327** 91
- [53] Issariyakul T, Kulkarni M G, Meher L C, Dalai A K and Bakhshi N N 2008 *Chem. Eng. J.* **140** 77
- [54] Du L X, Li Z, Ding S X, Chen C, Qu S K, Yi W M *et al* 2019 *Fuel* **258** 116122
- [55] Esmaeili H, Yeganeh G and Esmaeilzadeh F 2019 *Int. Nano Lett.* **9** 257
- [56] Basyouny M G, Abukhadra M R, Alkhaledi K, El-Sherbeeney A M, El-Meligy M A, Soliman A T A *et al* 2021 *Mol. Catal.* **500** 111340
- [57] Xu J, Xu D F, Zhu B C, Cheng B and Jiang C J 2018 *Appl. Surf. Sci.* **435** 1136
- [58] Zheng Y J, Cao L Y, Xing G X, Bai Z Q, Huang J F and Zhang Z P 2019 *RSC Adv.* **9** 7338
- [59] Hornak J 2021 *Int. J. Mol. Sci.* **22** 12752
- [60] Julkapli N M and Bagheri S 2016 *Rev. Inorg. Chem.* **36** 1

- [61] Karkalos N E, Markopoulos A P and Kundrak J 2017 *Proceedings of 16th Cirp conference on modelling of machining operations* (Cluny, France) p 281
- [62] Zhao Y N and Zhu G C 2014 *Int. J. Miner. Process.* **126** 35
- [63] Rezaei M, Khajenoori M and Nematollahi B 2011 *Mater. Res. Bull.* **46** 1632
- [64] Yan C L, Xue D F and Zou L J 2006 *Mater. Res. Bull.* **41** 2341
- [65] Pilarska A A, Klapiszewski L and Jesionowski T 2017 *Powder Technol.* **319** 373
- [66] Peng W C, Li J, Chen B J, Wang N, Luo G H and Wei F 2016 *Catal. Commun.* **74** 39
- [67] Sutradhar N, Sinhamahapatra A, Roy B, Bajaj H C, Mukhopadhyay I and Panda A B 2011 *Mater. Res. Bull.* **46** 2163
- [68] Man L F, Kwong T L, Wong W T and Yung K F 2021 *Nanomaterials* **11** 16
- [69] Wong C W, Chan Y S, Jeevanandam J, Pal K, Bechelany M, Elkodous M A *et al* 2020 *J. Cluster Sci.* **31** 367
- [70] Cui W W, Li P, Wang Z M, Zheng S L and Zhang Y 2018 *J. Hazard. Mater.* **341** 268
- [71] Alavi M A and Morsali A 2010 *Ultrason. Sonochem.* **17** 441
- [72] Li S, Zhou B J, Ren B, Xing L, Tan L X, Dong L C *et al* 2016 *Mater. Lett.* **171** 204
- [73] Kumar K S, Narayanan K R R, Siddarth S, Kumar R P, Narayan R B, Goutham R *et al* 2017 *Int. J. Chem. React. Eng.* **16** 8
- [74] Yin Y D, Zhang G T and Xia Y N 2002 *Adv. Funct. Mater.* **12** 293
- [75] Huang Y, Cheng X M, Li Y Y, Yu G M, Xu K and Li G 2018 *Sol. Energy* **160** 208
- [76] Masindi V 2021 *Mater. Today* **38** 1077
- [77] Rashad M, Tekin H O, Zakaly H M H, Pyshkina M, Issa S A M and Susoy G 2020 *Nucl. Eng. Technol.* **52** 2078
- [78] Zhou J J, Xia Y, Gong Y Y, Li W B and Li Z J 2020 *Sci. Total Environ.* **711** 135120
- [79] Shao J Q, Song M Y, Wu G, Zhou Y H, Wan J F, Ren X *et al* 2018 *Energy Storage Mater.* **13** 57
- [80] Devaraja P B, Avadhani D N, Prashantha S C, Nagabhushana H, Sharma S C, Nagabhushana B M *et al* 2014 *Spectrochim. Acta Part A* **118** 847
- [81] Zhao X, Ji G Z, Liu W, He X, Anthony E J and Zhao M 2018 *Chem. Eng. J.* **332** 216
- [82] Mastuli M S, Ansari N S, Nawawi M A and Mahat A M 2012 *Proceedings of 2nd International conference on chemistry and chemical process* (Kuala Lumpur, Malaysia) p 93
- [83] Kumar A and Kumar J 2008 *J. Phys. Chem. Solids* **69** 2764
- [84] Tang Z X and Shi L E 2008 *Ecl. Quím., São Paulo* **33** 15
- [85] Han D Y, Yang H Y and Shen C 2005 *Mater. Sci. Forum* **475** 3543
- [86] Cvetkovic V S, Vukicevic N M, Nikolic N D, Bascarevic Z, Barudzija T S and Jovicevic J N 2019 *J. Electroanal. Chem.* (Nachang, China) **842** 168
- [87] Kuang M J, Yang G L, Xie Z M, Su Q and Liu B X 2018 *Proceedings of 4th International conference on applied materials and manufacturing technology* p 012085
- [88] Modwi A, Khezami L, Taha K K and Idriss H 2018 *Z. Naturforsch., A: Phys. Sci.* **73** 975
- [89] Cao X P, Zhao H, Liu X Y, Luo H H and Liu R J 2020 *J. Cryst. Growth* **550** 125841
- [90] Ahmed S, Pan J S, Ashiq M N, Li D Q, Tang P G and Feng Y J 2019 *Inorg. Chem. Front.* **6** 1952
- [91] Ahmad K and Mobin S M 2019 *Nanoscale Adv.* **1** 719
- [92] Cui Z M, Chen Z, Cao C Y, Song W G and Jiang L 2013 *Chem. Commun.* **49** 6093
- [93] Lee J H, Jeon H, Park J T and Kim J H 2020 *Biomass Bioenergy* **142** 105788
- [94] Liu X M, Liao C Z, Le Lina, Gao H Q, Zhoua J, Feng Z *et al* 2015 *Surf. Interfaces* **21** 100701
- [95] Fernandes M, Singh K R B, Sarkar T, Singh P and Singh R P 2020 *Adv. Mater. Lett.* **11** 20081543
- [96] Bandara J, Kuruppu S S and Pradeep U W 2005 *Colloids Surf. A* **276** 197
- [97] Zheng X G, Huang M, You Y H, Fu X J, Liu Y and Wen J 2017 *Chem. Eng. J.* **334** 1399
- [98] An X F, Chen Y, Ao M H, Jin Y H, Zhan L W, Yu B *et al* 2022 *Chem. Eng. J.* **435** 135087
- [99] Du L X, Li Z, Ding S X, Chena C, Qua S K, Yi W M *et al* 2019 *Fuel* **258** 116122
- [100] Abukhadra M R, Mohamed A S, El-Sherbeeney A M, Soliman A T A and Abd Elgawad A E 2020 *Chem. Eng. Process.* **154** 108024