SCIENCEFORECAST
A digital science library

Review Article
Published: 16 Apr, 2018

SF Journal of Material and Chemical Engineering

Microwave Assisted Technology for Transparent Conducting Oxides Synthesis

Jayathilake DSY and Peiris TAN**

Department of Chemistry, Loughborough University, Loughborough, UK

Abstract

Transparent conducting oxides are essential component in large number of modern devices. Co-precipitation, sol-gel synthesis, hydrothermal and solvothermal methods are the common methods use to synthesize transparent conducting oxide (TCO) materials. The microwave assisted synthesis has already been used to synthesize inorganic materials with unique properties. Though, transparent conducting materials synthesis using microwave radiation is emerging as a novel and innovative technology that shows a great potential to be useful in a range of applications with many advantages over conventional thermal synthesis. Microwave synthesis provides new approaches for enhancing the physical, chemical and optical properties of TCO materials as well as economic advantages through energy savings. The fundamentals of microwave synthesis and a summary of recent developments in microwave synthesis of TCO materials are presented in this review. This review helps to guide researchers who are interested in using microwaves to synthesize low cost alternative TCO materials and improve their properties by making full use of the capabilities of microwave radiation.

Keywords: Transparent Conducting Oxides; Microwaves; Synthesis; Energy saving; Low-cost

Introduction

In recent years, microwaves have been explored as an efficient alternative energy source to traditional forms of heating (i.e. isomantles, oil baths, hot plates etc.) in materials synthesis [1]. It has been shown that the use of microwave radiation for material synthesis has shown promising results over conventional heating methods in terms of the product yield and the reaction rate [2]. This is due to deference in the two heating mechanisms (i.e. microwave heating and conventional heating) [3,4]. In the microwave process, the heat is produced within the material instead of external heat source. Particularly, microwave heat generation is due to an energy conversion rather than a heat transfer process. As the material is being treated under microwaves, the absorbed radiation is transformed to heat energy and the material turn into its own heating source [5,6]. Hence, the thermal gradient in a microwave processed material is the reverse of that in a material processed by conventional heating [7,8]. The temperature profiles of microwave and conventional annealing for a reaction are shown in Figure 1.

Microwave Absorbing Characteristics of Materials

The interaction of microwaves with matter is quantified by two complex physical quantities; dielectric permittivity, ε, and permeability (magnetic susceptibility), μ [9]. In reality, the permittivity and permeability are complex quantities which are defined as ε^* and μ^* respectively as below equations 1 and 2 [10],

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_o\left(\varepsilon_r' - i\varepsilon_{eff}''\right) \quad (1)$$

$$\mu^* = \mu' - i\mu'' = \mu_o\left(\mu_r' - i\mu_{eff}''\right) \quad (2)$$

where ε' is the dielectric constant which represents the time-independent polarizability of a material in the presence of an external electric field, that is to say it measures the resistance encountered when forming an electric field in a medium. ε'' is the dielectric loss or loss factor of the material, and indicates the time-dependent component of the permittivity which quantifies the ability of the material to convert absorbed energy into heat. ε_r' is the relative permittivity of the material which is the ratio of the permittivity of a substance to that of free space or vacuum. ε''_{eff} is the effective relative loss factor. μ' is the magnetic permeability, μ'' magnetic loss factor, μ_o the permeability of free space ($\mu_o = 4\pi \times 10^{-7}$ Hm^{-1}), μ_r' is the relative permeability of the material and μ''_{eff} is the effective relative

OPEN ACCESS

**Correspondence:*
Jayathilake DSY, Department of Chemistry, Loughborough University, Loughborough, LE113TU, UK.
E-mail: *dsyjayathilake@gmail.com*
Peiris TAN, Department of Chemistry, Loughborough University, Loughborough, LE113TU, UK.
E-mail: *nirmalprs@gmail.com*

Received Date: *09 Mar 2018*
Accepted Date: *11 Apr 2018*
Published Date: *16 Apr 2018*

Citation: *Jayathilake DSY, Peiris TAN. Microwave Assisted Technology for Transparent Conducting Oxides Synthesis. SF J Material Chem Eng. 2018; 1(1): 1006.*

