

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Doping of Semiconductors at Nanoscale with Microwave Heating (Overview)

Sandhya K. M., Litty Thomas Manamel and Bikas C. Das

Abstract

Incorporation of dopants efficiently in semiconductors at the nanoscale is an open challenge and is also essential to tune the conductivity. Typically, heating is a necessary step during nanomaterials' solution growth either as pristine or doped products. Usually, conventional heating induces the diffusion of dopant atoms into host nanocrystals towards the surface at the time of doped sample growth. However, the dielectric heating by microwave irradiation minimizes this dopant diffusion problem and accelerates precursors' reaction, which certainly improves the doping yield and reduces processing costs. The microwave radiation provides rapid and homogeneous volumetric heating due to its high penetration depth, which is crucial for the uniform distribution of dopants inside nanometer-scale semiconducting materials. This chapter discusses the effective uses of microwave heating for high-quality nanomaterials synthesis in a solution where doping is necessary to tune the electronic and optoelectronic properties for various applications.

Keywords: conductivity tuning, microwave heating, doping at the nanoscale, dopant diffusion, nanocrystals, solution growth

1. Introduction

The discovery of microwave cooking by Percy Spencer marked the dawn of a new era in microwave heating technology, which has gained huge attention in the scientific areas, especially in synthetic chemistry [1]. Numerous factors enabled the microwave technique to become a breakthrough technology in the complex synthesis process [2]. The significance of microwave heating for the synthesis of high-quality semiconducting nanomaterials, pristine or doped ones, is a subject that needs to be profoundly studied and explored due to its capability to revolutionize the semiconductor industry. The synthesis of high-quality nanocrystals primarily relies on controlled reactions of molecular precursors in a liquid medium at an adequate temperature in the presence of stabilizing agents [3, 4]. Most of the synthetic methods such as wet chemical process [5], emulsion methods, anti-solvent precipitation methods [6], have studied only the impact of the chemical process and parameters, on the properties of as-synthesized nanocrystals. Of late, the effect of additional external stimulations like microwave irradiation [7, 8], ultraviolet/visible light irradiation, ultrasound, etc. is also studied [5]. Microwave heating increases the rate of reaction, thereby considerably decreasing the reaction time without

altering the kinetics and chemical reaction [9–11]. The rate accelerations caused by “specific microwave effect” as well as “non-thermal effects” have to be considered in the microwave heating mechanism. Baghbanzadeh *et al.* propose that microwave dielectric heating can be termed as “specific microwave effects” by which one can achieve rate accelerations that cannot be attained by the conventional methods [12]. In the case of “non-thermal microwave effects”, the heating mechanism arises as a result of the direct interaction of microwaves with specific molecules or materials in the reaction medium [2, 12]. Jacob *et al.* report that the enhancement rate of reaction with microwave heating compared to conventional heating is mainly due to the thermal effects which arise due to three significant factors. Firstly, the localized heating effect is a consequence of superheating phenomena due to the abundant ions present in the medium. Secondly, the molecular agitation due to lag of dipole, in following the fast-moving EM wave. Thirdly, increase of diffusion rate of reactants [13].

Earlier, the synthesis of high-quality semiconducting quantum dots was very tough and the process of doping at this length scale makes it even more challenging. Erwin *et al.* reported that the difficulty in doping at nanoscale regime is due to the difference in mechanisms involved in doping at bulk and at the nanoscale, while other reports in literature claim the process of ‘self-purification’ as the leading cause for de-doping during the growth process [14]. The major daunting challenges arise mostly due to the lack of a comprehensive understanding of all the fundamental mechanisms associated with dopants incorporation and the absence of reliable synthetic procedures where the temperature-dependent dopant impurity atoms diffusion will be minimal [15]. Another challenge involved in doping at the nanoscale is the inherent statistical inhomogeneity of dopants among the nanocrystals. The doped nanomaterials always tend to exhibit a broad range of dopant populations per nanocrystal, which results in effective inhomogeneity in concentration of dopants among nanocrystals. Providing a uniform and instantaneous heating during the reaction process can minimize this problem to a great extent [16]. In this context, microwave heating became the suitable thermal energy source for doping the semiconducting nanocrystals, as it provides rapid and instantaneous heating. Short reaction time, faster reaction rate, uniform volumetric heating, cost-effective and eco-friendly method are the other remarkable features which make microwave heating a prime superior choice over other conventional methods of heating like a hot plate, oil bath, etc. [8]. Moreover, heating by means of conventional methods always results in ‘a self-purification’ mechanism where the dopants are diffused towards the surface of nanocrystals at the time of growth [14]. By adopting microwave-assisted techniques the aforementioned problems encountered while doping at the nanoscale can be eliminated to a great extent and the synthesized products are found to excel both in quality as well as quantity [17].

2. Physics behind the microwave heating

Microwave is an electromagnetic wave having low energy with a wavelength and a frequency in the range of 1 m to 1 mm and 300 MHz to 300 GHz, respectively as shown in **Figure 1**. Mainly, the laboratory and household microwave oven operate at a frequency of 2.45 GHz, which corresponds to a wavelength of 11.2 cm. It can travel at the speed of light (~ 30 cm/nanosecond) like any other electromagnetic wave and consists of electric and magnetic fields oscillating in a direction perpendicular to each other. One can also define it as a Multiphysics phenomenon in which the heating arises due to interaction between matter and electromagnetic radiation.

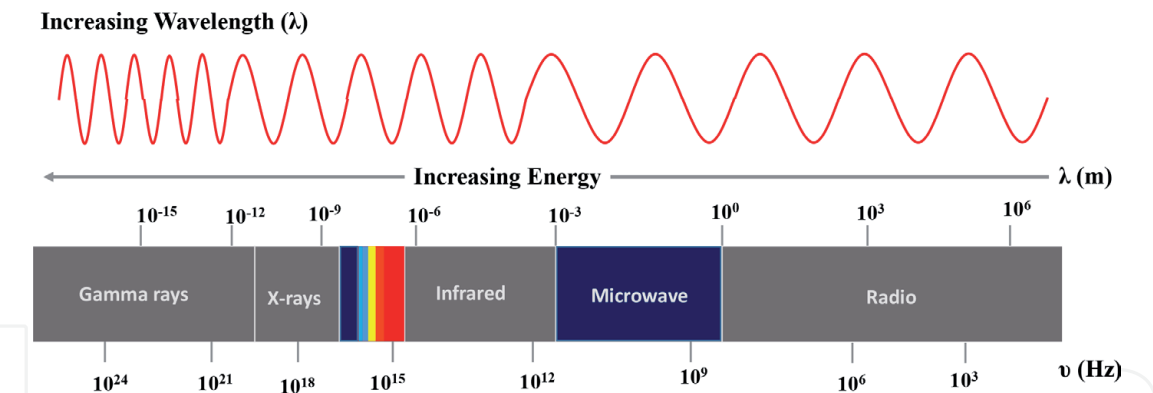


Figure 1.
Schematic representation of the electromagnetic spectrum in terms of wavelengths and frequencies.

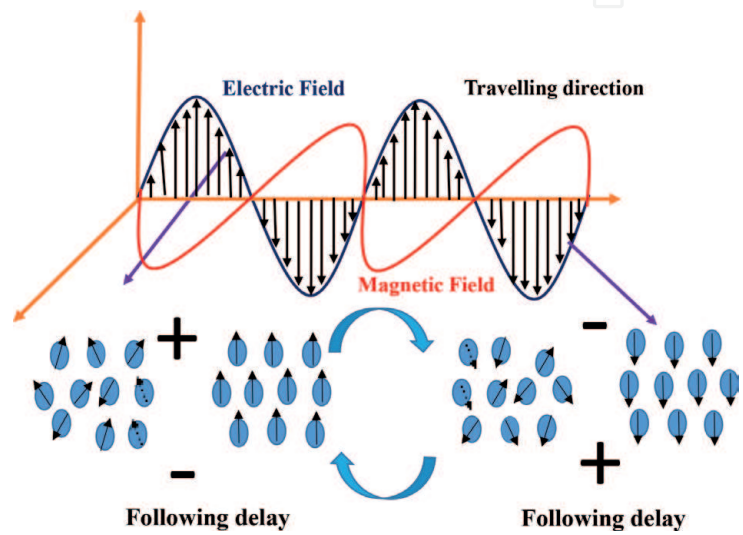


Figure 2.
Schematic diagram of the interaction of an electric component of the microwave radiation with matter.

