1. INTRODUCTION

In the past decade, the synthesis, characterizations, and applications of nanodimensional materials have been the focus of interest of many researchers in various fields including chemistry, physics, materials science, biology, and corresponding engineering [1–4]. Nanoparticles usually exhibit unusual electronic, optical, magnetic, and chemical properties significantly different from those of corresponding bulk materials due to their extremely small sizes and large surface-to-volume ratio. They have various potential applications such as catalysis, electronic, optical, and mechanical devices, magnetic recording media, superconductors, high-performance engineering materials, dyes, pigments, adhesives, photographic suspensions, drug delivery, and so on [5]. The rapid development of nanoscience and nanotechnology will bring us a new world [6]. Exploring new methods that involve mild conditions and convenient operations for the preparation of nanosized materials with desirable properties and controllable dimensions and morphologies is currently a great challenge to both synthetic chemists and materials scientists.

Over the past two decades, the synthesis of chalcogenides has attracted significant interest and is still the subject of intense investigations. Conventionally, metal chalcogenides can be prepared in a variety of ways, the most straightforward of which is the direct combination of the elements at elevated temperatures [7]. This process requires a significant energy input, lasts for a long period of reaction time, and gives little control in material stoichiometry [8]. A low-energy approach is the precipitation of metal chalcogenides from aqueous solutions of metal cations by use of H₂E (E = S, Se, or Te) [9]. Problems with this method include the use of very toxic reagents and consistently obtaining the product with a high degree of impurity. Molecular precursor methods [10] involve thermal decomposition of a compound containing a M-S or M-Se bond, or involve H₂E as the chalcogenide source [11]. These methods have already been thoroughly investigated and found to be reliable at relatively low temperature (200–350 °C). Bulk materials have also been prepared from the elements by self-propagating high-temperature synthesis [12] and from the reactions of alkali-metal sulfides and metal halides by solid-state metathesis [13]. In recent years, emphasis has been devoted to the synthesis of metal chalcogenides in their nanophased form. This is due to the modern trend of miniaturization, on one hand, and to the unique properties associated with the nanostructures, on the other hand. In the past few years, a number of new methods have been established for the preparation of nanocrystalline metal chalcogenides. Their appearance gives great impetus to the development of nanoscience and nanotechnology. The application of these novel technologies provides convenient and efficient routes to produce nanocrystalline metal chalcogenides with desirable properties and controllable sizes and morphologies. These synthetic methods have already shown their advantages and will play a more and more important role in materials science in the future.

Herein, we present a review about the latest progress in the field of synthesis of metal chalcogenide nanoparticles. This review mainly focuses on some novel synthetic methods for nanocrystalline metal chalcogenides that have been established in the past decade including microwave assisted heating, sonochemical method, sonoelectrochemical method, photochemical synthesis, γ-irradiation method, etc.
microwave route, low-temperature solid-state synthesis, solvothermal technique, electrochemical template synthesis, and sol-gel method.

2. SYNTHETIC METHODS

2.1. Microwave Assisted Heating

Microwave heating has been known since the 1940s and widely used in the food industry. Microwaves are electromagnetic waves containing electric and magnetic field components. It is well known that the interaction of dielectric materials, liquids or solids, with microwaves leads to what is generally known as dielectric heating. Electric dipoles present in such materials respond to the applied electric field. In liquids, this constant reorientation leads to the friction between molecules, which subsequently generate heat. Claimed effects of microwave irradiation include thermal effects and nonthermal effects. Microwave irradiation as a heating method has found a number of applications in chemistry. The frequencies allotted for microwave assisted heating are 918 MHz and 2.45 GHz, with the latter frequency being most often used. The latter is also applied in domestic microwave ovens. The microwave ovens used in microwave chemistry range from simple household multimode ovens to large-scale batch as well as continuous multimode ovens. The microwave synthesis, which is generally quite fast, simple, and efficient in energy, has been developed and is widely used in fields such as molecular sieve preparation, radiopharmaceuticals, the preparation of inorganic complexes and oxide, organic reactions, plasma chemistry, analytical chemistry, and catalysis [14]. Though the number of publications related to the application of microwave irradiation in organic chemistry has shown an exponential growth over the past two decades, its extension to inorganic chemistry, on the other hand, has been much slower. It is only quite recently that microwave irradiation has been used in the synthesis of inorganic nanoparticles and keeps showing rapid growth in its application to materials science. Compared with conventional heating methods, microwave assisted heating presents a more rapid and simultaneous environment for the formation of nanoparticles due to the fast and homogeneous heating effects of microwave irradiation. Therefore, microwave assisted heating methods have the advantages of short reaction time, high-energy efficiency, and the ability to induce the formation of particles with small size, narrow size distribution, and high purity. In the past few years, microwave assisted heating has been applied in the soft chemical synthesis of various nanocrystalline metal chalcogenides and presents a promising trend in its future development.