ISSN 2643-8100

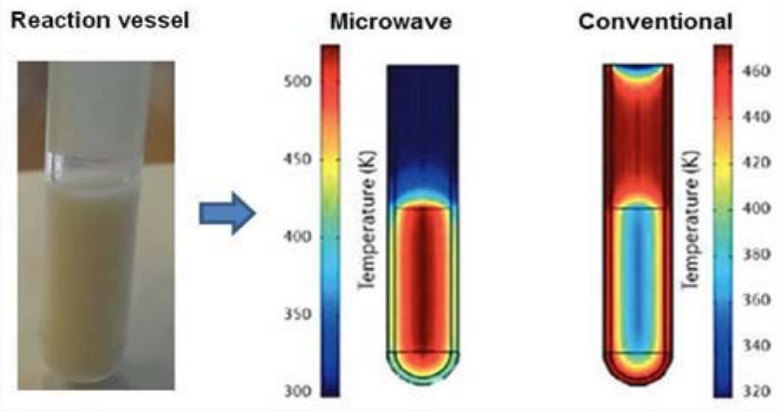

Figure 1: The temperature profiles of microwave and conventional annealing methods of the reaction mixture in the vessel.

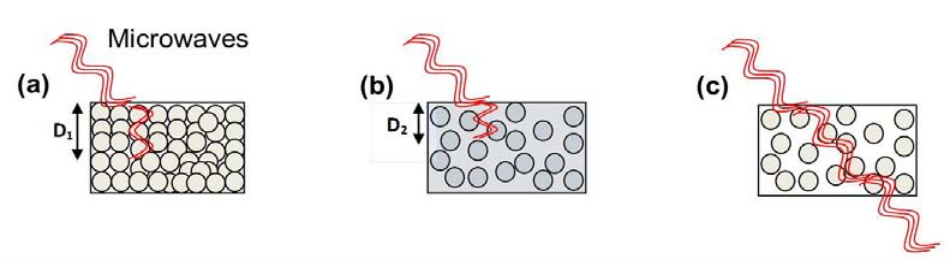

Figure 2: The variation in the penetration depth of microwaves with the density and the dispersion medium of SiC (a) Highly dense SiC (Tile) (b) SiC particles dispersed in dielectric medium (c) SiC particles dispersed in air [22].

magnetic loss factor.

The ratio of the dielectric loss to the dielectric constant is known as the loss tangent (*tanδ*) or dissipation factor which is given in equation 3 [11],

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (3)$$

The angle δ represents the phase lag between the polarization of the material and the applied electric field. The loss tangent is an indicator of the ability of the material to convert absorbed energy into heat. A good microwave absorber has $tan\delta \geq 0.1$ while those with $tan\delta \leq 0.01$ are transparent to microwaves. The heat generation by microwave energy can be quantified by equation 4 [12],

$$P = \sigma|E|^2 = 2\pi f \varepsilon_o \varepsilon'' |E|^2 = 2\pi f \varepsilon_o \varepsilon'' \tan\delta |E|^2 \quad (4)$$

where, P is power dissipation (W/cm^3), σ is the total effective conductivity, E is the magnitude of the internal electric field, and f is the microwave frequency.

The intensity of heat evolution in a sample depends on the materials properties, the frequency and intensity of the applied field, penetration depth of microwaves into the substance and geometric size of the sample [13]. The distribution of energy within a material can be determined by the attenuation factor, α' expressed as equation 5,

$$\alpha' = \frac{2\pi}{\lambda}\left[\frac{\varepsilon'}{2}\left\{\sqrt{\left(1+\tan^2\delta\right)}-1\right\}\right]^{\frac{1}{2}} \quad (5)$$

The attenuation factor can be used to calculate the penetration depth (D) as suggested by von Hippel [14]. It is inversely proportional to the penetration depth of the material as shown in the below equation (6),

$$D = \frac{1}{\alpha'} \quad (6)$$

Penetration depth is an important parameter which determines the heat generation of materials by microwaves. When microwaves are incident perpendicularly to the surface of the materials, its intensity decreases progressively due to dissipation inside the volume of the materials. The penetration depth is defined as the distance from the surface of the material at which the power drops to 1/e from its value at the surface. This can be also expressed as equation 7 [15],

$$D = \frac{3\lambda_o}{8.686\pi \tan\delta\sqrt{\varepsilon'}} \quad (7)$$

At a frequency of 2.45 GHz, the free space wavelength λ_o is 12.24 cm. Penetration depth ranges between several micro metres to several tens of meters depending on the dielectric nature of the material.

