

REVIEW

The Sol-Gel Method: Pathway to Ultrapure and Homogeneous Mixed Metal Oxide Nanoparticles

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Received: 31 December 2017;

Accepted: 22 April 2018;

Published online: 31 May 2018;

AJC-18903

This article includes an overview of current research on metal oxides and mixed (heterobi-) metal oxides prepared by sol-gel method using variety of precursors which created interest among scientists and technologists due to their structure, reactivity as well as application in almost every field of science. Sol-gel method is a soft-chemistry method requires mild reaction conditions, less equipments as well as produces materials with ultra purity and therefore, widely used as compared to other methods. Authors have explained hydrolytic sol-gel method with examples in the first section and compared the method with conventional solid state method. This section is further divided into subsections explaining the process using metal salts such as chlorides, nitrates, *etc.* and metal-organic compounds as precursor with chelating ligands, polyols, *etc.* The importance of using heterometallic alkoxides as precursor rather than using two different metal precursors is also explained and finally the new advancement in sol-gel method.

Keywords: Hydrolytic sol-gel, Metal oxide, Mixed metal oxide, Sol-gel, Nanoparticles.

INTRODUCTION

Over past few years, sol-gel method have been attracted key attention among scientists and technologists due to the wide applications of metal oxide in almost every areas of science such as medical science, life science, material science, nano-science, *etc.* Earlier, metal oxides were prepared by mixing two or more metal powder reactants followed by heating (furnace heating) to obtain desired product. But this method had some drawbacks which include inhomogeneity of starting material, lack of complete conversion to desired product, high temperature required, release of ash particles which create air pollution and difficult to control the morphology of the particles. Recently, solid state reaction has been used for the preparation of metal oxides using their hydrated metal salts with either NaOH or NH_4HCO_3 in the solid form. Han *et al.* [1] prepared various monometallic (Zn, In, Bi and Sn) oxides using solid state method by mixing their chlorides with NaOH at room temperature whereas Woodfield *et al.* [2] prepared several transition metal oxides such as Fe, Cu, Ag, Zn, Mn, Co, Ni, Pd, Y, *etc.* by solid mixing of their chlorides or nitrates and NH_4HCO_3 at room temperature and characterized them by various techniques.

A wide range of solid, solution and vapour phase techniques are available in literature for preparation of metal oxides include co-precipitation [3-5], hydro- and solvo-thermal method [6-9], sonochemical [10,11], microemulsion method [12,13],

sol-gel method, *etc.* Among these methods, sol-gel method offers many advantages over conventional heating method (solid-state method) *viz.*, (a) high purity and homogeneous starting materials give high purity and ultra homogeneous product, (b) oxides prepared at much lower temperature and show greater homogeneity than prepared by traditional processes such as heating the mixture of oxides around 1100-1300 °C. Hence prevents air pollution and save energy and, (c) product of desired forms (monolith fibres, films, powder) can be obtained using controlled conditions.

Sol-gel method has a long history, starting with synthesis of glass like material about 170 years ago. The term "Sol-Gel" was first proposed by Graham in 1864 [14] while doing research on silica sols, but actual sol-gel experiment was first carried out by Ebelman [15] in 1846 when he observed that on exposure of atmospheric moisture, $\text{Si}(\text{OEt})_4$ was converted into "glass like material". Later on, this process was used in the 1930 by the Schott glass company in Germany to produce metal oxides.

Thousands of papers, books and reviews [16-29] have been published on sol-gel method. A new journal "Journal of Sol-gel Science and Technology" has been launched since 1993, in which the significance of this simple technique has been emphasized by Sakka [30] in 1995. This method is not only for the preparation of metal oxides but also for non-oxide materials such as nitrides, carbides, sulphides, fluorides, *etc.* In present review, our emphasis is on the preparation of metal oxide which

is basically an ionic bonded compound having electrostatic interaction between positively charged metal ions and negatively charged oxide anions. In metal oxides, *s*-orbitals are completely filled which makes them thermally and chemical stable and presence of vacant *d*-orbitals makes them excellent catalysts and their use in electronic devices. Because of their good electrochromic and optical properties, super-conductivity as well as high band gap, metal oxides exhibit wide range of applications in the area of cosmetics [31,32], electroceramics [33,34], colour pigments [35,36] in glass and ceramic industry, catalysis [37-39], batteries [40,41], water and air purification [42-44], removal of heavy metal ions [45,46], decontamination of chemical warfare agents [47-49] and hence, their commercial value is increasing tremendously. Large amount of literature is available on monometallic oxides but less work has been done on the preparation of mixed metal oxides. Mixed metal oxides have improved properties as compared to monometallic oxides. Now-a-days, these materials are prepared in nanosize rather than bulk material. Nanoparticles are those particles whose one of the dimensions (length, width or diameter) is in the range of 1-100 nm. These nanoparticles exhibit unique chemical and physical properties because of their high surface to volume ratio. They show excellent properties as compared to properties of same oxide in bulk.

Two types of sol-gel methods are available in the literature based on the solvent used. Non-hydrolytic (non-aqueous) sol-gel (NHSG) method uses organic solvent whereas hydrolytic (aqueous) sol-gel (HSG) method, as name suggests water is used as a solvent. In this review, authors have explained hydrolytic sol-gel method in detail using all possible precursors with examples in the following sub-headings.

Hydrolytic (aqueous) sol-gel method (HSG): Hydrolytic sol-gel method can be defined as the formation of metal oxide by some chemical reactions including hydrolysis and condensation in aqueous medium under mild condition followed by thermal treatment. In this process, precursor/s as source of cations of required oxide, water as hydrolyzing agent, alcohol as solvent and acid or base as a catalyst or without catalyst are mixed together nearly at room temperature.

Precursors: In conventional heating method, the precursor minerals used were obtained by digging out from earth. These minerals contained mixture of compounds, whereas in HSG method, precursors used are synthetic chemical precursors which are pure and reproducible in their composition. Generally, in sol-gel method, precursors used are either inorganic metal salts such as chlorides, sulphates, nitrates, soluble inorganic oxide or metal organic compounds (containing M-O-C bond) such as alkoxides, acetylacetonates, carboxylates, acetates, *etc.* From all possible precursors, metal alkoxides are considered as suitable precursor mainly due to their easy purification, solubility in organic solvents, high volatility and their extremely facile hydrolyzability. Purification is generally carried out by distillation or recrystallization. Earlier, mixed metal oxide by sol-gel method were prepared by complexation of two homometallic alkoxide precursors but later on preparation of heterometallic alkoxides [50-59] has opened the possibility of using it as "single source precursors" and give ultra homogeneous mixed metal oxide. Mehrotra *et al.* [60-68] prepared alkoxides of most of the elements in the periodic table and published several articles, books and reviews on homo, hetero (bi, tri, tetra)-metallic alko-

xides and suggested that these can be used as precursors for mixed metal oxide. Heterometallic alkoxides have stronger M-O-M' bond. These will certainly produce ultra homogeneous and pure mixed metal oxide, which can be used in electronics especially in semiconductors where ultra purity is required.