Water has a very high dipole moment, which makes it one of the best solvents for microwave assisted reactions. A series of sulfide and selenide nanoparticles have been synthesized by microwave assisted heating method in aqueous solutions. Zhu and co-workers [15] have prepared CdS and ZnS nanoparticles by refluxing aqueous solutions containing CdCl₂ or Zn(Ac)₂ and thioacetamide in the presence of microwave irradiation. The average sizes of the as-prepared CdS and ZnS nanoparticles were ca. 9 nm and ca. 3 nm, respectively, and both products displayed conspicuous quantum size effects. The reactions occurring during microwave irradiation are believed to be

\[ \text{CH}_3\text{CSNH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3(\text{NH}_2)\text{C(OH)}\text{SH} \quad (1) \]

\[ \text{CH}_3(\text{NH}_2)\text{C(OH)}\text{SH} + \text{H}_2\text{O} \rightarrow \text{CH}_3(\text{NH}_2)\text{C(OH)}_2 + \text{H}_2\text{S} \quad (2) \]

\[ \text{CH}_3(\text{NH}_2)\text{C(OH)}_2 \rightarrow \text{CH}_3(\text{NH}_2)\text{C}=\text{O} + \text{H}_2\text{O} \quad (3) \]

\[ \text{H}_2\text{S} + \text{CdCl}_2 \rightarrow \text{CdS} + 2\text{HCl} \quad (4) \]

\[ \text{H}_2\text{S} + \text{Zn(Ac)}_2 \rightarrow \text{ZnS} + 2\text{HAc} \quad (5) \]

Equation (1) represents that H₂O reacts with CH₃CSNH₂ to form CH₃(NH₂)C(OH)SH by microwave heating. Repeating this process would then result in the formation of CH₃(NH₂)C(OH)₂ and H₂S. CH₃(NH₂)C(OH)₂ would immediately lose water to give CH₃CONH₂ (Eq. (3) shows the results). The further H₂S reacts with CdCl₂ or Zn(Ac)₂ to yield CdS or ZnS, respectively. Liao et al. [16] extended this methodology to the microwave assisted preparation of various metal sulfide nanoparticles including CdS, ZnS, CuS, HgS, and Bi₂S₃ by choosing 37.5% formaldehyde aqueous solution as solvent. During the microwave-induced formation of the sulfide nanoparticles, HCHO did not take part in the reactions. However, it acts as the dispersion stabilizer. It was found that the size and morphology of the as-prepared sulfide nanoparticles were different though the same irradiation time and intensity were used. This work showed that microwave irradiation could influence selective nucleation and growth rates of different compounds. Gedanken and co-workers [17] reported the microwave assisted preparation of nanocrystalline selenide semiconductors including CdSe, Cu₂₋ₓSe, and PbSe. In this method, CdSO₄, Pb(Ac)₂, or Cu(Ac)₂ reacted with Na₂SeSO₃ in water in the presence of complexing agents with induction of microwave irradiation to fabricate selenide nanoparticles. In the experiments, several factors were found to have influence on the nature and morphology of the products, such as the pH value, irradiation time, complexing agents, and so on.