In metals, microwave propagation is usually described in terms of skin depth (δ) which is defined as the depth at which the magnitude of electric field drops to 1/e of the value at the surface and it is expressed as,

$$\delta = \frac{1}{\sqrt{f\pi\mu_{o\sigma}}} \quad (8)$$

In general, if the penetration depth exceeds the sample thickness, the material behaves as if it is transparent to microwaves. Volumetric heating only results when the penetration depth is comparable to the sample thickness. If the sample is too thick, absorption is limited to the surface [16].

Microwave interaction with materials can be predicted if dielectric properties such as dielectric constant and dielectric loss are known. The loss tangent is an indicator of the ability of the material to convert absorbed energy into heat and the penetration depth determines the penetration ability of microwaves into the material.

Table 1: Transparent conducting metal oxides synthesized using microwave radiation are listed by the dopant, synthesis/thin film fabrication method, reported conductivity/resistivity with the references.

Metal Oxide	Dopant	Synthesis method and additives	Precursors	Specialty and reaction conditions	Reference
ZnO	Al	Glycolysis, H_2O	$Zn(OAc)_2$	Spheres ca. 12 nm MW - 30 min	[26]
		DEG	$AlCl_3$	200°C	
ZnO	In	Glycolysis, H_2O	$Zn(OAc)_2$	Spheres 15 nm, 30 min	[26]
		DEG	$InCl_3$	200°C	
In_2O_3	Sn	Alkaline hydrolysis, DMF/EtOH	$InCl_3$	Irregular polyhedrons 25 nm, 3–15 s	[27]
		$N(CH_3)_4OH$	$SnCl_4$	300°C	
In_2O_3	Sn	Glycolysis	$InCl_3$	Spheres15–19 nm, 120 min	[28]
		DEG $N(CH_3)4OH$	$SnCl_4$	200°C, 1 atm	
$ZnGa_2O_4$	Cu	Alkaline Hydrolysis, H_2O	$Ga_2(SO_4)_3$ $ZnSO_4$	Aggregates of spherical 10–20 nm Particles, 30 min	[29]
		NH_4OH	$CuCl_2$	150°C	
ZnO	Au	Alkaline hydrolysis, EtOH	$Zn(NO_3)_2$,	Nanorods 10–15 nm x 100–600 nm 10 min	[30]
		NaOH, PEG	$H[AuCl_4]$	MW cycles: 10 s on/20 s off	
TiO_2	La, Zr	Acidic hydrolysis, iPrOH	$Ti(OiPr)_4$, $ZrCl_4$	Aggregates of15–25 nm particles	[31]
		AcOH, citric acid, PEG, H_2O	$La(NO_3)_3$	4 min	
ZnO	Al, Ga	Glycolysis, H_2O	$Zn(OAc)_2$ $AlCl_3$	Smallest spherical particle size 80 nm, 30 min	[24]
		DEG	$Ga(NO_3)_3$	200°C	

The power required to raise the temperature of material from initial (T) to final temperature (T_o) is given by equation 9,

$$P' = mC_P\left(T - T_o\right)/t \qquad (9)$$

where, P' is the required power to raise the temperature in Js^{-1}, m is the mass, C_p the specific heat capacity and t is the time taken. If the microwave frequency is constant and the variations of materials density (ρ) and specific heat capacity are relatively small, the temperature increase by microwave irradiation will be a function of ε'' as shown by the below derived equation from equations 4 and 9,

$$\frac{2\pi f \varepsilon_o |E|^2 \varepsilon''}{\rho C_P} = \frac{(T-T)}{t} \qquad (10)$$

This confirms that materials' dielectric loss plays an important role in elevating the temperature of the material by absorbing microwave energy. Microwave penetration is determined by the material's dielectric constant. The optimum combination of these two properties (expressed by tanδ) along with the matching of the penetration depth and the sample thickness enables efficient heat generation throughout the material.

Microwave Assisted Synthesis of TCOs

Over the past few decades, most of the microwave heating in chemistry has been limited to organic synthesis. More recently the use of microwave radiation for heating reactions in the laboratory has expanded to inorganic and materials chemistry. Reviews by Bilecka [17] and Rao [18] give an overview of microwave-assisted liquid phase routes to synthesize inorganic nanomaterials. A review by Kitchen et al [19], analyses the significant advances in the area of solid-state microwave synthesis. Hoz et al. provides an overall picture of non-thermal microwave effects on organic synthesis [20] whilst Lidström [21] delivers a critical review on microwave assisted organic synthesis and its advantages over conventional synthesis methods.