Hydrolysis and condensation: The main steps involved in this method using metal alkoxide as precursor are hydrolysis and condensation. The first step is hydrolysis and partial condensation which results in the formation of homogeneous solution (without precipitation). This homogeneous solution with chain like material called sol on mixing precursor, water, alcohol and with or without catalyst. A sol is actually a colloidal suspension of solid particles in liquid. This colloidal suspension (sol) on aging undergoes polycondensation to form thick, viscous or gelatinous material known as gel. High molecular weight intermediates in sol lead to the formation of cross-linked three dimensional gel containing metal-oxygen-metal or metal-hydroxy-metal bond. Gel is a two-component system that consists of a continuous solid and fluid phase of colloidal dimensions. Gel consists of two parts one is solid part which contain three dimensional cross linked high molecular weight material full with solvent, second part is the liquid part *i.e.* solvent which is filled in the vacant space (pores) between the solid part. Method of removal of solvent from the gel strongly affects the properties of oxidic material. Removal of solvent from gel is done either by evaporation or by supercritical drying (Fig. 1). When solvent is removed by simple evaporation at ambient temperature, the pores shrink which result in the formation of xerogel [69], which on calcination forms dense ceramic or glass, whereas on drying under supercritical conditions results in the formation of an extremely porous form of light material called aerogel (Fig. 1). Last step of HSG method is calcination or sintering by which surface M-OH group can be removed by heating.

Prof. Pierre-Gilles de Gennes, a Nobel prize winner (1991) in Physics, wrote a famous book "Scaling concepts in polymer Physics" (Cornel University Press, 1979). In that book, he mentioned sol phase as "polymer solution" and conversion of sol to gel as "sol-gel transition". Earlier, HSG method was used for the preparation of dense and bulk material. Now-a-day, this method is vastly used in the preparation of mixed metal oxide nanoparticles as their activity is enhanced many times because high surface to volume ratio. One of the highly attractive features of sol-gel process is the formation of material of desired physical forms such as monoliths [70], films, fibers, monosized powders, spheres, *etc.*

Hydrolytic sol-gel method occurs in two ways depending on the nature of precursor. With inorganic metal salt as precursor in aqueous medium form a complicated condensed species on changing the oxidation state, temperature and adjusting pH of the solution. Furthermore, the role of counter ion is not exactly known which can change the morphology and chemical composition of the final metal oxides. Removal of these counter ions from metal oxide is also very difficult. Many drawbacks using metal salts as precursors for oxide preparation can be avoided by using metal organic precursors. In another method, precursor is metal organic compound such as metal alkoxides or their derivatives.

Because of extremely hydrolyzable nature of metal alkoxides, Mehrotra *et al.* [71,72] suggested oxo-alkoxides as better precursors for the preparation of mixed metal oxide. They

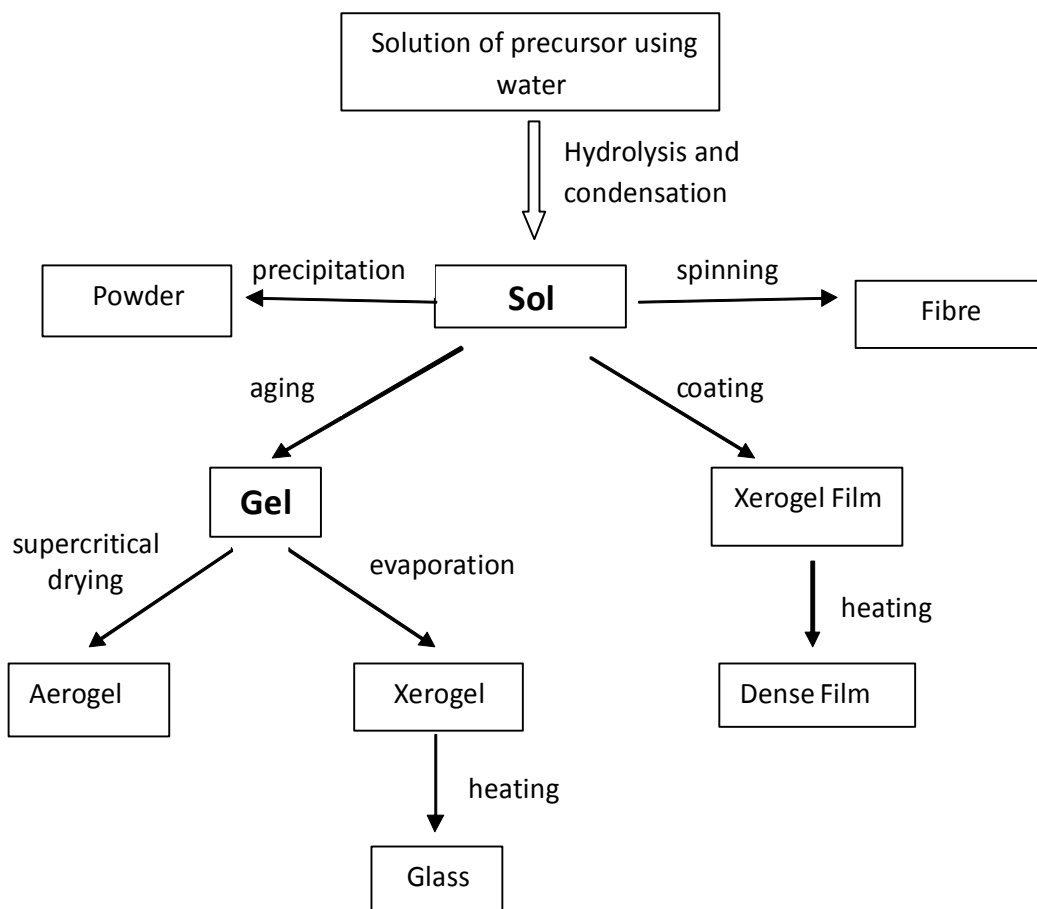


Fig. 1. Scheme showing the formation of variety of forms by sol-gel process

called alkoxides and oxo-alkoxides as "single source precursors" for preparation of mixed metal oxide. Kapoor *et al.* [73,74] as well as other researchers [75-78] also prepared mixed metal oxide using alkoxides or oxo-alkoxide precursor.