In contrast to other conventional methods of heating, here the medium itself gets self-heated as a result of the alignment of molecular dipoles present in it with respect to the field associated. The electric and magnetic components in microwave interact with matter in different manners as discussed below [1].

2.1 Influence of electric field component

The polar molecules are sensitive to an electric field, and thus as a result of force exerted by the field on the charged particles, they start to migrate or rotate in order to align along the field (**Figure 2**). Since the electric and magnetic components reverse direction rapidly with a frequency of 2.45 GHz, the electric dipoles have no time to orientate to the direction of electric field. As a result, there occurs the angle between the orientation of the dipoles in space and the direction of the electric field and the energy loss by the dipoles occurs resulting in to rise of dielectric heating. Reflection, absorption, and transmission are the three modes by which the medium reacts to the electromagnetic waves, either in a single or combined fashion [18]. The effective dielectric loss factor for the dielectric heating can be expressed in terms of dipolar polarization, ionic conduction as follows

$$\epsilon''_{ff} = \epsilon''_{polarisation} + \epsilon''_{dipolar} = \epsilon''_{interfacial} + \frac{\sigma}{\omega\epsilon_0} + \epsilon''_{dipolar} \quad (1)$$

where $\epsilon''_{\text{polarisation}}$, $\epsilon''_{\text{dipolar}}$, $\epsilon''_{\text{interfacial}}$, σ , ω , and ϵ_0 represent the polarization dielectric loss, dipolar dielectric loss, interfacial dielectric loss, electrical conductivity (S/m), angular frequency (Hz), and permittivity of free space (8.854×10^{-12} F/m), respectively [19].

2.2 Influence of magnetic field component

Like an electric field, a magnetic field interacts too with matter and induces heat through magnetic loss, joule heating, and so on. However, sufficient studies apart from dielectric heating are still very rare. Meanwhile, Cheng *et al.* reported that magnetic loss contributes significantly to microwave heating compared to dielectric heating [20]. The necessary physical processes generating heat energy as a result of interaction between material medium and the magnetic field component are the eddy current loss, hysteresis loss, and magnetic resonance loss [21, 22]. The overall losses that constitute the effective magnetic permeability ($\mu''_{\text{effective}}$) we may define as

$$\mu''_{\text{effective}} = \mu''_{\text{hysteresis}} + \mu''_{\text{eddy current}} + \mu''_{\text{residual}} \quad (2)$$

where $\mu''_{\text{hysteresis}}$, $\mu''_{\text{eddy current}}$, and μ''_{residual} represent the hysteresis magnetic loss (H/m), eddy current magnetic loss (H/m), and residual magnetic loss (H/m), respectively [18].

3. Doping at the nanoscale and microwave heating

Microwave heating has been the subject of interest for doping semiconductors at nanoscale owing to its ability to control the synthesis process explicitly. Apart from being cost-effective, the dielectric heating by microwave irradiation minimizes the dopant diffusion problem and provides quick reaction among precursors. The process of nucleation and growth of nanocrystals have been described in theories like LaMer burst nucleation [23], Watzky and Finke's slow nucleation followed by autocatalytic growth [24], and LSW theory, etc. [25, 26]. Nucleation is the process where nuclei act as a template for nanocrystal growth. Uniform formation of nuclei throughout the growth medium defined as 'homogeneous nucleation' can be easily and efficiently achieved by microwave irradiation in contrast to conventional methods of heating. Volumetric heating provided by microwave irradiation raises

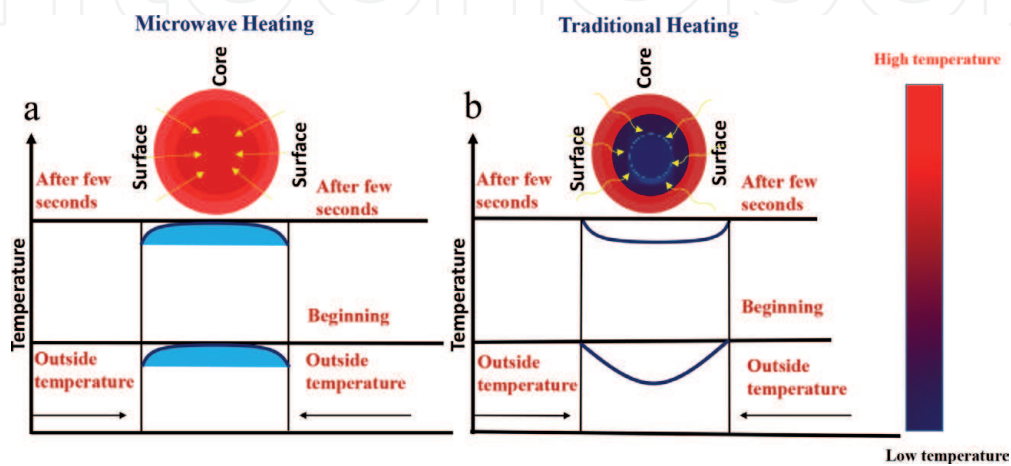


Figure 3. Schematic illustration of main differences between the microwave heating (a) and traditional heating method (b).

the internal temperature of the whole medium simultaneously and homogeneously as illustrated in **Figure 3**. This favors a quick nucleation process which results in solution supersaturation leading to homogeneous nucleation. Microwave-assisted technique aids to measure, manipulate, and thereby optimize the nucleation process and parameters that in turn influences the stability of the synthesized particles along with an added advantage of automatic data recording [12]. Efficient doping is determined by the surface morphology and shape of nanocrystals and the presence of surfactants in the reaction medium. Temperature plays a significant role in molding the aforementioned factors [27]. This demands the necessity for a proper thermal energy source like microwave heating while synthesizing nanocrystals. High penetration depth (d) offered by microwave heating is yet another factor that distinguishes it from the conventional methods of heating. It is defined as the distance at which the microwave power reduces to $1/e$ of its incident power. It has inverse proportionality with oscillating frequency, dielectric, and magnetic loss factor. The formula for determinate a penetration depth (d) may be written as

$$d = \frac{1}{\alpha} = \sqrt{\frac{2}{\omega^2 \mu_0 \mu' \varepsilon_{eff}'' \varepsilon_0}} \quad (3)$$

where α is the absorption coefficient of microwaves, ω is the oscillating frequency, μ_0 is the permeability, ε_{eff}'' is the dielectric loss factor, ε_0 is the vacuum permittivity, μ' is the magnetic loss factor, etc. [19]. In addition to the above-mentioned factors, the specific interaction of electromagnetic wave with the precursors plays a significant role in the formation of nanocrystals.

The efficient absorption of the EM wave by the solvent is determined by its loss tangent factor. It is defined as the ability of a material to convert electromagnetic energy into heat energy at a given frequency and temperature [1]. A high value is desired for maximum absorption, however, heating aided by microwave radiation is achievable even in the presence of a low $\tan(\delta)$ solvent provided there exists either a polar reactant or reagent such that the overall dielectric nature of the reaction medium favors the microwave heating. In the case of conventional heating methods, the transfer of heat is slow and inefficient, resulting in a huge temperature gradient owing to the different thermal conductivity of materials. However, in the case of microwave radiation, there is a direct coupling between the microwave energy and the molecules resulting in core volumetric heating. The most commonly used frequency of the microwave is 2.45 GHz, possessing an energy of 0.0016 eV, which is lower than that of Brownian motion and therefore insufficient to break the bonds. This property of microwaves makes them incapable of carrying out any unwanted reactions and thereby solely ensuring effective doping at nanoscale materials.

3.1 Doping of semiconducting nanomaterials

Nanocrystals are broadly classified as nanoparticles and quantum dots. Generally, tiny particles of a dimension of 100 nm or below are termed as nanoparticles. However, quantum dots (QDs) are a class of nanomaterials with their charge carriers confined in all three dimensions of the length scale of exciton Bohr radius [28]. While doping the QDs, the dopants have a high tendency to come out of it due to the thermal diffusion because their size is in the nanometer range. This problem can be resolved greatly by having a comprehensive idea about the various mechanisms involved during doping and following a proper synthesis process [29]. However, various properties, including optical, magnetic, and electronic, of semiconducting quantum dots can be tailored in a desired fashion by the incorporation

of impurity dopant atoms [30]. Moreover, this can also generate some new physical properties, including spin-polarizable excitonic photoluminescence, exciton storage, excitonic magnetic polaron formation, and magnetic circular dichroism so on. The proper incorporation of impurity atoms into the semiconducting QDs is a tough job but can be identified by observing the following features like red-shifted PL emission and large Zeeman splitting of excitonic excited states that are a result of strong exchange coupling between dopant and the carrier [31, 32]. In the year 2000, Mikulec *et al.* reported the most significant result on QDs doping; in which they reported manganese (Mn) doped CdSe nanocrystals with the evidential result obtained from electron paramagnetic resonance (EPR) [33]. Later, a variety of doped semiconducting material were reported by tailoring both the host atoms such as ZnS, PbS, MgO, Al_2O_3 , $\alpha\text{-Fe}_2\text{O}_3$, CdS, ZnSe, etc. and dopant atoms such as Mn, Cu, Ag, Fe, Zn, Cr, Er, etc. [34, 35]. However, there is a limitation to select the host system and the respective dopant atoms. Suppose, incorporation of Mn into nanocrystals of CdS and ZnSe easy but not into CdSe even though the bulk solubility almost equal to 50% for all three [27, 36].