In organic and inorganic material synthesis, some or all the reactants involved in the reaction should have a high coupling efficiency with microwaves. This provides adequate energy to overcome the activation energy barrier, allowing the reaction to proceed. The microwave absorbing properties of the reactants facilitate the rapid heating and lead to the successful synthesis of the target material within a very short period. In microwave-assisted synthesis, one often selects alternative reactants with favorable dielectric properties to achieve the maximum product yield. If there are no alternative microwave absorbing reactants available for material synthesis, it is usually possible to find a secondary material that can act as a heating source; this is commonly referred to as a microwave susceptor. Microwave susceptors are substances that have the ability to absorb microwave energy and convert it to heat. In other words, a susceptor is a material that has a high dielectric loss tangent. Graphitic or amorphous carbon, silicon carbide (SiC) and copper (II) oxide are some examples of commonly used susceptors [22,23]. These susceptor materials can be kept either in direct contact with the sample (by mixing with the other regents) or placed outside (surrounding the sample). In some cases, adding a susceptor into a reaction mixture can cause problems with the final product purity, yield and reaction rate. Microwave susceptors can also be used in material post heat treatments to ramp up the temperature of poorly microwave absorbing materials [24]. In such cases, the penetration depth plays a vital role in the heat generation. If the penetration depth exceeds susceptor thickness, the susceptor behaves as if it is transparent to microwaves. Volumetric heating only occurs when the penetration depth is comparable to the sample thickness. If the sample is too thick, absorption is limited to the surface. The physical nature of materials, such as particle size, density and the medium the material is present in, also determines the microwave penetration depth [25].

The variation of the penetration depth of SiC with the above physical properties is shown in figure. As indicated in the Figure 2, the penetration depth of microwaves in to SiC varies with the density and the nature of the particle dispersion in the medium. This affects the microwave coupling and heat generation. Generally, SiC

is an abrasive material with a high density. The microwaves couple with SiC as a whole and penetrate well into the material to generate heat effectively because of its high density (Figure 2a). When the SiC particles are dispersed in a dielectric medium, (such as water, ethanol etc.) microwaves interact with SiC particles as well as the dielectric medium to generate heat. Since both media couple well with microwaves, the penetration depth of such a system (which is determined by the sum of the contributions from each material's dielectric properties) are reasonably high, and this leads to heat generation (Figure 2b). In the case of SiC powders the voids between the particles are filled with air, which is transparent to microwaves. Thus, heat generation is only influenced by the particle size of SiC (figure 2c). To generate volumetric heating in SiC powders the penetration depth of microwaves needs to be comparable with the particle size of the SiC (diameter of the particles). Therefore, it is not possible to heat SiC nanoparticles (<100nm) by microwaves unless they are mixed with another dielectric matrix.

Over the past decade many colloidal inorganic metal nanocrystals, metal oxides and chalogenides have been synthesized using microwave radiation. Table 1 gives an idea about the transparent conducting metal oxides synthesized using microwave radiation.

In most of the literature it is claimed that use of microwaves in microwave-assisted synthesis shortens the reaction times and reaction temperatures significantly compared to conventional synthetic techniques [32]. According to the reports, microwave synthesized TCO materials possess significantly improved conducting properties by enhancing crystallinity and modifying the intrinsic defects. For instance, Feldmann et al. stated ITO (Sn doped In_2O_3) and AZO (Al doped ZnO) pelleted powders, microwave synthesized in polyol media with resistivity values of 1.1 x 10^{-2} Ω.cm and 5.1 x 10^{-1} Ω.cm, respectively [26,28]. Niederberger et al. synthesized AZO by a microwave-assisted non-aqueous sol–gel route in benzyl alcohol and then processed it into a TCO thin film. They stated a minimum resistivity value of 2.35 x 10^{-2} Ω.cm for their AZO thin film after post-synthesis heat treatment [33]. Furthermore, a recent study reported a lower resistivity of 5.6 x 10^{-4} Ω.cm for the microwave synthesized AGZO (Al and Ga co-doped ZnO) powders signifying the microwave assisted technology could be a promising way forward on producing low-cost electrical conducting materials for TCO applications [24].