Hydrolytic sol-gel using metal salts as precursor: Metal salts (chlorides, sulphates, nitrates, *etc.*) in aqueous medium form hydrated species by coordination with water and form hydrated metal cation. This occurs *via* coordination of electrons to bonding orbitals of metal ion. In the case of transition metals, electron density is transferred to vacant *d*-orbitals. This weakens the O-H bond by the removal of H⁺ with the formation of hydroxo species. Hydrated metal cation acts as Lewis acid hence undergoes polymerization (formation of metal-hydroxy-metal bond) and oxolation (formation of metal-oxy-metal bond) which results ultimately in the formation of polymeric oxides in the solution. The exact series of reactions that takes place in aqueous medium are complex. It may involve the formation of following hydrated species such as aquo $[M(H_2O)_n]^{z+}$, hydroxo $[M(H_2O)_n(OH)_{m-n}]^{z+}$ and oxo $[M(H_2O)_n(O)_{m-n}]^{z+}$ ligands, *etc.* In these reactions, basic aquo species $[M(H_2O)_n]^{z+}$ displaces water from same neighbouring species with the formation of hydroxo- $[M(H_2O)_n(OH)_{m-n}]^{z+}$ species and proton is released in aqueous medium. Hydroxy group in above species is bridged between two hydrated metal complexes $[(H_2O)_nM(OH)_m(H_2O)_n]^{(2z-1)+}$. Subsequently, deprotonation of hydroxyl species led to the formation of M-O-M bond. Polymerization in aqueous medium rarely proceeds smoothly, hence produce heterogeneous metal oxides. If metal in salt is more reactive then rate of hydrolysis will be very

high. But for less reactive metals, rate of hydrolysis can be controlled by pH. In basic solution, reaction moves in the forward direction with the formation of oxo-bridged complex whereas in acidic solution, hydrolysis is either prevented or there will be a hydroxyl complex formation.

Aqueous solution of many metal salts is very stable. Their solution is homogeneous and does not resemble with gel. On heating or drying in air results either the formation of original metal salt or amorphous hydroxide/oxide with irregular particles. To avoid this, small molecules such as chelating ligands or gelators such as EDTA, citric acid, tartaric acid [79], glycolic acid [80], oxalic acid [81], synthetic [82] as well as biopolymers such as starch [83], chitosan [84], dextran [85], *etc.* and synthetic polymers are added with metal salt. These chelating ligands form stable complex with metal ion and the resulting homogeneous solution which resembles with gel. Removal of solvent from the solution results in the formation of glassy solid which on heating gives more ordered metal oxides rather than precipitate. More detail information was explained by Livage *et al.* [86].

Citric acid, a weak tribasic acid, is the most common, low-cost and easily available gelator used in sol-gel method with metal nitrates. In the preparation of metal oxides, metal salt especially metal nitrate is mixed with citric acid and heated to form viscous gel which on pyrolysis in air affords crystalline metal oxide powder. By this method, binary, ternary and quaternary metal oxides can also be prepared. Generally, type of materials obtained by this method is porous and spongy because large amount of gases are released on heating nitrates with organic

material. Some authors reported the use of ammonia and ethylene diamine as base to modify the pH of the solution and to enhance the complexation between metal ion and citrate. The pH of the solution has an important role in the synthesis to prevent the precipitation of hydroxides and stabilize the metal-citrate complex. Yue *et al.* [87] reported the synthesis of NiCuZn ferrite using nitrate/citrate precursors affords porous and more open metal oxide at higher pH. The main advantage of this method is the homogeneity of the starting material. Morphology of nanoparticles is dependent on the concentration of reactants [88], pH, nature of the solvent, type and concentration of additive temperature of the reaction medium as well as pre- and post-heat treatment to the material which has been proved in literature by their SEM studies. Some literature reported the synthesis of ceramic/carbon composites carbon/FePO₄ [89], an important cathode material for lithium ion batteries, using citrate method in inert atmosphere where citrate provides the carbon source. In citrate method, metal nitrates are preferred over other metal salts because of very sharp mass loss step with an exothermic peak is involved in thermogravimetric analysis using nitrate/citrate precursor. The mass loss occurs mainly at around 200 °C in DTA which is associated with fast and self-propagating combustion where counter ion, nitrate and citrate act as oxidant and organic fuel, respectively.

In order to get homogeneous gel, some researchers used synthetic polymers or polyols such as poly(vinyl alcohol) [82], poly(vinyl pyrrolidone) [90], triethylene glycol [91] and poly(ethylene glycol) [92]. Functional groups present in polymers have a strong tendency to form complex in which metal is homogeneously stabilized within the matrix. Cai *et al.* [91] prepared magnetite nanoparticles (Fig. 2) by using triethylene glycol which acted as reducing agent, high boiling solvent as well as stabilizer to prevent agglomeration of nanoparticles.

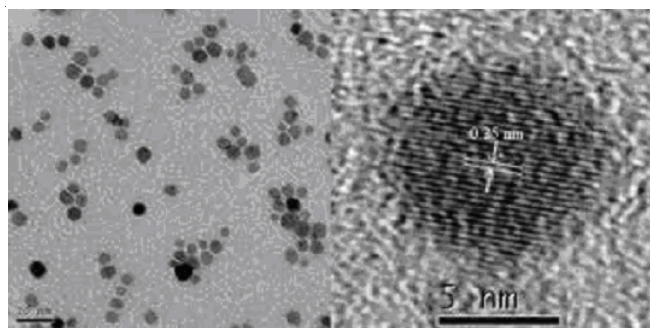


Fig. 2. TEM and HRTEM images of magnetite NPs prepared by SG method. Reproduced from [Ref. 91] with the permission of The Royal Society of Chemistry