Depending on dopants' diffusivity, the dopant precursors are injected at different time intervals, suppose along with the host precursors or at the time of nucleation or growth as shown in **Figure 4** [37]. The major problem involved in doping at the nanoscale is that many dopants fail to be incorporated within the host lattice and instead get adsorbed on the surface [38]. High formation energy for defects renders the impurity atoms to be thermodynamically unstable, resulting in the expulsion of dopants from the host lattice, in turn leading to self-purification [14, 27, 39]. Apart from thermodynamics, kinetics also play a significant role in determining the stability of added impurities in solution phase synthesis. Chen *et al.* have reported a detailed study regarding all the elemental processes involved with doping, such as surface adsorption, lattice incorporation, lattice diffusion, and lattice ejection as represented schematically in **Figure 5** [40]. Maintenance of appropriate temperature is a crucial factor even in the phenomena mentioned above.

The high cost of commercially doped QDs is one reason that limits its wide range of applications. Therefore, cost-effective synthesis protocols need to be developed to produce high-quality doped QDs. This limitation and the ones mentioned above are lifted off using microwave heating for doping the QDs. It is also found to be an economical and eco-friendly method in line with green chemistry. Now let us discuss some semiconducting QDs systems where doping has been performed with microwave heating technique.

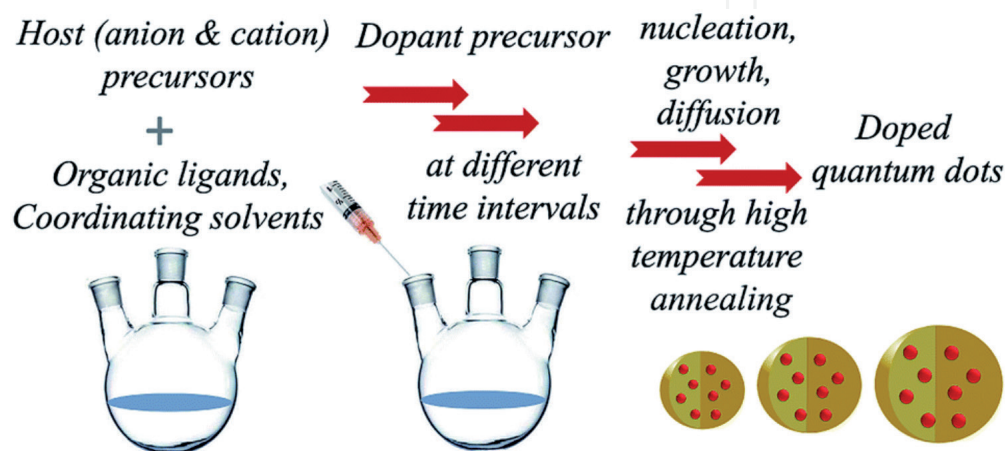


Figure 4.
General schematic model of the colloidal synthesis of doped quantum dots [37].

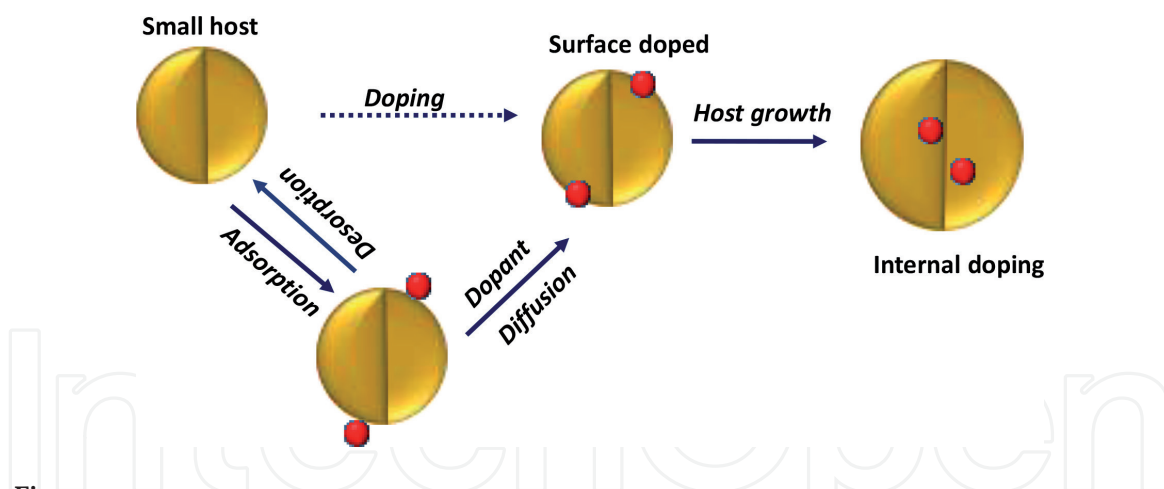


Figure 5.
 Schematic diagram showing temperature-dependent dopant lattice diffusion [37].

3.1.1 Mn-doped CdSe quantum dots

CdSe QDs is n-type intrinsically, and a flagship candidate in nanoscale research history shows several novel properties as a member of the II-VI binary semiconductor group. It was attractive to the researchers to demonstrate various optoelectronic applications as its energy band overlaps nicely with the solar energy spectrum [41]. The fundamental properties of CdSe are enhanced via doping, which further increases its demand in the semiconductor industry. However, doping of CdSe by Mn^{2+} ions is challenging due to the self-purification effect, as reported by Erwin *et al.* [27, 29, 42]. The doping process is mainly governed by the surface kinetic effect. Microwave heating helps one to have exquisite control over this surface kinetics that eases the doping process.

Meladom *et al.* developed a robust synthesis protocol for efficient doping of Mn^{2+} into CdSe QDs in an aqueous medium with mild microwave heating as a final step [17]. A household microwave oven was used to heat the CdSe QDs solution for 60 seconds duration with the set point of 450 W (operational frequency 2.45 GHz). This heating step was repeated three times by giving 5 minutes intervals. The motivation was to tune the electrical conductivity of CdSe QDs thin film by varying doping concentration only as the size of QDs kept similar for all the samples. Microwave heating improves the quality of QDs in terms of optical properties, which was confirmed by recording UV-vis absorbance and photoluminescence both excitation and emission spectra, as shown in **Figure 6(a)** and **(b)**, respectively. In all the cases, peak intensities were enhanced and bandwidth reduced, which indicates the reduction of surface defects of QDs. The chemical composition of the doped CdSe QDs sample was confirmed with X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS), and inductively coupled plasma - atomic emission spectroscopy (ICP-AES) measurements data. XPS result confirmed the efficient incorporation of Mn atoms as dopants inside the host CdSe QDs (**Figure 7**).

3.1.2 More examples on doped binary nanocrystals

Microwave-assisted synthesis has also been utilized by many research groups around the world to dope various other binary II-VI semiconductor-based nanocrystals. Molaei *et al.* reported the synthesis of copper (Cu) doped ZnSe nanocrystals in the aqueous medium to study the doping effect on the optical properties [43]. Synthesis of Mn^{2+} ion-doped ZnS quantum dots was reported by Joicy *et al.* using a rapid microwave irradiation step without any surfactants, which showed photocatalytic activity by observing photodegradation of methyl orange dye under

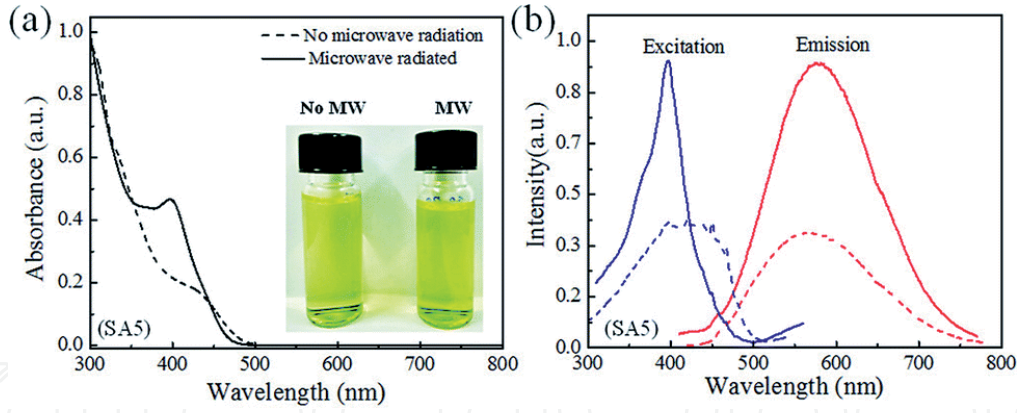


Figure 6. Electronic UV-vis (a) and photoluminescence (b) spectrum of Mn²⁺ doped CdSe QDs sample with and without microwave irradiation [17].