Conclusions

Over the past few years there has been a significant increase in research into the synthesis and thin film fabrication of doped metal oxides for transparent conducting applications. The demand for low-cost conducting thin films has pushed research towards new TCO materials. Similarly, efforts to reduce the costs associated with TCO fabrication have driven research towards low-cost energy efficient synthesis technologies. Hence, recent research has directed towards microwave synthesis of TCO materials. Since microwave synthesis is a relatively new technology for transparent conducting materials, more research is required to understand the nature of interaction and heat generation with different TCO materials. It is hoped that significant advancements will take place in microwave assisted synthesis of TCOs because of the unique advantages which cannot be achieved by the conventional radiant heating techniques. This review demonstrates that microwave assisted synthesis is a promising alternative method to conventional synthesis as it opens up a new research strategy for the engineering of TCO materials properties for use in advanced electronic and optoelectronic devices.

Acknowledgments

The authors gratefully acknowledge Professor Upul Wijayantha and Dr Darren Southee for their kind support. All the partners of TCO consortia and the industrial collaborators of the UK Engineering and Physical Sciences Research Council (EPSRC) project under grant number EP/ L017709/1 are also acknowledged. The authors also thank the Energy Research Laboratory in the Department of Chemistry, Loughborough University.

References

1. Manseki K, Sugiura T, Yoshida T. Microwave synthesis of size-controllable SnO_2 nanocrystals for dye-sensitized solar cells. New J. Chem. 2014; 38: 598.
2. Lagashetty A, Havanoor V, Basavaraja S, Balaji SD, Venkataraman A. Microwave-assisted route for synthesis of nanosized metal oxides. Sci. Technol. Adv. Mater. 2007; 8: 484–493.
3. Nirmal Peiris TA, Ghanizadeh S, Jayathilake DSY, Hutt DA, Wijayantha KGU, Conway PP, et al. Aerosol-assisted fabrication of tin-doped indium oxide ceramic thin films from nanoparticle suspensions. J. Mater. Chem. C. 2016; 4: 5739–5746.
4. Bhatti IA, Nirmal Peiris TA, Smith TD, Upul Wijayantha KG. Hierarchical ZnO nanorod electrodes: Effect of post annealing on structural and photoelectrochemical performance. Mater. Lett. 2013; 93: 333–336.
5. Jayathilake DSY, Nirmal Peiris TA. Overview on Transparent Conducting Oxides and State of the Art of Low-cost Doped ZnO Systems. SF J Mater. Chem Eng. 2018; 1: 7.
6. Tahir AA, Peiris TAN, Wijayantha KGU. Enhancement of Photoelectrochemical Performance of AACVD-produced TiO2 Electrodes by Microwave Irradiation while Preserving the Nanostructure. Chem. Vap. Depos. 2012; 18: 107–111.
7. Peiris TAN, Sagu JS, Hazim Yusof Y, Wijayantha KGU. Microwave-assisted low temperature fabrication of ZnO thin film electrodes for solar energy harvesting. Thin Solid Films. 2015; 590: 293–298.
8. Kappe CO, Dallinger D. The impact of microwave synthesis on drug discovery. Nat. Rev. Drug Discov. 2006; 5: 51–63.
9. Stuerga D. Microwave-Material Interactions and Dielectric Properties Key Ingredients for Mastery of Chemical Microwave Processes. In Microwaves in Organic Synthesis Wiley-VCH Verlag GmbH: Weinheim Germany. 2006; pp 1–61.
10. Bruce RW. New Frontiers in the Use of Microwave Energy: Power and Metrology. MRS Proc. 1988; 124-123.
11. Chen M, Siochi EJ, Ward TC, McGrath JE. Basic ideas of microwave processing of polymers. Polym. Eng. Sci. 1993; 33: 1092–1109.
12. Hong S. M. Park J. K. Teeradej N. Lee Y. O. Cho Y. K. Park C. H. Pretreatment of sludge with microwaves for pathogen destruction and improved anaerobic digestion performance. Water Environ. Res.2006 78 (1) 76–83.
13. Meredith RJ, (Roger J. Institution of Electrical Engineers. Engineers' handbook of industrial microwave heating Institution of Electrical Engineers. 1998.
14. von Hippel Arthur Robert. Dielectrics and waves John Wiley New York. 1954.
15. Rao KJB, Vaidhyanathan M, Ganguli A, Ramakrishnan PA. Synthesis of Inorganic Solids Using Microwaves. Chem. Mater. 1999; 11: 882–895.
16. Ramesh PD, Brandon D, Schächter L. Use of partially oxidized SiC particle bed for microwave sintering of low loss ceramics. Mater. Sci. Eng. A. 1999; 266: 211–220.