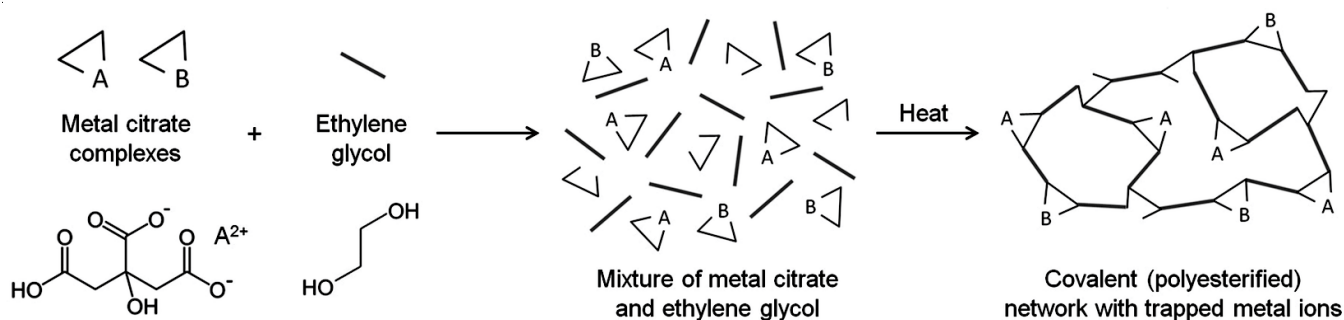


Fig. 3. Formation of MO by Pechini method {reproduced from [Ref. 94]}

Pechini method: Pechini [93] developed this method for the synthesis of lead niobates and titanates. In a typical reaction, aqueous solution of metal salt in the first step mixed with α -hydroxy carboxylic acid such as citric acid, tartaric acid, *etc.* or EDTA as chelating ligands to form complex. Stability of complex depends on pH and concentration of chelating ligand. Most of the transition metals form stable complex with citric acid but some metals like barium does not form stable complex hence an additional complexing agent EDTA also added. Formed complex is then heated with polyol such as ethylene glycol (Fig. 3) to form homogeneous gel. This is the key step of this method [94] *i.e.* trans-esterification (Fig. 4) which occur between citrate complex and ethylene glycol and form covalently bonded polymeric network in which metal ions are trapped. The purpose of adding ethylene glycol is to form more controlled growth of ceramic materials by delaying thermal decomposition of organic surrounding. Recently, it has been observed that a mixture of -OH containing, poly(vinyl alcohol) and poly(ethylene glycol) proved good complexing agents as compared to carboxylic acid for the preparation of homogeneous oxide material such as indium tin oxide [95] and BiFeO₃ [96].

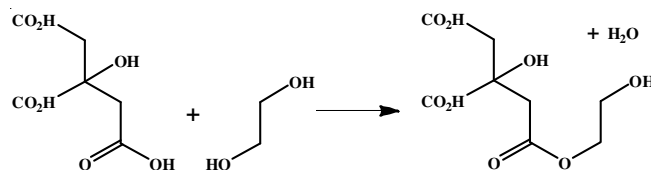


Fig. 4. Trans-esterification reaction between citric acid and ethylene glycol

Homogeneous gel is dried at 110-150 °C to remove water to get polymeric resin. During drying, precipitation is prevented otherwise, it will damage the homogeneity of the final product. Metal oxidic material is obtained after heating in furnace below 400 °C where all organic part decomposes. Earlier, the excess of polyol was added which required high temperature to remove large amount of organic molecules but now a days, polyol is added in the same ratio with that of carboxylic acid. Farbun *et al.* [97] reported the change in the morphology of ZnO (Fig. 5) with the change in the concentration of polyol [98].

Size of the final product particles and the stability of metal citrate complex is also dependent on pH. Many scientists used ammonium hydroxide, ammonia and other base used to optimize pH. Low pH in result in protonation of citrate complex whereas high pH lead to the formation of metal hydroxide precipitate. Abrue (Jr.) *et al.* [99] prepared Pb(Zr_{0.52}Ti_{0.48})O₃ using urea as a base to rise the pH which slowly released ammonia to form

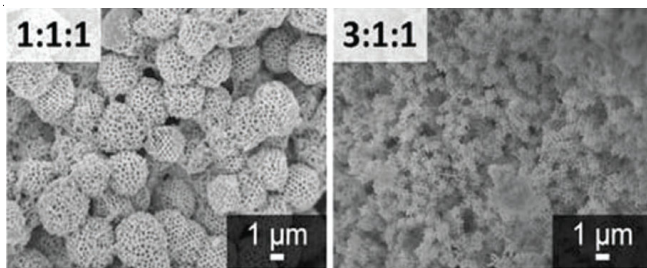


Fig. 5. SEM images of MO Nps prepared by using different ratio of ethylene glycol: citric acid: metal ion. Reproduced from Ref. [98], copyright (2012) ACS

much smaller crystallites. This method not only used for the preparation of metal oxides but also carbides.

Advanced Pechini method has been reported by some group of scientists [100], where they had prepared YBCO superconductor $YBa_2Cu_3O_{7-x}$ by replacing citric acid by tartaric acid or EDTA. This resulted in the formation of homogeneous and larger particles which indicated that branching in polyester is responsible for altering the particles size [101].

Hydrolytic sol-gel using alkoxides as precursor: Metal alkoxides $M(OR)_n$ are versatile molecular precursors for sol-gel synthesis of metal oxides. Many alkoxides are soluble in organic solvents, volatile and highly reactive towards nucleophilic attack. Metal alkoxides are highly moisture sensitive compounds. They readily form precipitate rather than gels when water is added. Hydrolysis undergoes by S_N^2 mechanism. In hydrolysis, water is an essential solvent which initiate the reaction by coordinating itself through oxygen which contains partial positive charge to the central metal centre. This coordination causes instability in precursor molecule and immediately undergoes transfer of proton from oxygen of water to oxygen of alkoxy group. Cleavage of σ -bond between metal and oxygen in $M-OR$ then occurs by the addition of proton from water. Both steps (proton transfer and cleavage) takes place simultaneously, led to the formation of $M-OH$ bond and release of water. In HSG method, water is added just to initiate the reaction. Subsequent condensation step produces water itself. Both hydrolysis and condensation are chain reactions. Very less amount of water is needed which depends upon the amount of reactant. Addition of large amount of water may get precipitation immediately, which then difficult to form homogeneous metal or mixed metal oxides.

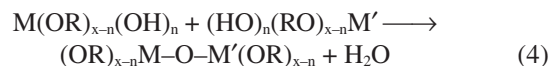


Number of alkoxy group replaced by $-OH$ group depends upon the amount of water added forming $-M(OH)_x(OR)_{n-x}$. Terminal alkoxy groups in precursor hydrolyse first. Condensation reaction takes place by ololation, oxolation or alkoxolation. Ololation is the condensation step in which hydroxyl group is bridged between two metal atoms. There are various types of hydroxyl bridge forms reported in literature [86]. In general, smaller the charge, larger the size of metal, greater will be the rate of ololation. Oxolation (reaction 2) is the condensation step in which oxo bridge is formed between two metal centres.

Rate of hydrolysis is not same for all metal alkoxides. It depends on the electronegativity of central metal, its ability to increase coordination number, steric hinderence of alkoxy group and molecular structure (whether monomeric or polymeric) of metal alkoxides. Generally, coordinatively unsaturated, monomeric alkoxides with small or less sterically crowded alkoxy group undergo fast hydrolysis. According to Livage *et al.* [86], the rate of both hydrolysis and condensation in transition metal alkoxides is five times higher than in silicon alkoxides. In transition metals, low electronegativity and presence of vacant d -orbitals make metal a highly electrophilic centre. Transition metals are coordinatively unsaturated hence increase their coordination number by several numbers when reacted with water. As a result, transition metal alkoxides are much more reactive.