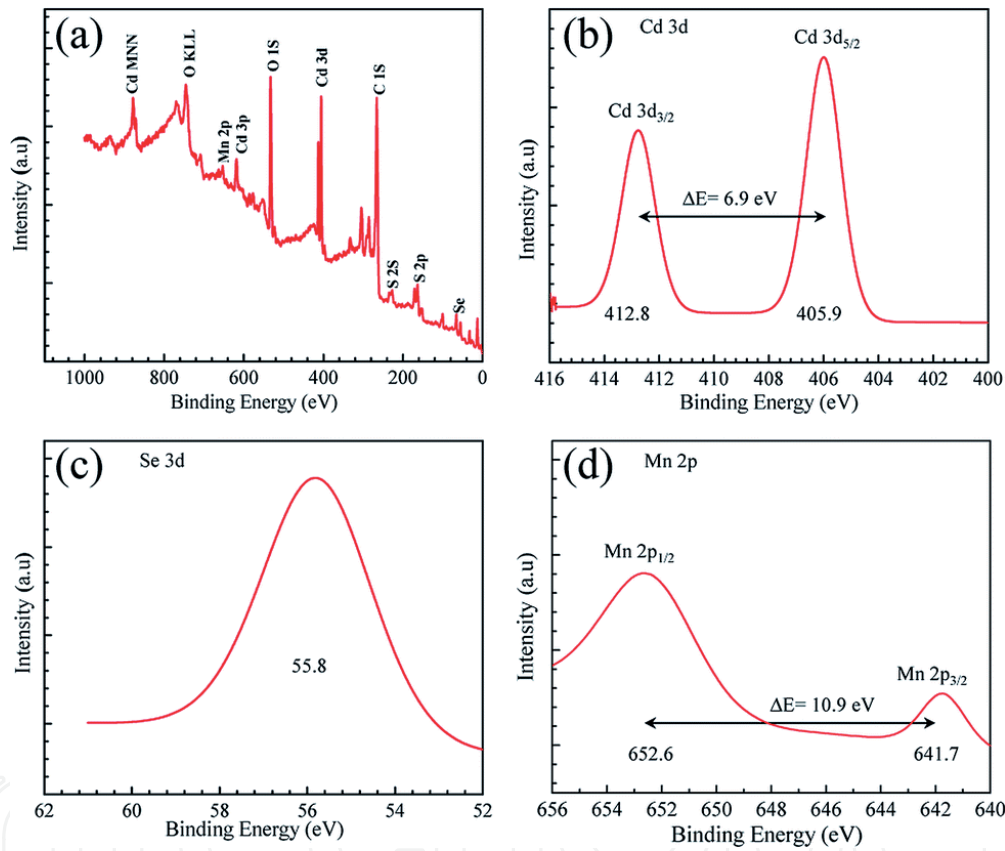


Figure 7. (a) Survey scan of the X-ray photoelectron spectrum of 2% Mn²⁺-doped CdSe QDs. (b, c) high-resolution spectrum of Cd 3d electrons depicting doublet splitting with binding energies separated by 6.9 eV and Se 3d, respectively. (d) the high-resolution spectrum of Mn 2p core electrons showing doublet splitting with binding energy separated by 10.9 eV [17].

UV light irradiation [44]. Here, the zinc blende crystal phase of ZnS was important for the efficient incorporation of Mn atoms. In the same year, Zhu *et al* reported the synthesis of Mn-doped ZnS via green and rapid microwave-assisted approach and they also developed indapamide drug detector by recording room-temperature phosphorescence (RTP) with that doped material [45].

Later, Zhang *et al.* reported the aqueous synthesis of Mn and Cu doped ZnSe QDs by microwave radiation with higher quantum yields (QYs) and they have further extended this work to grow the white-light-emitting ZnSe/ZnS core/shell QDs via the co-doping of Mn and Cu [46]. Lead sulphide (PbS) QD are still emerging various applications in optoelectronics and its property was further tuned with a

silver (Ag) atom doping. It is also reported by Shkir *et al.* that the bandgap of PbS QDs was increased with Ag atom incorporation, which was predicted without mentioning the influence of size variation between the samples used [47]. Recently, another work reported on facile microwave synthesis of CdS quantum dots doped with Cr atoms as impurity doping and they have studied various properties like structural, opto-dielectric, electrical, and so on [48].

3.1.3 Doped oxide nanomaterials

Various metal oxides nanomaterials play a major role in the development of different novel daily life applications in the fields of display, sensors, medicine, biomedical devices, agriculture, information technology, optical, energy, electronics, and so on. Efforts are ongoing to tune their properties and applications further with incorporating impurity as dopants. For that reason, microwave heating based synthesis protocols is developing as a potential alternative to the conventional heating based growth process. Kar *et al.* developed a microwave synthesis of rare-earth element Eu^{3+} doped tin oxide (SnO_2) to tune the optical and electrical properties of the host [49]. Jamatia *et al.* reported the microwave-assisted synthesis of Fe doped ZnO nanoparticles to show their application in polymer light-emitting diodes [50]. The wurtzite hexagonal crystal phase of ZnO nanoparticles and incorporation of the Fe dopant into the host ZnO crystal lattice was confirmed via X-ray diffraction analysis. This report claimed that the bandgap modification of ZnO via Fe doping is estimated from the Tauc plot without considering the influence of size. Similarly, many spinel structured metal oxides were also doped with different transition metal ions via microwave heating based synthesis technique with tunable structural, morphological, optical, vibrational, and magnetic properties and different potential applications like phosphor-based forensic testing and many more [51–54]. Interestingly, Er^{3+} doped $\alpha\text{-Fe}_2\text{O}_3$ and Fe doped TiO_2 nanoparticles were synthesized successfully with the help of microwave heating to study their crystal structure and optical properties [55, 56]. Recently, Yathisha *et al.* reported Zn^{2+} doped MgO nanoparticles utilizing microwave combustion route to study the influence on photovoltaic properties [57]. Therefore, microwave heating could explore further as a low-cost alternative synthesis protocol to design a new variant of nanomaterials.

3.1.4 Lanthanide ion doped lanthanum trifluoride (LaF_3)

Lanthanum trifluoride (LaF_3) is an ionic compound that is utilized as core-shell-up conversion nanoparticles (UCNPs) for different filed of applications like sensing, biomedical, and solar cells. Tek *et al.* reported Yb^{3+} ion-doped (active) and undoped (inert) LaF_3 shell coatings on a 20% Yb, 2% Tm codoped hexagonal phase LaF_3 core with the help of microwave -assisted synthesis route [58]. They observed higher optical enhancement of inert shell compared with the active shell at all prominent emission peaks, which is explained with the energy band diagram indicating the energy transfer pathways for the Yb^{3+} and Tm^{3+} – co-doping (Figure 8).