17. Bilecka I, Niederberger M. Microwave chemistry for inorganic nanomaterials synthesis. Nanoscale. 2010; 2: 1358.

18. Rao CNR, Müller A, Cheetham AK. The Chemistry of Nanomaterials: Synthesis Properties and Applications. The Chemical of Nanomaterials. 2004.

19. Kitchen HJ, Vallance SR, Kennedy JL, Tapia-Ruiz N, Carassiti L, Harrison A, et al. Modern microwave methods in solid-state inorganic materials chemistry: from fundamentals to manufacturing. Chem. Rev. 2014; 114: 1170–1206.

20. de la Hoz A, Díaz-Ortiz Á, Moreno A, Jiménez JL, Palacios JC, Cossío FP, et al. Microwaves in organic synthesis. Thermal and non-thermal microwave effects. Chem. Soc. Rev. 2005; 34: 164–178.

21. Lidström P, Tierney J, Wathey B, Westman J. Microwave assisted organic synthesis—a review. Tetrahedron. 2001; 57: 9225–9283.

22. Peiris TAN. Microwave-assisted processing of solid materials for sustainable energy related electronic and optoelectronic applications. Loughborough University. 2014.

23. Ghanizadeh S, Peiris TAN, Jayathilake DSY, Hutt DA, Wijayantha KGU, Southee DJ, et al. Dispersion and microwave processing of nano-sized ITO powder for the fabrication of transparent conductive oxides. Ceram. Int. 2016; 42: 18296–18302.

24. Jayathilake DSY, Peiris TAN, Sagu JS, Potter DB, Wijayantha KGU, Carmalt CJ, et al. Microwave-Assisted Synthesis and Processing of Al-Doped Ga-Doped and Al Ga Codoped ZnO for the Pursuit of Optimal Conductivity for Transparent Conducting Film Fabrication. ACS Sustain. Chem. Eng. 2017; 5: 4820–4829.

25. Shpil'ko AV, Kirilenko EV, Soltis MV, Petrovskii VY. Microwave absorptivity of refractory powders depending on particle size. Powder Metall. Met. Ceram. 2010; 49: 304–316.

26. Hammarberg E, Prodi-Schwab A, Feldmann C. Microwave-assisted polyol synthesis of aluminium- and indium-doped ZnO nanocrystals. J. Colloid Interface Sci. 2009; 334: 29–36.

27. Bühler G, Thölmann D, Feldmann C. One-Pot Synthesis of Highly Conductive Indium Tin Oxide Nanocrystals. Adv. Mater. 2007; 19: 2224–2227.

28. Hammarberg E, Prodi-Schwab A, Feldmann C. Microwave-assisted synthesis of indium tin oxide nanocrystals in polyol media and transparent conductive layers thereof. Thin Solid Films. 2008; 516: 7437–7442.

29. Conrad F, Zhou Y, Yulikov M, Hametner K, Weyeneth S, Jeschke G, et al. Microwave-Hydrothermal Synthesis of Nanostructured Zinc-Copper Gallates. Eur. J. Inorg. Chem. 2010; 2010: 2036–2043.

30. Glaspell G, Fuoco L, El-Shall MS. Microwave synthesis of supported Au and Pd nanoparticle catalysts for CO oxidation. J. Phys. Chem. B. 2005; 109: 17350–17355.

31. Shojaie AF, Loghmani MH. La^{3+} and Zr^{4+} co-doped anatase nano TiO_2 by sol-microwave method. Chem. Eng. J. 2010; 157: 263–269.

32. Baghbanzadeh M, Carbone L, Cozzoli PD, Kappe CO. Microwave-Assisted Synthesis of Colloidal Inorganic Nanocrystals. Angew. Chemie Int. Ed. 2011; 50: 11312–11359.

33. Luo L, Rossell MD, Xie D, Erni R, Niederberger M. Microwave-Assisted Nonaqueous Sol–Gel Synthesis: From Al:ZnO Nanoparticles to Transparent Conducting Films. ACS Sustain. Chem. Eng. 2013; 1: 152–160.