Precipitation during hydrolysis results due to high reactivity of alkoxides towards water which can be prevented by slowing down the hydrolysis process. This can be done by carrying out ligand exchange reaction [50,53,78]. In ligand exchange reactions, alkoxy group is replaced either by sterically more crowded group (such as 2-methoxyethanol, *tert*-amyl alcohol, *tert*-butyl alcohol, *etc.*) or by chelating ligand (diethanolamine, triethanolamine, β -diketones, *etc.*) which not only controls the reactivity but also sometimes solubilize the metal alkoxides.

Only few number of papers has been reported for the preparation of mixed metal oxides using heterobimetallic alkoxides and oxo-alkoxides [71-78] as precursors. Heterometallic alkoxides undergo hydrolysis *via* ligand exchange reaction and form alkoxy-hydroxy sol and gel on aging. Centrifugation followed by heating gives ultra-homogeneous mixed metal oxides. Alternatively, two different metal alkoxides upon hydrolysis followed by condensation gives $M-O-M'$ moiety (reaction 4).



Recent advances in sol-gel chemistry: Although this method is considered to be almost ecofriendly but scientists modified the process according as per their requirements. For example, fractures appear in the preparation of monolith silica gel so conventional heating was shifted to microwave. Some advancements in sol-gel methods are as follows:

Conventional to microwave heating: In HSG method, heating is required for the conversion of gel into desired material which is done either in air or in furnace. This takes more time with high energy consumption, sometimes reaction of gel with crucible may occur as well as inhomogeneity in heating which may afford inhomogeneity in product. Therefore, conventional heating methods were shifted to modern microwave method. Now a days, microwave assisted method is being used for the preparation of ceramic materials. The difference between conventional and microwave method is that in microwave assisted method reactants are heated by energy conversion which increases temperature of the reaction mixture very fast, uniformly as well as the heat is generated internally, whereas in conventional method heating is done by energy transfer and requires external source. For the first time, Komarneni and Roy [102,103] used the microwave in liquid state synthesis for titania gel spheres. Generally, in the preparation of monolith gel cracks appear during aging and drying. But using microwave [104] not only

pore size but also surface area also improved without cracking. Now days, heating method is shifted from conventional to microwave for the preparation of mixed metal oxides [105-107].

Hydrolytic to non-hydrolytic sol gel method: Although, HSG method is highly successful in bulk metal oxide preparation, but it has some drawbacks. In HSG method, chemistry of hydrated metals is complex. All the three steps (*i.e.* hydrolysis, condensation and aggregation) take place simultaneously and are not controllable. Slight changes in the experimental conditions modify the morphology (size and shape), texture and composition of the product. So reproducibility is the major issue *i.e.* HSG method is now replaced by non-hydrolytic sol-gel method in which organic solvent is used rather than water. This method is also known as non-aqueous sol-gel method. There is a tremendous increase in publications including books, reviews and research articles [108-111] based on non-hydrolytic sol-gel in last few years. Role of organic solvent in non-hydrolytic sol-gel method is manifold. It is not only an oxygen provider in metal oxides formation but also modify particle morphology, composition and surface property. In NHSG, oxygen suppliers are either solvents such as alcohol, aldehyde, ketone, ether or organic part of precursor such as alkoxides, acetylacetonates, *etc.* Reactions are much slower than in aqueous medium as they involve breakage of C-O bond rather than O-H. Furthermore, moderate reactivity of C-O bond as well as stabilizing effect of organic groups lead to the formation of materials with improved texture, composition and morphology. Chemistry of C-O bond is well-established so progress of the reaction can be monitored easily.

Preparation of new materials: Earlier, only simple homo- and hetero-metallic oxides were prepared using sol-gel method. Now variety of materials has been prepared for examples, organic-inorganic hybrid materials [112], composite materials, atomic layer deposition materials, *etc.*

Conclusion

Nanoparticles prepared by hydrolytic sol gel method have been described. This process was started using metal precursor with water and alcohol which is now modified to great distinct. Now heating is done using microwave and in place of water, other organic solvents such as acetone, aldehyde, benzyl alcohol, polyols, polymers (bio as well as synthetic) and even chelating ligands are used to get improved properties of mixed metal oxides nanoparticles.