3.2 Doping of carbon based nanomaterials

Carbon-based materials like graphene can also be doped via microwave (MW) heating. Since the nanocarbon materials are found to be sensitive to microwave radiation [59, 60], the technique of MW heating was employed in the modification of graphene materials. It is also reported that by the use of microwave heating, hollow carbon nanospheres can be synthesized within a short time which can be effectively used as a host material for doping [61, 62]. Figure 9 shows the

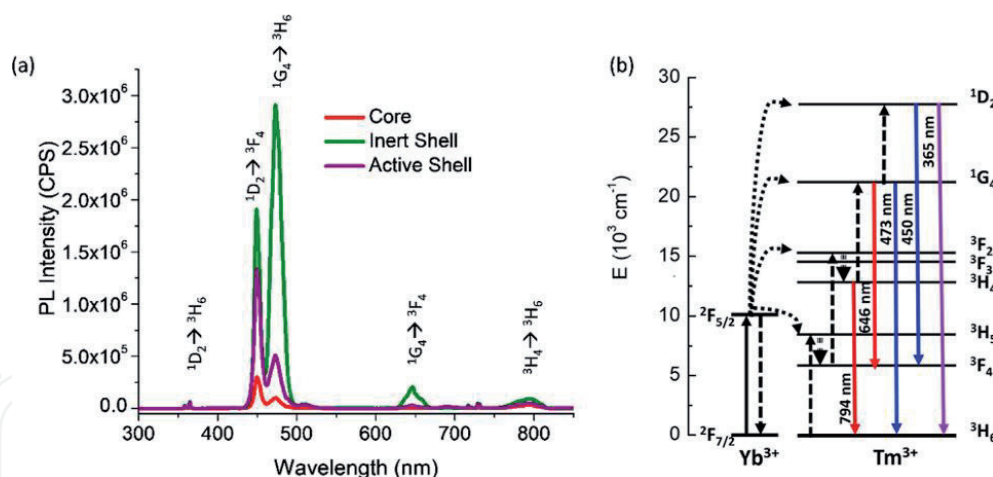


Figure 8.

(a) UCPL data for core, active shell, and inert shell nanoparticles under 980 nm continuous-wave excitation. (b) Energy diagram showing the corresponding transition of UCPL of (a) where the energy transfer pathways for the Yb^{3+} and Tm^{3+} -codoped up conversion nanoparticles are depicted [58].

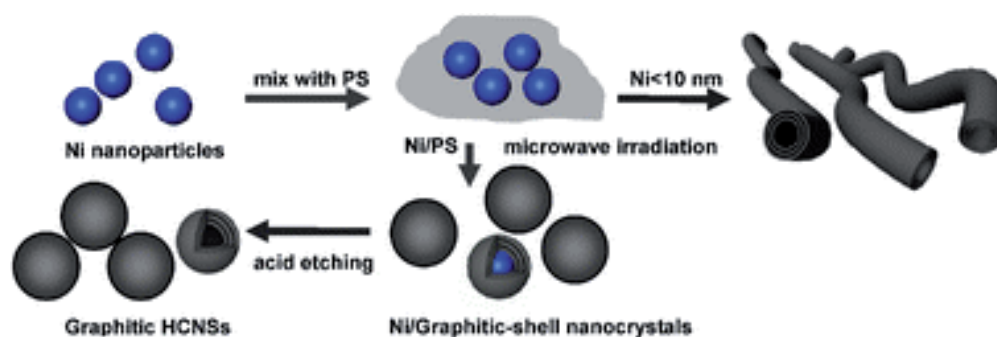


Figure 9.

Microwave-induced synthesis of Ni/graphitic-shell nanocrystals and graphitic hollow carbon Nano spheres [61].

microwave-assisted approach to prepare metal/graphitic shell nanocrystals and CNT in a very short time using ordinary carbon precursor.

The microwave-assisted technique facilitates the growth of heteroatom-doped graphene with better catalytic activity as well. Nitrogen doping up to 8.1% on graphene was achieved by Kwang *et al* within a minute with the aid of the microwave radiation. The binding configuration of nitrogen over graphitic basal planes can be varied with the irradiation power of microwave. The conductivity enhancement upto 300 Scm^{-1} was obtained in this case in comparison to nitrogen-doped via arc discharge method, nitrogen plasma process, etc. showing a lesser conductivity [63]. The dielectric heating of MW induces a high energy state that helps the graphitic basal plane to accommodate the dopants in order to convert graphite to N-doped graphene. The selective dielectric heating, which arises due to the difference in the dielectric constants of solvent and reactant can enhance the efficiency of doping without the rise of a thermal gradient [64]. The solid phase microwave-assisted synthetic method is adopted for the large-scale production of N-doped carbon nanodots (CNDs) using different citric acid/urea (C/U) weight ratios, which result in size variation of CNDs as shown in **Figure 10** with the transmission electron microscope (TEM) images. The dopant ion concentration can be varied in a precise manner that results in N-doped graphene QDs and graphitic-carbon nitride quantum dots (g-CNQD). The doped material is found to exhibit a 38.7% quantum yield due to the presence of N and O rich edge groups resulting from the interaction of microwave on graphene [65].

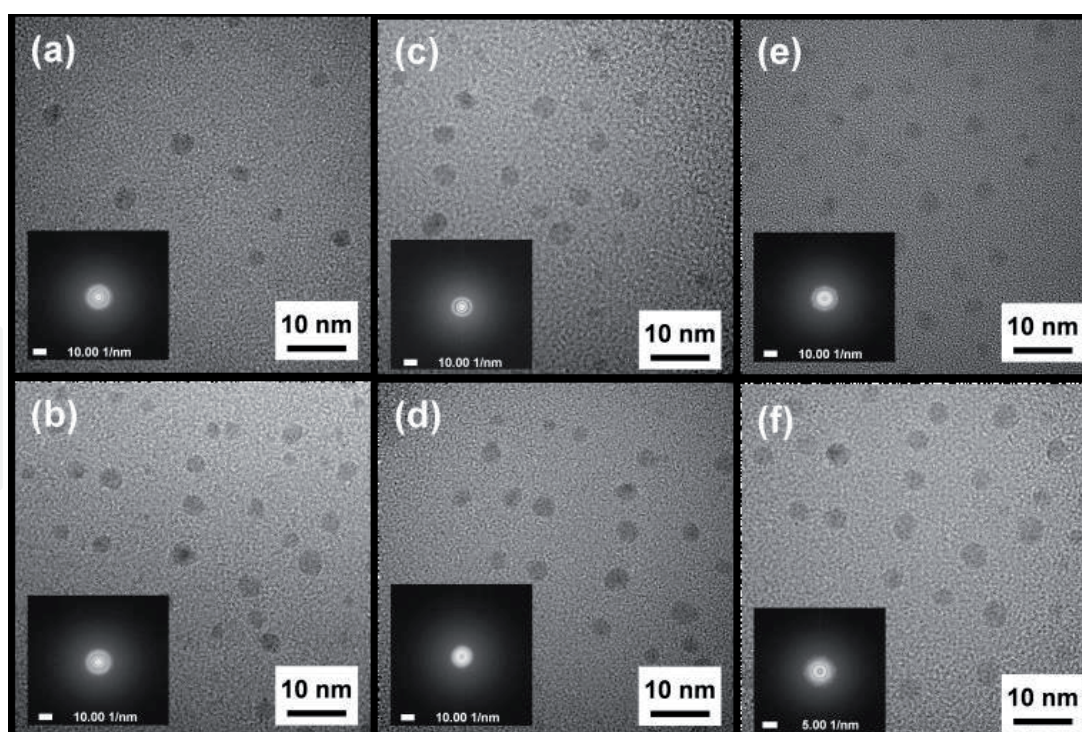
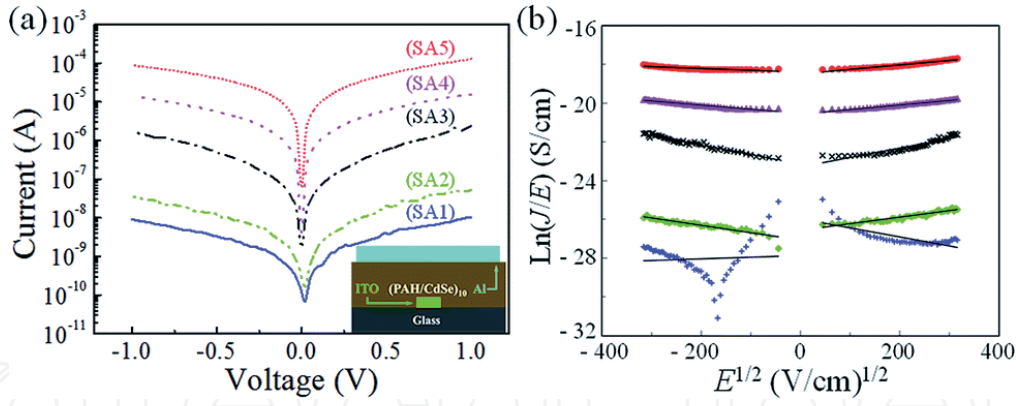


Figure 10.
 HR-TEM micrographs of N-doped carbon nanodots (CNDs) samples prepared using the SPMA method for different citric acid /urea (C/U) weight ratios of 3/1 (a), 2/1 (b), 1/1 (c), 1/1.5 (d), 1/2 (e), and 1/3 (f). Inset shows the corresponding selected-area diffraction pattern [65].