Currently, one-dimensional (1D) nanostructured materials have been the focus of scientific research due to their unusual properties and potential use in both mesoscopic research and the development of nanodevices. Synthesis of metal chalcogenide nanorods (nanowires) or nanoribbons and investigations of their properties arouse considerable interests. Zhu's group has successfully applied microwave irradiation to induce the one-dimensional preferential growth of some II-VI and V-VI group semiconductors and prepared Bi₁S₃ [18] and Sb₂S₃ [19] nanorods and CdS nanoribbons [20] by microwave-induced decomposition of single-source precursors. It was found that microwave-induced decomposition of Bi-thiourea complex in formaldehyde solution and Sb-thiourea complex in N,N-dimethylformamide would lead to the formation of Bi₁S₃ and Sb₂S₃ nanorods, respectively. The observed rod type morphology of the as-prepared Bi₁S₃ and Sb₂S₃ is probably due to the chain type structures of such kind of materials. The formation of uniform nanosized particles demands
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a uniform growth environment, and microwave heating afforded this. With microwave irradiation of reactants in polar solvents, temperature and concentration gradients can be avoided, providing a uniform environment for the nucleation. During the process, microwaves not only provided the energy for the decomposition of the complexes, but also greatly accelerated the nucleation. All these were favorable for the formation of uniform and small-sized nanorods. CdCl₂ and 1-pyrrolidine dithio carboxylic acid ammonium salt (APDTC) would react with each other to form an inorganic core cluster complex [Cd(APDTC)₂]₂, which was unstable. Nucleophilic attack by ethylenediamine with the induction of microwave irradiation would lead to the formation of Cd₃S₂ crystal nuclei. These nuclei were not stable and had the tendency to combine with each other to grow into larger crystals. During the crystal growth process, these Cd₃S₂ nuclei preferentially grew along a unique direction grid, which resulted in the formation of a 1D structure. It was also found that ethylenediamine, which was a strong coordination Lewis base and N-chelation reagent, played an important role in the formation of CdS nanoribbons. When other solvent such as water or ethanol was utilized to replace ethylenediamine, CdS nanoribbons could not be obtained. These results showed that ethylenediamine probably served as a director for the preferential 1D growth of the CdS nanoribbons.

During the formation of the nanoparticles under microwave irradiation, solvents have important influence on the size and morphology of the final products. In different solvents, the collision rate between reactant molecules, the heating rate, and the temperature of the reaction are different. As a result, nanocrystalline particles with different sizes and morphologies could be obtained by using different solvents. Wang et al. [21] established a microwave assisted heating method for the rapid synthesis of spherical β-HgS nanoparticles with different sizes. By using different solvents, the average sizes of the HgS nanoparticles could be controlled in the range of 8 to 23 nm. Murugan and co-workers [22] used a combination of microwave and solvothermal techniques for the synthesis of CdS nanocrystalline powders. The effects of different parameters such as reaction time, temperature, solvent, and molar ratio of CdS to thiourea on the formation of CdS powders under microwave-solvothermal conditions were investigated in detail. It was found that solvents had significant effects not only on the different particle sizes, but also on the morphologies and phases of the products.