REFERENCES

- S.A. Patil, D.V. Shinde, D.Y. Ahn, D.V. Patil, K.K. Tehare, V.V. Jadhav, J.K. Lee, R.S. Mane, N.K. Shrestha and S.-H. Han, *J. Mater. Chem. A Mater. Energy Sustain.*, **2**, 13519 (2014); <https://doi.org/10.1039/C4TA02267J>.
- S.J. Smith, B. Huang, S. Liu, Q. Liu, R.E. Olsen, J. Boerio-Goates and B.F. Woodfield, *Nanoscale*, **7**, 144 (2015); <https://doi.org/10.1039/C4NR04964K>.
- N.D. Kandpal, N. Sah, R. Loshali, R. Joshi and J. Prasad, *J. Sci. Ind. Res.*, **73**, 87 (2014).
- J. Balavijayalakshmi, *J. Environ. Nanotechnol.*, **2**, 53 (2013); <https://doi.org/10.13074/jent.2013.06.132015>.
- W.S. Peternele, V.M. Fuentes, M.L. Fascineli, J.R. de Silva, R.C. Silva, C.M. Lucci and R.B. De Azevedo, *J. Nanomater.*, Article ID 682985 (2014); <https://doi.org/10.1155/2014/682985>.
- J. Li, Q. Wu and J. Wu, Handbook of Nanoparticles, Springer International Publishing, Switzerland, pp. 295-328 (2015). https://doi.org/10.1007/978-3-319-13188-7_17-1.
- Z. Liu, M. Li, F. Pu, J. Ren, X. Yang and X. Qu, *J. Mater. Sci.*, **22**, 2935 (2012); <https://doi.org/10.1039/C1JM14088D>.
- N. Soultanidis, W. Zhou, C.J. Kiely and M.S. Wong, *Langmuir*, **28**, 17771 (2012); <https://doi.org/10.1021/la3029462>.
- Y. Tian, B. Yu, X. Li and K. Li, *J. Mater. Chem.*, **21**, 2476 (2011); <https://doi.org/10.1039/c0jm02913k>.
- C.J. Mao, H.C. Pan, X.C. Wu, J.J. Zhu and H.Y. Chen, *J. Phys. Chem. B*, **110**, 14709 (2006); <https://doi.org/10.1021/jp061809m>.
- D.P. Dutta, V. Sudarsan, P. Srinivasu, A. Vinu and A.K. Tyagi, *J. Phys. Chem. C*, **112**, 6781 (2008); <https://doi.org/10.1021/jp800576y>.
- A. Bumajdad and M. Madkour, *Nanoscale Res. Lett.*, **10**, 19 (2015); <https://doi.org/10.1186/s11671-015-0730-9>.
- A. Kumar, A. Saxena, A. De, R. Shankar and S. Mozumdar, *RSC Adv.*, **3**, 5015 (2013); <https://doi.org/10.1039/c3ra23455j>.
- T.J. Graham, *Chem. Soc.*, **17**, 318 (1864); <https://doi.org/10.1039/JS8641700318>.
- J.J. Ebelmen, *Liebigs Ann. Chem.*, **57**, 319 (1846); <https://doi.org/10.1002/jlac.18460570303>.
- I. Bilecka and M. Niederberger, *Electrochim. Acta*, **55**, 7717 (2010); <https://doi.org/10.1016/j.electacta.2009.12.066>.
- A. Vious and P.H. Mutin, eds.: L. Klein, M. Aparicio and A. Jitianu, Handbook of Sol-Gel Science and Technology, Springer International Publishing, pp. 1-27 (2016). https://doi.org/10.1007/978-3-319-19454-7_28-1.
- A.E. Danks, S.R. Hall and Z. Schnepp, *Mater. Horiz.*, **3**, 91 (2016); <https://doi.org/10.1039/C5MH00260E>.
- R. Deshmukh and M. Niederberger, "The Sol-Gel Handbook - Synthesis, Characterization, and Applications: Synthesis, Characterization and Applications", ed. D. Levy and M. Zayat, **2015**, Vol. 1: Synthesis and Processing. Wiley-VCH, Weinheim, 29.
- M. Niederberger and G. Garnweitner, *Chem. Eur. J.*, **12**, 7282 (2006); <https://doi.org/10.1002/chem.200600313>.
- M. Niederberger, *Acc. Chem. Res.*, **40**, 793 (2007); <https://doi.org/10.1021/ar600035e>.
- A. Vioux and D. Leclercq, *Heterog. Chem. Rev.*, **3**, 65 (1996); [https://doi.org/10.1002/\(SICI\)1234-985X\(199603\)3:1<65::AID-HCR57>3.0.CO;2-7](https://doi.org/10.1002/(SICI)1234-985X(199603)3:1<65::AID-HCR57>3.0.CO;2-7).
- A. Vioux, *Chem. Mater.*, **9**, 2292 (1997); <https://doi.org/10.1021/cm970322a>.
- P.H. Mutin and A. Vioux, *Chem. Mater.*, **21**, 582 (2009); <https://doi.org/10.1021/cm802348c>.
- L.L. Hench and J.K. West, *Chem. Rev.*, **90**, 33 (1990); <https://doi.org/10.1021/cr00099a003>.
- A.C. Pierre, Introduction to Sol-Gel Processing, Kluwer, Boston (1998).
- H. Kozuka, Sol-Gel Processing, In: Handbook of Sol-Gel Science and Technology, Kluwer Academic Publishers, vol. 1 (2005).
- C.J. Brinker and G.W. Scherrer, Sol-Gel Science: The Physics and Chemistry of Sol Gel Processing, Academic Press Limited, London (1990).
- A. Styskalik, D. Skoda, C.E. Barnes and J. Pinkas, *Catalysts*, **7**, 168 (2017); <https://doi.org/10.3390/catal7060168>.
- S. Sakka, *J. Sol-Gel Sci. Technol.*, **4**, 5 (1995); <https://doi.org/10.1007/BF00486696>.
- P. Singh and A. Nanda, *Int. J. Cosmet. Sci.*, **36**, 273 (2014); <https://doi.org/10.1111/ics.12124>.
- P.-J. Lu, S.-C. Huang, Y.-P. Chen, L.-C. Chiueh and D.Y.-C. Shih, *J. Food Drug Anal.*, **23**, 587 (2015); <https://doi.org/10.1016/j.jfda.2015.02.009>.
- J.S. Park, H. Kim and I.D. Kim, *J. Electroceram.*, **32**, 117 (2014); <https://doi.org/10.1007/s10832-013-9858-0>.
- A.J. Moulson and J.M. Herbert, Electroceramics: Materials, Properties, Applications, John Wiley & Sons Ltd., II Edition, England (2003).
- G. Buxbaum, Industrial Inorganic Pigments, Wiley-VCH, edn 3, p. 315 (1998).
- C.B. Carter and M.G. Norton, Materials, Science and Engineering, Springer, New York (2007).