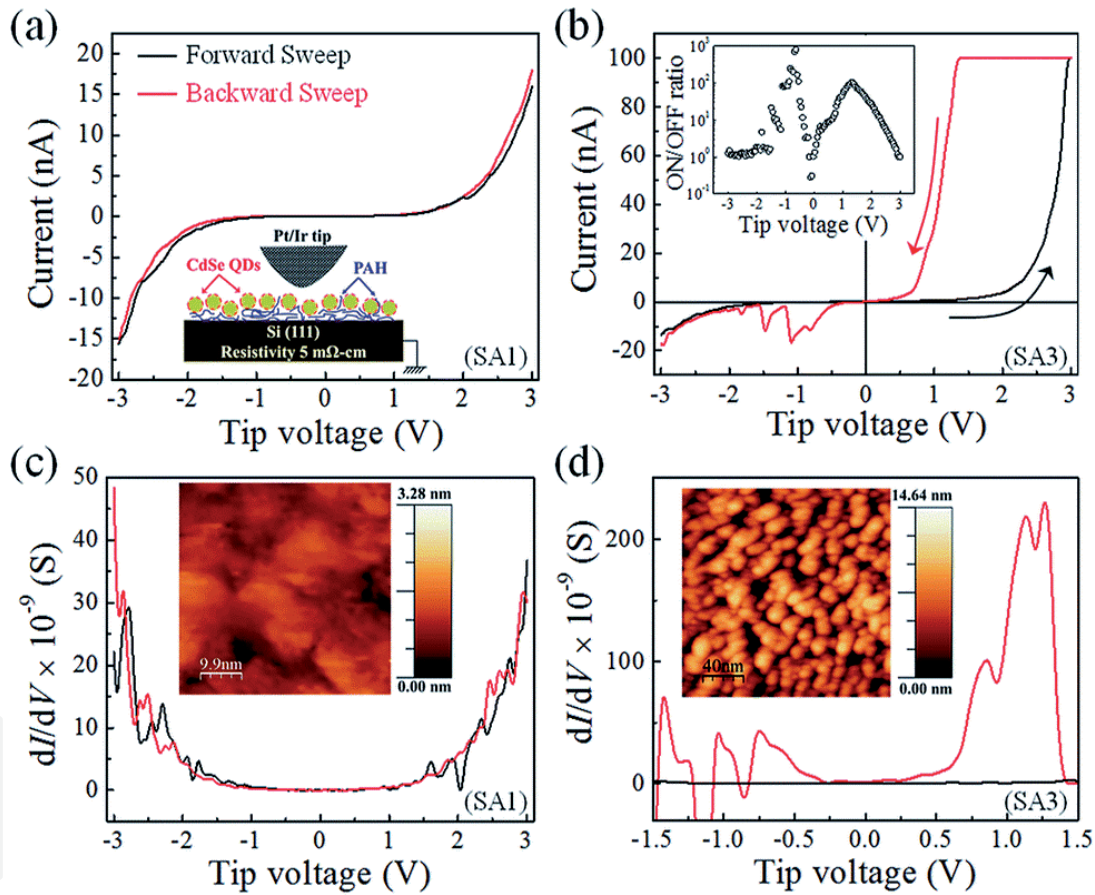
4. Electrical and memristor property of Mn^{2+} doped CdSe QDs

Huge enhancement in the conductivity of microwave-assisted doped QDs has been reported in many pieces of literature. Microwave heating enables the tuning of electrical conductivity in a desired manner by proper incorporation of dopants into the desired locations of the host material. This is evidenced by the rise in the electrical conductivity to the order of 10^4 for 2% Mn^{2+} doped CdSe over undoped one as shown in **Figure 11(a)** [17]. Here, the conduction mechanism is controlled by the electric field-assisted thermal ionization of trapped charge carriers in CdSe QDs as described in Poole–Frenkel effect as shown in **Figure 11(b)** [66]. The bandgap has no role in the conductivity and the observed colossal conductivity enhancement is solely due to the concentration of Mn^{2+} dopant ions.

The STM study performed on a monolayer device of Mn^{2+} doped CdSe QDs synthesized via microwave method founds to exhibit excellent memory characteristics as described in **Figure 12** [17]. This memristor property is evident from **Figure 12(b)** where the doped CdSe QDs switched to a high conducting state at the bias of 2.5 V. It is also observed that the device switched back to its low conducting state when the tip swept towards 3 V and the ON/OFF ratio obtained was higher than 10^2 . The reproducible nature of the resistive switching property over many cycles further confirms the reliability of the measurement. The threshold voltage at which the device switches to a high conducting state is found to be decreasing with an increase in the dopant concentration. Thus the notable electric bistability and the low threshold voltage of as synthesized doped CdSe QDs with the aid of simple and domestic microwave method promises its application in vivid area of future technologies which ensures minimum energy consumption per byte of the resistive data storage devices in future.


Figure 11.

(a) Current–voltage characteristics of Mn-doped CdSe QDs for the samples with varying dopant concentrations. (b) Poole–Frenkel fitting for all samples with respective straight trend line [17].


Figure 12.

(a, b) The Tunneling current–voltage (I – V) characteristics of a monolayer of undoped and 0.2% Mn^{2+} -doped CdSe QDs. Doped CdSe is showing low conducting state (OFF state, black line) and high conducting state (ON state, red line) for forward and backward voltage sweep direction respectively. (c, d) The differential conductance–voltage characteristics of a monolayer of undoped and 0.2% Mn^{2+} -doped CdSe QDs respectively in their forward (black line) and backward (red line) sweep direction. The topographic images of bare Si(111) and monolayer of undoped CdSe QDs deposited on Si(111) are shown on the insets within (c) and (d) [17].

5. Conclusion

In this chapter, we mainly discussed the incorporation of impurity dopant atoms into a host semiconducting quantum dots system very efficiently using microwave heating strategy with the help of a large number of examples from the literature. It has also been observed that the zinc blend crystal phase is very efficient for the


dopant incorporation than the hexagonal one. This also reflects that microwave heating can be utilized to synthesize various classes of doped zero-dimensional (0D) nanomaterials or quantum dots of many chalcogenides, oxides, carbon dots, and more with the large numbers of dopant atoms easily and more cheaply. Literature shows that the research related to two-dimensional (2D) transition metal dichalcogenides (TMDs) is booming up due to having tunable physical, electronic, and optoelectronic properties. Therefore, it would be intriguing to grow various 2D TMDs, both intrinsic and impurity-doped, via microwave heating, which will definitely reduce cost and different health and environmental hazards.

Author details

Sandhya K. M., Litty Thomas Manamel and Bikas C. Das*
School of Physics, Indian Institute of Science Education and Research
Thiruvananthapuram (IISER TVM), Maruthamala PO, Vithura, Trivandrum,
Kerala, India