Metal tellurides are relatively more difficult to prepare than sulfides and selenides due to their much lower reactivity and high toxicity. Palchik et al. [23] used microwave irradiation to activate the reaction between elemental Te and Cu(AC)₂ or Hg(AC)₂ in ethylenediamine and synthesized Cu₂−xTe and HgTe nanoparticles. The copper telluride prepared by this method was a complex of Cu₂−xTe and ethylenediamine, which decomposed into pure Cu₂−xTe following annealing at 280 °C. Two probable mechanisms were proposed for the formation of the telluride by microwave irradiation. The first one could be described as a direct interaction between the tellurium and the microwave irradiation. Microwave irradiation could be used to heat metallic powders to very high temperatures, even if they were dispersed in low-boiling-point solvents. Since Te has some metallic characteristics (resistivity ρ = 2 × 10⁻⁶ Ω cm), its heating can be a major driving force for the reaction. Te would probably be heated to reach temperatures higher than the boiling point of ethylenediamine (118 °C), leading to the interfacial overheating of the solvent and facilitating the reactions. At an elevated temperature the ethylenediamine could reduce the Te to Te²⁻, which subsequently reacts with the metallic ions. A second possibility is based on the observation that in microwave boiled solvents, the solvents themselves can undergo profound overheating. This localized overheating effect can reach 13–26 °C in the case of organic solvents. Such an increase in the boiling point has been known to result in an approximately eightfold reaction rate enhancement. Such overheating effects can increase the reduction power of the solvent and reduce the metal ions to the metal in the zero oxidation state. Such metallic powders will strongly interact with microwaves, yielding very high temperatures, which enhance the solid-state reaction of metal with Te. Research is still underway to assess the relative importance of the solvent overheating and microwave-induced “solid-state reactions” in the microwave assisted preparation of metal tellurides.

In the 1980s, Fievet et al. used ethylene glycol as a solvent and reducing agent for the preparation of submicrometer particles of the transition metals. This method is known as the polyol process [24–27]. The mechanism of this reaction, however, is still only poorly understood even though it is known that the reduction is based on the decomposition of the ethylene glycol and its conversion to diacetyl. It has been discovered that the temperature is a dominant factor affecting the reactivity. In these reactions, the temperature influences three factors: (1) reducing potential of polyol compound; (2) rupture and creation of chemical bond; and (3) diffusion. All these factors make the microwave assisted heating method favorable for the fabrication of chalcogenides using ethylene glycol as a solvent. Gedanken’s group has already applied microwave irradiation to induce the formation of a series of binary and ternary chalcogenide nanoparticles via the so-called polyol process [28–31]. Polyol solvents like ethylene glycol are very suitable for microwave assisted reactions because of their relatively high dipole moment. Another advantage of using ethylene glycol as a solvent is its reducing power, which can be enhanced with the induction of microwave irradiation. Palchik et al. [28] prepared CdSe “nanoballs” by a microwave assisted polyol reduction method. The cubic and hexagonal forms of CdSe nanoparticles could be obtained by choosing triethylene glycol and ethylene glycol as the solvent, respectively. The as-prepared “nanoballs” were actually built up of clusters of CdSe with sizes of a few nanometers. Kerner et al. [29] used the microwave assisted polyol reduction method to synthesize agglomerated PbSe and PbTe nanoparticles. It is noteworthy that they also found that such polyol reactions could be induced by ultrasound irradiation and the PbSe and PbTe nanoparticles prepared sonochemically were monodisperse. Grisaru et al. [30, 31] reported the extension of this method to the preparation of ternary selenide nanoparticles, Cd₁−xZn₅Se (Fig. 1). Changing the preparation conditions,
such as the ratio of Cd and Zn, makes it possible to turn the electronic properties of Cd$_{1-x}$Zn$_x$Se. Further extension of this method may lead to the fabrication of some other ternary chalcogenide nanoparticles.