37. M. Andrianainarivelo, R. Corriu, D. Leclercq, P.H. Mutin and A. Vioux, *J. Mater. Chem.*, **6**, 1665 (1996); <https://doi.org/10.1039/JM9960601665>.
38. K. Bouchmella, P. Hubert Mutin, M. Stoyanova, C. Poleunis, P. Eloy, U. Rodemerck, E.M. Gaigneaux and D.P. Debecker, *J. Catal.*, **301**, 233 (2013); <https://doi.org/10.1016/j.jcat.2013.02.016>.
39. J.C. Védrine and I. Fecheté, *C.R. Chim.*, **19**, 1203 (2016); <https://doi.org/10.1016/j.crci.2015.09.021>.
40. H. Su, S. Jaffer and H. Yu, *Energy Storage Mater.*, **5**, 116 (2016); <https://doi.org/10.1016/j.ensm.2016.06.005>.
41. M.V. Reddy, G.V. Subba Rao and B.V.R. Chowdari, *Chem. Rev.*, **113**, 5364 (2013); <https://doi.org/10.1021/cr3001884>.
42. F. Jinbo and J. Li, ed.: C.S.S.R. Kumar, Nanomaterials for the Life Sciences, In: Nanostructured Oxides, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, vol. 2, p. 287 (2009).
43. S. Pande, H. Swaruparani, M.D. Bedre, R. Bhat, R. Deshpande and A. Venkataraman, *Nanosci. Nanotechnol. Asia*, **2**, 90 (2012); <https://doi.org/10.5923/j.nn.20120204.01>.
44. A. Khaleel, P.N. Kapoor and K.J. Klabunde, *Nanostruct. Mater.*, **11**, 459 (1999); [https://doi.org/10.1016/S0965-9773\(99\)00329-3](https://doi.org/10.1016/S0965-9773(99)00329-3).
45. L. Chen, H. Xin, Y. Fang, C. Zhang, F. Zhang, X. Cao, C. Zhang and X. Li, *J. Nanomater.*, **Article ID 793610** (2014) <http://dx.doi.org/10.1155/2014/793610>.
46. D. Pathania and P. Singh, Advanced Materials for Agriculture, Food, and Environmental Safety, John Wiley & Sons Inc., pp. 243-263 (2014).
47. N. Sharma and R. Kakkar, *Adv. Mater. Lett.*, **4**, 508 (2013); <https://doi.org/10.5185/amlett.2012.12493>.
48. B. Singh, G.K. Prasad, K.S. Pandey, R.K. Danikhel and R. Vijayaraghavan, *Def. Sci. J.*, **60**, 428 (2010); <https://doi.org/10.14429/dsj.60.487>.
49. G.W. Wagner, L.R. Procell, R.J. O'Connor, S. Munavalli, C.L. Carnes, P.N. Kapoor and K.J. Klabunde, *J. Am. Chem. Soc.*, **123**, 1636 (2001); <https://doi.org/10.1021/ja003518b>.
50. M. Bhagat, A. Singh and R.C. Mehrotra, *Main Group Met. Chem.*, **20**, 89 (1997); <https://doi.org/10.1515/MGMC.1997.20.2.89>.
51. M. Bhagat, A. Singh and R.C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem.*, **28**, 997 (1998); <https://doi.org/10.1080/00945719809351684>.
52. M. Bhagat, A. Singh and R.C. Mehrotra, *Indian J. Chem.*, **37A**, 820 (1998).
53. M. Sharma, A. Singh and R.C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem.*, **30**, 1331 (2000); <https://doi.org/10.1080/00945710009351837>.
54. M. Sharma, A. Singh and R.C. Mehrotra, *J. Chem. Res.*, 191 (2003); <https://doi.org/10.3184/030823403103173697>.
55. M. Sharma, A. Singh and R.C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1223 (2002); <https://doi.org/10.1081/SIM-120014299>.
56. M.K. Sharma, M. Sharma, A. Singh and R.C. Mehrotra, *Indian J. Chem.*, **40A**, 1226 (2001).
57. R.C. Mehrotra, A. Singh and S. Sogani, *Chem. Rev.*, **94**, 1643 (1994); <https://doi.org/10.1021/cr00030a008>.
58. H.K. Sharma and P.N. Kapoor, *Indian J. Chem.*, **43A**, 566 (2004).
59. H.K. Sharma and P.N. Kapoor, *Polyhedron*, **7**, 1389 (1988); [https://doi.org/10.1016/S0277-5387\(00\)80390-3](https://doi.org/10.1016/S0277-5387(00)80390-3).
60. R.C. Mehrotra, A. Singh and S. Sogani, *Chem. Soc. Rev.*, **23**, 215 (1994); <https://doi.org/10.1039/c9942300215>.
61. R.C. Mehrotra and A. Singh, *Prog. Inorg. Chem.*, **46**, 239 (1997);
62. R.C. Mehrotra, A. Singh, M. Bhagat and J. Godhwani, *J. Sol-Gel Sci. Technol.*, **13**, 45 (1998); <https://doi.org/10.1023/A:1008690903037>.
63. D.C. Bradley, R.C. Mehrotra, I.P. Rothwell and A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Academic Press, London (2001).
64. K. Sharma, M. Sharma, A. Singh and R.C. Mehrotra, *Main Group Met. Chem.*, **26**, 131 (2003); <https://doi.org/10.1515/MGMC.2003.26.2.131>.
65. K. Sharma, M. Sharma, A. Singh and R.C. Mehrotra, *Indian J. Chem.*, **42A**, 493 (2003).
66. M. Sharma, A. Singh and R.C. Mehrotra, *Polyhedron*, **19**, 77 (2000); [https://doi.org/10.1016/S0277-5387\(99\)00327-7](https://doi.org/10.1016/S0277-5387(99)00327-7).
67. A. Singh and R.C. Mehrotra, *Coord. Chem. Rev.*, **248**, 101 (2004); <https://doi.org/10.1016/j.cct.2003.09.004>.
68. R.C. Mehrotra, A. Singh and U.M. Tripathi, *Chem. Rev.*, **91**, 1287 (1991); <https://doi.org/10.1021/cr00006a007>.
69. A.T. Bolsoni, J.S. Dos Santos, M.D. Assis and H.P. Oliveira, *J. Non-Cryst. Solids*, **357**, 3301 (2011); <https://doi.org/10.1016/j.jnoncrysol.2011.05.022>.
70. R. Gvishi, eds.: D. Levy and M. Zayat, The Sol-Gel Handbook: Synthesis, Characterization and Applications, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, vol. 2, Chap. 10, pp. 317-344 (2015). <https://doi.org/10.1002/9783527670819>.
71. R.C. Mehrotra and A. Singh, *Chem. Soc. Rev.*, **25**, 1 (1996); <https://doi.org/10.1039/cs9962500001>.
72. R.C. Mehrotra, *Proc. Indian Natl. Sci. Acad. Part A*, **61**, 253 (1995).
73. P.N. Kapoor, D. Heroux, R.S. Mulukutla, V. Zaikovskii and K.J. Klabunde, *J. Mater. Chem.*, **13**, 410 (2003); <https://doi.org/10.1039/b205743n>.
74. P.N. Kapoor, S. Uma, S. Rodriguez and K.J. Klabunde, *J. Mol. Catal. A*, **229**, 145 (2005); <https://doi.org/10.1016/j.molcata.2004.11.008>.
75. S. Mathur, M. Veith, M. Haas, H. Shen, N. Lecerf, V. Huch, S. Hüfner, R. Haberkorn, H.P. Beck and M. Jilavi, *J. Am. Ceram. Soc.*, **84**, 1921 (2001); <https://doi.org/10.1111/j.1151-2916.2001.tb00938.x>.
76. I.H. Mutlu, H. Acun, E. Celik and H. Turkmen, *Physica C*, **451**, 98 (2007); <https://doi.org/10.1016/j.physc.2006.10.010>.
77. M. Toyoda and D.A. Payne, *Mater. Lett.*, **18**, 84 (1993); [https://doi.org/10.1016/0167-577X\(93\)90062-3](https://doi.org/10.1016/0167-577X(93)90062-3).
78. A. Suárez-Gómez, M. Sanchez-Tizapa, R. Castañeda-Valderrama and M.A. Carreón-Álvarez, *Bull. Mater. Sci.*, **37**, 1123 (2014); <https://doi.org/10.1007/s12034-014-0052-z>.
79. A. Kareiva, M. Karppinen and L. Niinistö, *J. Mater. Chem.*, **4**, 1267 (1994); <https://doi.org/10.1039/JM9940401267>.
80. S.H. Park and Y.K. Sun, *J. Power Sources*, **119**, 161 (2003); [https://doi.org/10.1016/S0378-7753\(03\)00171-X](https://doi.org/10.1016/S0378-7753(03)00171-X).
81. R. Thirunakaran, K.T. Kim, Y.M. Kang and J. Young Lee, *Mater. Res. Bull.*, **40**, 177 (2005); <https://doi.org/10.1016/j.materresbull.2004.08.013>.
82. K. Hayat, M.A. Gondal, M.M. Khaled, S. Ahmed and A.M. Shemsi, *Appl. Catal. A Gen.*, **393**, 122 (2011); <https://doi.org/10.1016/j.apcata.2010.11.032>.
83. D. Visinescu, C. Paraschiv, A. Ianculescu, B. Jurca, B. Vasile and O. Carp, *Dyes Pigments*, **87**, 125 (2010); <https://doi.org/10.1016/j.dyepig.2010.03.006>.
84. S.R. Hall, *Adv. Mater.*, **18**, 487 (2006); <https://doi.org/10.1002/adma.200501971>.
85. D. Walsh, L. Arcelli, T. Ikoma, J. Tanaka and S. Mann, *Nat. Mater.*, **2**, 386 (2003); <https://doi.org/10.1038/nmat903>.
86. J. Livage, M. Henry and C. Sanchez, *Prog. Solid State Chem.*, **18**, 259 (1988); [https://doi.org/10.1016/0079-6786\(88\)90005-2](https://doi.org/10.1016/0079-6786(88)90005-2).
87. Z. Yue, J. Zhou, L. Li, H. Zhang and Z. Gui, *J. Magn. Magn. Mater.*, **208**, 55 (2000); [https://doi.org/10.1016/S0304-8853\(99\)00566-1](https://doi.org/10.1016/S0304-8853(99)00566-1).
88. S. Thiagarajan, A. Sanmugam and D. Vikraman, ed.: U. Chandra, Recent Application in Sol Gel Synthesis, InTech, Chap. 1, pp. 308 (2017).
89. K.F. Hsu, S.Y. Tsay and B.J. Hwang, *J. Mater. Chem.*, **14**, 2690 (2004); <https://doi.org/10.1039/B406774F>.
90. S. Kandhasamy, A. Pandey and M. Minakshi, *Electrochim. Acta*, **60**, 170 (2012); <https://doi.org/10.1016/j.electacta.2011.11.028>.
91. J. Wan, W. Cai, X. Meng and E. Liu, *Chem. Commun.*, 5004 (2007); <https://doi.org/10.1039/b712795b>.
92. S.R. Lukic, D.M. Petrovic, M.D. Dramic'anin, M. Mitric and L. Đaëanin, *Sci. Mater.*, **58**, 655 (2008); <https://doi.org/10.1016/j.scriptamat.2007.11.045>.
93. M.P. Pechini, Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor, US Patent 3330697A (1967).
94. L. Dimesso, eds.: L. Klein, M. Aparicio and A. Jitianu, Handbook of Sol-Gel Science and Technology, Springer, pp. 1-22 (2016).