*Address all correspondence to: bikas@iisertvm.ac.in

IntechOpen

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] S. A. Galema, "Microwave chemistry," *Chemical Society Reviews*, vol. 26, pp. 233-238, Jun 1997.
- [2] Y. J. Zhu and F. Chen, "Microwave-Assisted Preparation of Inorganic Nanostructures in Liquid Phase," *Chemical Reviews*, vol. 114, pp. 6462-6555, Jun 25 2014.
- [3] M. Niederberger, G. Garnweitner, J. Buha, J. Polleux, J. H. Ba, and N. Pinna, "Nonaqueous synthesis of metal oxide nanoparticles: Review and indium oxide as case study for the dependence of particle morphology on precursors and solvents," *Journal of Sol-Gel Science and Technology*, vol. 40, pp. 259-266, Dec 2006.
- [4] M. Casavola, R. Buonsanti, G. Caputo, and P. D. Cozzoli, "Colloidal strategies for preparing oxide-based hybrid nanocrystals," *European Journal of Inorganic Chemistry*, pp. 837-854, Feb 2008.
- [5] P. D. Cozzoli and L. Manna, "Synthetic strategies to size and shape controlled nanocrystals and nanocrystal heterostructures," *Bio-Applications of Nanoparticles*, vol. 620, pp. 1-17, 2007.
- [6] E. Reverchon, "Supercritical antisolvent precipitation of micro- and nano-particles," *Journal of Supercritical Fluids*, vol. 15, pp. 1-21, May 1 1999.
- [7] I. Bilecka and M. Niederberger, "Microwave Chemistry: Towards Predictable Nanoparticle Synthesis," *Chimia*, vol. 63, pp. 581-581, 2009.
- [8] I. Bilecka and M. Niederberger, "Microwave chemistry for inorganic nanomaterials synthesis," *Nanoscale*, vol. 2, pp. 1358-1374, 2010.
- [9] C. O. Kappe, "Controlled microwave heating in modern organic synthesis," *Angewandte Chemie-International Edition*, vol. 43, pp. 6250-6284, 2004.
- [10] F. Langa, P. Delacruz, A. DelaHoz, A. DiazOrtiz, and E. DiezBarra, "Microwave irradiation: more than just a method for accelerating reactions," *Contemporary Organic Synthesis*, vol. 4, pp. 373-386, Oct 1997.
- [11] D. Obermayer, B. Gutmann, and C. O. Kappe, "Microwave Chemistry in Silicon Carbide Reaction Vials: Separating Thermal from Nonthermal Effects," *Angewandte Chemie-International Edition*, vol. 48, pp. 8321-8324, 2009.
- [12] M. Baghbanzadeh, L. Carbone, P. D. Cozzoli, and C. O. Kappe, "Microwave-Assisted Synthesis of Colloidal Inorganic Nanocrystals," *Angewandte Chemie-International Edition*, vol. 50, pp. 11312-11359, 2011.
- [13] A. de la Hoz, A. Diaz-Ortiz, and A. Moreno, "Microwaves in organic synthesis. Thermal and non-thermal microwave effects," *Chemical Society Reviews*, vol. 34, pp. 164-178, 2005.
- [14] G. M. Dalpian and J. R. Chelikowsky, "Self-purification in semiconductor nanocrystals," *Physical Review Letters*, vol. 96, Jun 9 2006.
- [15] J. B. Li, S. H. Wei, S. S. Li, and J. B. Xia, "Origin of the doping bottleneck in semiconductor quantum dots: A first-principles study," *Physical Review B*, vol. 77, Mar 2008.
- [16] J. D. Bryan and D. R. Gamelin, "Doped Semiconductor Nanocrystals: Synthesis, Characterization, Physical Properties, and Applications," *Progress in Inorganic Chemistry*, Vol 54, vol. 54, pp. 47-126, 2005.
- [17] S. K. Meladom, S. Arackal, A. Sreedharan, S. Sagar, and B. C. Das, "Microwave assisted robust aqueous synthesis of Mn²⁺-doped CdSe QDs with enhanced electronic properties,"

Rsc Advances, vol. 8, pp. 26771-26781, 2018.

[18] D. El Khaled, N. Novas, J. A. Gazquez, and F. Manzano-Agugliaro, "Microwave dielectric heating: Applications on metals processing," *Renewable & Sustainable Energy Reviews*, vol. 82, pp. 2880-2892, Feb 2018.

[19] J. Sun, W. L. Wang, and Q. Y. Yue, "Review on Microwave-Matter Interaction Fundamentals and Efficient Microwave-Associated Heating Strategies," *Materials*, vol. 9, Apr 2016.

[20] J. P. Cheng, R. Roy, and D. Agrawal, "Experimental proof of major role of magnetic field losses in microwave heating of metal and metallic composites," *Journal of Materials Science Letters*, vol. 20, pp. 1561-1563, 2001.

[21] J. P. Cheng, R. Roy, and D. Agrawal, "Radically different effects on materials by separated microwave electric and magnetic fields," *Materials Research Innovations*, vol. 5, pp. 170-177, Feb 2002.

[22] R. Roy, R. Peelamedu, C. Grimes, J. P. Cheng, and D. Agrawal, "Major phase transformations and magnetic property changes caused by electromagnetic fields at microwave frequencies," *Journal of Materials Research*, vol. 17, pp. 3008-3011, Dec 2002.

[23] C. B. Whitehead, S. Ozkar, and R. G. Finke, "LaMer's 1950 Model for Particle Formation of Instantaneous Nucleation and Diffusion-Controlled Growth: A Historical Look at the Model's Origins, Assumptions, Equations, and Underlying Sulfur Sol Formation Kinetics Data," *Chemistry of Materials*, vol. 31, pp. 7116-7132, Sep 24 2019.

[24] M. A. Watzky and R. G. Finke, "Nanocluster size-control and "magic number" investigations, experimental tests of the "living-metal polymer" concept and of mechanism-based

size-control predictions leading to the syntheses of iridium(0) nanoclusters centering about four sequential magic numbers," *Chemistry of Materials*, vol. 9, pp. 3083-3095, Dec 1997.

[25] I. M. Lifshitz and V. V. Slyozov, "The kinetics of precipitation from supersaturated solid solutions," *Journal of Physics and Chemistry of Solids*, vol. 19, pp. 35-50, 1961/04/01/ 1961.

[26] J. A. Marqusee and J. Ross, "Kinetics of Phase-Transitions - Theory of Ostwald Ripening," *Journal of Chemical Physics*, vol. 79, pp. 373-378, 1983.

[27] S. C. Erwin, L. J. Zu, M. I. Haftel, A. L. Efros, T. A. Kennedy, and D. J. Norris, "Doping semiconductor nanocrystals," *Nature*, vol. 436, pp. 91-94, Jul 7 2005.

[28] N. Razgoniaeva, P. Moroz, M. R. Yang, D. S. Budkina, H. Eckard, M. Augspurger, *et al.*, "One-Dimensional Carrier Confinement in "Giant" CdS/ CdSe Excitonic Nanoshells," *Journal of the American Chemical Society*, vol. 139, pp. 7815-7822, Jun 14 2017.

[29] D. J. Norris, A. L. Efros, and S. C. Erwin, "Doped nanocrystals," *Science*, vol. 319, pp. 1776-1779, Mar 28 2008.

[30] S. Gilje, S. Han, M. Wang, K. L. Wang, and R. B. Kaner, "A chemical route to graphene for device applications," *Nano Letters*, vol. 7, pp. 3394-3398, Nov 2007.

[31] C. J. Barrows, V. A. Vlaskin, and D. R. Gamelin, "Absorption and Magnetic Circular Dichroism Analyses of Giant Zeeman Splittings in Diffusion-Doped Colloidal Cd_{1-x}Mn_xSe Quantum Dots," *Journal of Physical Chemistry Letters*, vol. 6, pp. 3076-3081, Aug 6 2015.

[32] R. Beaulac, L. Schneider, P. I. Archer, G. Bacher, and D. R. Gamelin, "Light-Induced Spontaneous Magnetization in Doped Colloidal

Quantum Dots,” *Science*, vol. 325, pp. 973-976, Aug 21 2009.

Journal of the American Chemical Society, vol. 133, pp. 1666-1669, Feb 16 2011.

[33] F. V. Mikulec, M. Kuno, M. Bennati, D. A. Hall, R. G. Griffin, and M. G. Bawendi, “Organometallic synthesis and spectroscopic characterization of manganese-doped CdSe nanocrystals,” *Journal of the American Chemical Society*, vol. 122, pp. 2532-2540, Mar 22 2000.

[40] D. A. Chen, R. Viswanatha, G. L. Ong, R. G. Xie, M. Balasubramanian, and X. G. Peng, “Temperature Dependence of “Elementary Processes” in Doping Semiconductor Nanocrystals,” *Journal of the American Chemical Society*, vol. 131, pp. 9333-9339, Jul 8 2009.

[34] C. J. Barrows, P. Chakraborty, L. M. Kornowski, and D. R. Gamelin, “Tuning Equilibrium Compositions in Colloidal Cd_{1-x}Mn_xSe Nanocrystals Using Diffusion Doping and Cation Exchange,” *Acs Nano*, vol. 10, pp. 910-918, Jan 2016.

[41] V. Chikan, “Challenges and Prospects of Electronic Doping of Colloidal Quantum Dots: Case Study of CdSe,” *Journal of Physical Chemistry Letters*, vol. 2, pp. 2783-2789, Nov 3 2011.

[35] C. B. Murray, D. J. Norris, and M. G. Bawendi, “Synthesis and Characterization of Nearly Monodisperse Cde (E = S, Se, Te) Semiconductor Nanocrystallites,” *Journal of the American Chemical Society*, vol. 115, pp. 8706-8715, Sep 22 1993.

[42] L. G. Gutsev, N. S. Dalal, and G. L. Gutsev, “Structure and Properties of a (CdSe)(6)@(CdSe)(30) Cluster Doped with Mn Atoms,” *Journal of Physical Chemistry C*, vol. 119, pp. 6261-6277, Mar 19 2015.