95. T.O.L. Sunde, M.-A. Einarsrud and T. Grande, *J. Eur. Ceram. Soc.*, **33**, 565 (2013);
<https://doi.org/10.1016/j.jeurceramsoc.2012.09.023>.
96. T. Liu, Y. Xu and J. Zhao, *J. Am. Ceram. Soc.*, **93**, 3637 (2010);
<https://doi.org/10.1111/j.1551-2916.2010.03945.x>.
97. I.A. Farbut, I.V. Romanova and S.A. Kirillov, *J. Sol-Gel Sci. Technol.*, **68**, 411 (2013);
<https://doi.org/10.1007/s10971-013-3024-7>.
98. S.G. Rudisill, N.M. Hein, D. Terzic and A. Stein, *Chem. Mater.*, **25**, 745 (2013);
<https://doi.org/10.1021/cm303761z>.
99. S.M. Abreu Jr., S.M. Zanetti, M.A.S. Oliveira and G.P. Thim, *J. Eur. Ceram. Soc.*, **25**, 743 (2005);
<https://doi.org/10.1016/j.jeurceramsoc.2004.02.021>.
100. Y.K. Sun and I.H. Oh, *Ind. Eng. Chem. Res.*, **35**, 4296 (1996);
<https://doi.org/10.1021/ie950527y>.
101. M. Motta, C. Deimling, M. Saeki and P. Lisboa-Filho, *J. Sol-Gel Sci. Technol.*, **46**, 201 (2008);
<https://doi.org/10.1007/s10971-007-1673-0>.
102. S. Komarneni and R. Roy, *Mater. Lett.*, **3**, 165 (1985);
[https://doi.org/10.1016/0167-577X\(85\)90151-X](https://doi.org/10.1016/0167-577X(85)90151-X).
103. S. Komarneni, *Chem. World*, **6**, 38 (2009).
104. G.M. Neves, R.F.S. Lenza and W.L. Vasconcelos, *Mater. Res.*, **5**, 447 (2002);
<https://doi.org/10.1590/S1516-14392002000400009>.
105. D. He, H. Hao, D. Chen, J. Lu, L. Zhong, R. Chen, F. Liu, G. Wan, S. He and Y. Luo, *J. Environ. Chem. Eng.*, **4**, 311 (2016);
<https://doi.org/10.1016/j.jece.2015.11.019>.
106. H. Yang, X. Zhang, Q. Tao and A. Tanga, *J. Optoelectron. Adv. Mater.*, **9**, 2493 (2007).
107. H. Mirzaei and A. Davoodnia, *Chin. J. Catal.*, **33**, 1502 (2012);
[https://doi.org/10.1016/S1872-2067\(11\)60431-2](https://doi.org/10.1016/S1872-2067(11)60431-2).
108. R. Deshmukh and M. Niederberger, *Chem. Eur. J.*, **23**, 8542 (2017);
<https://doi.org/10.1002/chem.201605957>.
109. M. Karmaoui, S.G. Leonardi, D.M. Tobaldi, N. Donato, R.C. Pullar, M.P. Seabra, J.A. Labrincha and G. Neri, *J. Mater. Chem. B Mater. Biol. Med.*, **3**, 399 (2015);
<https://doi.org/10.1039/C4TB01177E>.
110. R. Deshmukh, G. Zeng, E. Tervoort, M. Staniuk, M. Niederberger and D. Wood, *Chem. Mater.*, **27**, 8282 (2015);
<https://doi.org/10.1021/acs.chemmater.5b03444>.
111. D. Skoda, A. Styskalik, Z. Moravec, P. Bezdicka, J. Bursik, P.H. Mutin and J. Pinkas, *RSC Adv.*, **6**, 68739 (2016);
<https://doi.org/10.1039/C6RA16556G>.
112. P. Jittiarporn, S. Badilescu, M.N. Al Sawafta, L. Sikong and V.-V. Truong, *J. Sci.: Adv. Mater. Devices*, **2**, 286 (2017);
<https://doi.org/10.1016/j.jsamd.2017.08.005>.