[36] N. Pradhan, D. M. Battaglia, Y. C. Liu, and X. G. Peng, “Efficient, stable, small, and water-soluble doped ZnSe nanocrystal emitters as non-cadmium biomedical labels,” *Nano Letters*, vol. 7, pp. 312-317, Feb 2007.

[43] M. Molaei, A. R. Khezripour, and M. Karimipour, “Synthesis of ZnSe nanocrystals (NCs) using a rapid microwave irradiation method and investigation of the effect of copper (Cu) doping on the optical properties,” *Applied Surface Science*, vol. 317, pp. 236-240, Oct 30 2014.

[37] M. Makkar and R. Viswanatha, “Frontier challenges in doping quantum dots: synthesis and characterization,” *Rsc Advances*, vol. 8, pp. 22103-22112, 2018.

[44] S. Joicy, R. Saravanan, D. Prabhu, N. Ponpandian, and P. Thangadurai, “Mn²⁺ ion influenced optical and photocatalytic behaviour of Mn-ZnS quantum dots prepared by a microwave assisted technique,” *Rsc Advances*, vol. 4, pp. 44592-44599, 2014.

[38] M. van Schilfgaarde and O. N. Mryasov, “Anomalous exchange interactions in III-V dilute magnetic semiconductors,” *Physical Review B*, vol. 63, Jun 15 2001.

[45] D. Zhu, W. Li, H. M. Wen, Q. Chen, L. Ma, and Y. Hu, “Microwave-assisted aqueous synthesis of Mn-doped ZnS quantum dots and their room-temperature phosphorescence detection of indapamide,” *Analytical Methods*, vol. 6, pp. 7489-7495, 2014.

[39] N. S. Karan, S. Sarkar, D. D. Sarma, P. Kundu, N. Ravishankar, and N. Pradhan, “Thermally Controlled Cyclic Insertion/Ejection of Dopant Ions and Reversible Zinc Blende/Wurtzite Phase Changes in ZnS Nanostructures,”

[46] J. Zhang, Q. H. Chen, W. L. Zhang, S. L. Mei, L. J. He, J. T. Zhu, *et al.*,

“Microwave-assisted aqueous synthesis of transition metal ions doped ZnSe/ZnS core/shell quantum dots with tunable white-light emission,” *Applied Surface Science*, vol. 351, pp. 655-661, Oct 1 2015.

- [47] M. Shkir, M. T. Khan, I. M. Ashraf, S. AlFaify, A. M. El-Toni, A. Aldalbahi, *et al.*, “Rapid microwave-assisted synthesis of Ag-doped PbS nanoparticles for optoelectronic applications,” *Ceramics International*, vol. 45, pp. 21975-21985, Dec 1 2019.
- [48] M. Shkir, Z. R. Khan, K. V. Chandekar, T. Alshahrani, A. Kumar, and S. AlFaify, “A facile microwave synthesis of Cr-doped CdS QDs and investigation of their physical properties for optoelectronic applications,” *Applied Nanoscience*, vol. 10, pp. 3973-3985, Oct 2020.
- [49] A. Kar and A. Patra, “Optical and Electrical Properties of Eu³⁺-Doped SnO₂ Nanocrystals,” *Journal of Physical Chemistry C*, vol. 113, pp. 4375-4380, Mar 19 2009.
- [50] T. Jamatia, D. Skoda, P. Urbanek, J. Sevcik, J. Maslik, L. Munster, *et al.*, “Microwave-assisted synthesis of Fe_xZn_{1-x}O nanoparticles for use in MEH-PPV nanocomposites and their application in polymer light-emitting diodes,” *Journal of Materials Science-Materials in Electronics*, vol. 30, pp. 11269-11281, Jun 2019.
- [51] S. G. Menon, A. K. Kunti, D. E. Motaung, and H. C. Swart, “A new recipe for the rapid microwave synthesis of high quantum yield Mn²⁺-doped ZnGa₂O₄ phosphors for potential forensic applications,” *New Journal of Chemistry*, vol. 43, pp. 17446-17456, Nov 28 2019.
- [52] A. T. Dhiwahar, M. Sundararajan, P. Sakthivel, C. S. Dash, and S. Yuvaraj, “Microwave-assisted combustion synthesis of pure and zinc-doped

copper ferrite nanoparticles: Structural, morphological, optical, vibrational, and magnetic behavior,” *Journal of Physics and Chemistry of Solids*, vol. 138, Mar 2020.

- [53] T. S. Nirmala, N. Iyandurai, S. Yuvaraj, and M. Sundararajan, “Effect of Cu²⁺ ions on structural, morphological, optical and magnetic behaviors of ZnAl₂O₄ spinel,” *Materials Research Express*, vol. 7, Apr 2020.
- [54] S. Ramachandran, C. S. Dash, A. Thamilselvan, S. Kalpana, and M. Sundararajan, “Rapid Synthesis and Characterization of Pure and Cobalt Doped Zinc Aluminate Nanoparticles via Microwave Assisted Combustion Method,” *Journal of Nanoscience and Nanotechnology*, vol. 20, pp. 2382-2388, Apr 2020.
- [55] M. Jahdi, S. B. Mishra, E. N. Nxumalo, S. D. Mhlanga, and A. K. Mishra, “Synergistic effects of sodium fluoride (NaF) on the crystallinity and band gap of Fe-doped TiO₂ developed via microwave-assisted hydrothermal treatment,” *Optical Materials*, vol. 104, Jun 2020.
- [56] L. E. Mathevula, B. M. Mothudi, and M. S. Dhlamini, “Effect of Er³⁺ on structural and optical properties of microwave synthesized alpha-Fe₂O₃ nanoparticles,” *Physica B-Condensed Matter*, vol. 578, Feb 1 2020.
- [57] R. O. Yathisha, Y. A. Nayaka, H. T. Purushothama, P. Manjunatha, K. V. Basavarajappa, and M. M. Vinay, “Investigation the influence of Zn²⁺ doping on the photovoltaic properties (DSSCs) of MgO nanoparticles,” *Journal of Molecular Structure*, vol. 1217, Oct 5 2020.
- [58] S. Tek, B. A. Vincent, L. C. Mimun, A. Ponce, and K. L. Nash, “Atomic-Scale Structural Analysis of Homoepitaxial LaF₃:Yb,Tm Core-Shell Upconversion Nanoparticles Synthesized through a

Microwave Route,” *Crystal Growth & Design*, vol. 20, pp. 2153-2163, Apr 1 2020.

[59] W. F. Chen, L. F. Yan, and P. R. Bangal, “Preparation of graphene by the rapid and mild thermal reduction of graphene oxide induced by microwaves,” *Carbon*, vol. 48, pp. 1146-1152, Apr 2010.

[60] P. Tang, G. Hu, Y. J. Gao, W. J. Li, S. Y. Yao, Z. Y. Liu, *et al.*, “The microwave adsorption behavior and microwave-assisted heteroatoms doping of graphene-based nano-carbon materials,” *Scientific Reports*, vol. 4, Aug 11 2014.

[61] K. Chen, C. L. Wang, D. Ma, W. X. Huang, and X. H. Bao, “Graphitic carbon nanostructures via a facile microwave-induced solid-state process,” *Chemical Communications*, pp. 2765-2767, 2008.

[62] C. L. Wang, D. Ma, and X. H. Bao, “Transformation of Biomass into Porous Graphitic Carbon Nanostructures by Microwave Irradiation,” *Journal of Physical Chemistry C*, vol. 112, pp. 17596-17602, Nov 13 2008.

[63] K. H. Lee, J. Oh, J. G. Son, H. Kim, and S. S. Lee, “Nitrogen-Doped Graphene Nanosheets from Bulk Graphite using Microwave Irradiation,” *Acs Applied Materials & Interfaces*, vol. 6, pp. 6361-6368, May 14 2014.

[64] J. A. Gerbec, D. Magana, A. Washington, and G. F. Strouse, “Microwave-enhanced reaction rates for nanoparticle synthesis,” *Journal of the American Chemical Society*, vol. 127, pp. 15791-15800, Nov 16 2005.

[65] S. Y. Gu, C. T. Hsieh, Y. A. Gandomi, J. K. Chang, J. Li, J. L. Li, *et al.*, “Microwave growth and tunable photoluminescence of nitrogen-doped graphene and carbon nitride quantum

dots,” *Journal of Materials Chemistry C*, vol. 7, pp. 5468-5476, May 14 2019.

[66] T. H. Chiang and J. F. Wager, “Electronic Conduction Mechanisms in Insulators,” *Ieee Transactions on Electron Devices*, vol. 65, pp. 223-230, Jan 2018.