2.2. Sonochemical Synthesis

Currently, ultrasound irradiation has become an important tool in chemistry. It provides an unusual mechanism for generating high-energy chemistry with extremely high local temperatures and pressures and an extraordinary heating and cooling rate. Sonochemistry drives principally from acoustic cavitations: the formation, growth, and implosive collapse of bubbles in liquids [32]. When solutions are exposed to strong ultrasound irradiation, bubbles are implosively collapsed by acoustic fields in the solution. High-temperature and high-pressure fields are produced at the centers of the bubbles. The implosive collapse of the bubbles generates a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubbles. The conditions formed in these hotspots have been experimentally determined, with the transient temperature of $\sim 5000 \text{ K}$, pressure of $>1800 \text{ atm}$, and cooling rates in excess of $10^{10} \text{ K/s}$. These extreme conditions enable many chemical reactions to occur. Ultrasound irradiation differs from traditional energy sources (such as heat, light, or ionizing radiation) in duration, pressure, and energy per molecule. The use of high-intensity ultrasound irradiation to enhance the reactivity of metals as stoichiometric reagent has become a synthetic technique for many heterogeneous organic and organometallic reactions [33], especially those involving reactive metals, such as Mg, Li, or Zn. This development originated from the early work of Renault and the more recent breakthrough of Luche [34]. The effects are fairly general and apply to reactive inorganic salts as well. Suslick and co-workers found a variety of sonochemical reactions in liquid-solid mixture synthesis, for example, intercalation into layered inorganic solids [35], synthesis of amorphous metal powders [32], and metal semicarbides [36]. Ultrasound irradiation has also been used to induce hydrolysis to produce various metal oxide nanoparticles [37].

Ultrasound irradiation also offers a very attractive method for the preparation of various nanosized metal chalcogenides. In recent years, it has shown very rapid growth in its application to materials science due to its unique reaction effects. The advantages of this method include a rapid reaction rate, controllable reaction conditions, and the ability to form nanoparticles with uniform shapes, narrow size distributions, and high purities. It has been extensively used to generate novel materials with unusual properties, because in many cases it causes the formation of particles with a much smaller size and higher surface area than those reported by other methods. It has been known that during the sonochemical process, three different regions [38] are formed: (a) the inner environment (gas phase) of the collapsing bubbles, where the elevated temperatures and pressures are produced; (b) the interfacial region between the cavitation bubbles and the bulk solution where the temperature is lower than in the gas-phase region but still high enough to induce a sonochemical reaction; (c) the bulk solution, which is at ambient temperature. Among the three regions mentioned above, it appears that the current sonochemical reaction occurs within the interfacial region, yielding nanoparticles, because of the very high quenching rate experienced by the products. These products present either nanoamorphous or nanocrystalline nature [39, 40], as the results of different conditions formed during ultrasound irradiation.

A wide range of commercial equipment is now readily available for sonochemical research. High-intensity ultrasonic probes (50 to 500 W/cm$^2$) of the type used for biological cell disruption are the most reliable and effective source for laboratory-scale sonochemistry and permit easy control over ambient temperature and atmosphere. Ultrasonic cleaning baths are less satisfactory, owing to their low intensities (about 1 W/cm$^2$). For larger-scale irradiations, flow reactors with high ultrasonic intensities are commercially available in 20-kW modular units [32].

Ultrasound waves that are intense enough to produce cavitations can drive chemical reactions such as oxidation, reduction, dissolution, and decomposition. Other reactions driven by high-intensity ultrasound irradiation, such as promotion of polymerization, have also been reported [32d]. It has been known that during an aqueous sonochemical process, the elevated temperatures and pressures inside the collapsing bubbles cause water to vaporize and further pyrolyze into H$^\bullet$ and OH$^\bullet$ radicals. The sonochemical formation of metal chalcogenide nanoparticles in aqueous solutions is related to the radical species generated from water molecules by the absorption of the ultrasound energy. The $\textit{in situ}$ generated H$^\bullet$ is highly reducing radicals that can reduce mercaptan or compounds containing C=S or C=Se bonds, such as thiourea, thioacetamide, and selenium, to produce H$_2$S or H$_2$Se. Then the released H$_2$S or H$_2$Se reacts with metal cations to yield metal sulfides.
or metal selenides. The sonochemical formation of metal chalcogenide nanoparticles in aqueous solution via such kind of reactions can be summarized as follows:

\[
\begin{align*}
\text{H}_2\text{O} & \longrightarrow \text{H}^+ + \text{OH}^- \\
\text{RS} + 2 \text{H}^+ & \rightarrow \text{R}^+ + \text{H}_2\text{S} \quad (\text{RS} = \text{CH}_3\text{CSNH}_2 \text{ or } \text{NH}_2\text{CSNH}_2) \\
\text{M}^{x^+} + y\text{H}_2\text{S} & \rightarrow \text{M}_y\text{S}_x + 2y\text{H}^+ \\
n\text{M}_y\text{S}_x & \rightarrow (\text{M}_y\text{S}_x)_n \\
or \quad \text{RSe} + 2 \text{H}^+ & \rightarrow \text{R}^+ + \text{H}_2\text{Se} \quad (\text{RSe} = \text{NH}_2\text{CSeNH}_2) \\
\text{M}^{x^+} + y\text{H}_2\text{Se} & \rightarrow \text{M}_y\text{Se}_x + 2y\text{H}^+ \\
n\text{M}_y\text{Se}_x & \rightarrow (\text{M}_y\text{Se}_x)_n
\end{align*}
\]

Zhu et al. [41] reported a sonochemical method for the preparation of nanophase ZnSe. ZnSe nanoparticles of about 3 nm in size have been prepared by the sonochemical irradiation of an aqueous solution of selenoure and zinc acetate under argon. This method is proposed as a general method for the preparation of selenides. It has also been employed for the preparation of CuSe and PbSe nanoparticles. Jeevanandam et al. synthesized nanocrystalline ruthenium sulfide sonochemically by using ruthenium chloride and thiourea as precursors [42]. Sonication of an aqueous solution of ruthenium chloride and thiourea yielded an X-ray amorphous product which yields nanocrystalline ruthenium sulfide of stoichiometry RuS\textsubscript{1.7} on heating at 650 °C. The H\textsuperscript{•} generated from water molecules by absorption of ultrasound not only reduced thiourea, but also triggered the reduction of Ru(III) to Ru(II). The RuS\textsubscript{2} formed an adduct with thiourea and water, RuS\textsubscript{2}(NH\textsubscript{2}CSNH\textsubscript{2})\textsubscript{1.5} (H\textsubscript{2}O)\textsubscript{1.2}, which on heating produced nanocrystals of ruthenium sulfide with nonstoichiometry, RuS\textsubscript{1.7}. Avivi et al. [43] reported the preparation of nanophased indium sulfide by sonicating an aqueous solution of indium chloride and thioacetamide, the latter serving as the sulfur source. The reaction was carried out at different temperatures. It was found that the sonication of InCl\textsubscript{3} with thioacetamide in an aqueous solution led to different products, depending on the sonication temperature. Sonication at 0 °C yielded In\textsubscript{2}O\textsubscript{3} as the major product and In\textsubscript{2}S\textsubscript{3} as a minor component. On the other hand, when the reaction is carried out at “room temperature,” nanocrystalline In\textsubscript{2}S\textsubscript{3} is obtained as the sole product. The products of sonication at 0 °C are obtained in the amorphous form. An explanation for this was offered based on the hot spot mechanism. CuS and NiS nanoparticles have also been synthesized by sonication of aqueous solutions containing metal acetate (Cu(CH\textsubscript{3}COO)\textsubscript{2} or Ni(CH\textsubscript{3}COO)\textsubscript{2}) and thioacetamide (TAA) in the presence of triethanolamine (TEA) as a complexing agent under ambient air [44]. Grieser and co-workers [45] described the sonochemical formation of Q-state CdS colloid and the sonochemical dissolution of larger colloid CdS particles. In a system containing mercaptopropionic acid, the action of ultrasound produces H\textsubscript{2}S and in the presence of Cd\textsuperscript{2+} (aq.) ions, colloidal CdS was formed. The mechanism for the production of H\textsubscript{2}S appeared to be predominantly H\textsuperscript{•} attack on the thio group of the mercaptan, although there was evidence that the local heating from ultrasound also contributed to H\textsubscript{2}S formation. The colloidal particles produced sonochemically clearly showed quantum size effects and were estimated to be less than 3 nm in diameter. The dissolution of colloidal CdS at pH 10.5 appeared to be due to the reaction of H\textsubscript{2}O\textsubscript{2} and O\textsubscript{2} with the colloids. The likely explanation for the dissolution process can be summarized as below:

\[
\begin{align*}
\text{H}_2\text{O} & \longrightarrow \text{H}^+ + \text{OH}^- \\
2 \text{H}^+/2 \text{OH}^- & \rightarrow \text{H}_2/\text{H}_2\text{O}/2 \text{H}_2\text{O} \\
\text{H}^+ + \text{O}_2 & \rightarrow \text{HO}_2 \\
\text{HO}_2 & \rightarrow \text{H}^+ + \text{O}_2^- \\
\text{CdS} + 2 \text{OH}^- & \rightarrow \text{Cd}^{2+} + \text{S}_0^+ + 2 \text{OH}^- \\
\text{CdS} + 2 \text{H}_2\text{O} & \rightarrow \text{Cd}^{2+} + \text{S}_0^+ + 2 \text{OH}^- \\
\text{CdS} + 2 \text{O}_2^- + 4 \text{H}_2\text{O} & \rightarrow \text{Cd}^{2+} + \text{S}_0^+ + 2 \text{H}_2\text{O}_2 + 4 \text{OH}^- \\
\text{H}^+ & \text{generated during an aqueous sonochemical process can also trigger the reduction of S}_2\text{O}_2^2^- or \text{SeSO}_2^2^- to produce S^- or \text{Se}^2^- ions. The main steps can be described as follows:}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O} & \longrightarrow \text{H}^+ + \text{OH}^- \\
2 \text{H}^+/2 \text{OH}^- & \rightarrow \text{H}_2/\text{H}_2\text{O}/2 \text{H}_2\text{O} \\
\text{H}^+ + \text{O}_2 & \rightarrow \text{HO}_2 \\
\text{HO}_2 & \rightarrow \text{H}^+ + \text{O}_2^- \\
\text{CdS} + 2 \text{OH}^- & \rightarrow \text{Cd}^{2+} + \text{S}_0^+ + 2 \text{OH}^- \\
\text{CdS} + 2 \text{H}_2\text{O} & \rightarrow \text{Cd}^{2+} + \text{S}_0^+ + 2 \text{OH}^- \\
\text{CdS} + 2 \text{O}_2^- + 4 \text{H}_2\text{O} & \rightarrow \text{Cd}^{2+} + \text{S}_0^+ + 2 \text{H}_2\text{O}_2 + 4 \text{OH}^- \\
\text{M}^{x^+} + y\text{H}_2\text{S} \text{ or } \text{H}_2\text{S} & \rightarrow \text{M}_y\text{S}_x \text{ or } \text{M}_y\text{S}_x \\
\text{Zhu} \text{ and co-workers [46] have successfully prepared monodisperse lead selenide nanoparticles via a sonochemical route from an aqueous solution of lead acetate and sodium selenosulfate in the presence of complexing agents under ambient air. It was found that when trisodium citrate was used as the complexing agent, the product was spherical nanoparticles with an average size of ca. 8 nm (Fig. 2a). If potassium nitrotriacetate was used, the product consisted of rectangles with an average size of ca. 25 nm (Fig. 2b). Several other factors also affected the nature and morphology of the products, such as the pH value, the complexing agents, and the intensity of the ultrasound irradiation.}
\end{align*}
\]

Figure 2. TEM images of (a) monodisperse spherical PbSe nanoparticles prepared sonochemically; (b) monodisperse rectangular PbSe nanoparticles prepared sonochemically. Reprinted with permission from [46], J. J. Zhu et al., Langmuir 18, 3306 (2002). © 2002, American Chemical Society.
Other selenide nanoparticles including HgSe [47], Cu3Se2, Cu2x.3Se, and CuSe [48], have also been synthesized sonochemically in aqueous solutions by using sodium selenosalicylate as the selenium source. It was interesting that the ratio between Cu2+ and SeSO2− concentrations played an important role in the phase transformation of copper selenides. In this system, copper selenides with different phases including Cu2−xSe, Cu2x−3Se2, and CuSe could be obtained selectively by changing the ratio between Cu2+ and SeSO2− concentrations. The explanation of this phenomenon was proposed by the authors based on the following reactions:

\[
\begin{align*}
2 \text{H}^+ + \text{SeSO}_2^− & \rightarrow \text{Se}^{2−} + \text{H}_2\text{SO}_3^- \\
2 \text{Cu}^{2+} + 2 \text{SO}_3^{2−} + 2 \text{OH}^− & \rightarrow 2 \text{Cu}^{+} + \text{SO}_4^{2−} + \text{H}_2\text{O} \\
\text{Cu}^{2+} + \text{Se}^{2−} & \rightarrow \text{CuSe} \\
2\text{Cu}^{2+} + 2\text{Cu}^{+} + 2\text{Se}^{2−} & \rightarrow \text{Cu}_2\text{Se}_2 \\
(2 − x)\text{Cu}^{2+} + \text{Se}^{2−} & \rightarrow \text{Cu}_x\text{Se}_2
\end{align*}
\]

The in situ-generated H• radicals can react with SeSO2− to give Se2−. Meanwhile, Cu2+ can be reduced by SO32− to generate Cu+. When the concentration of SeSO2− is high enough, the reaction (‘) may be the main reaction so that the product is CuSe. The rate of reaction (‘) decreased sharply with the decrease of the concentration of SeSO2−, and when the concentration of SeSO2− was decreased, the reaction (**) changed gradually to be the main reaction so that the Cu+ generated together with Cu2+, leading to the formation of Cu2−xSe2 and Cu2x−3Se2, as shown in reactions (**‘). The release of Se2− was a continuous process, which makes the gradual growth of copper selenides nanocrystals. Wang et al. [49] synthesized Bi2S3 nanorods (Fig. 3) by a sonochemical method from an aqueous solution of bismuth nitrate and sodium thiosulfate in the presence of complexing agents. Bismuth sulfide nanorods with different diameters and lengths could be obtained by using different complexing agents including ethylenediaminetetraacetic acid, triethanolamine, and sodium tartrate. When 20% N,N-dimethylformamide (DMF) was used as the solvent, higher yield was observed and smaller sizes of Bi2S3 nanorods were obtained. It has been known that in the bulk solution, factors favoring maximum acoustic cavitation and sonochemical yields are low viscosity, high surface tension, low vapor pressure, and high sound speed. DMF is favorable for sonochemical process for it fulfills all of the criteria mentioned. When 20% DMF-water solution was used as the solvent, better yield could be obtained. The DMF accumulated at the interfacial region is likely to outcompete the concurrent process of the removal of OH• radicals:

\[
\text{OH•} + (\text{CH}_3)_2\text{NCHO} \rightarrow \cdot\text{CH}_2\text{N}(\text{CH}_3)\text{CHO} + \text{H}_2\text{O}
\]

This is one of the most likely factors responsible for the continuing increase of the sonochemical radical yields. So when 20% DMF-water solution was used as the solvent instead of water alone, the sonochemical process was enhanced, which led to the better yields of the product. Furthermore, the existence of DMF in aqueous solution influences the size and morphology of the product. When 20% DMF-water solution was used as the solvent, the size of the Bi2S3 nanorods obtained became much smaller. The decrease in size may be attributed to the faster nucleation rate caused by the enhancement of the sonochemical process. Wang and co-workers [50] employed ultrasound irradiation to fabricate hexagonal and cubic CdS nanocrystallites in aqueous solutions with or without isopropyl alcohol addition at room temperature. If the reactions were carried out in pure aqueous solution, the as-prepared CdS crystallized in hexagonal structure. When the isopropyl alcohol, which was a scavenger of radicals, was added into pure aqueous solution, the final product was cubic phase CdS. In the presence of isopropyl alcohol, a secondary reducing radical (CH3)2(OH)C• was formed during sonication via hydrogen abstraction from the (CH3)2CH(OH) by OH• radicals though the following reaction:

\[
(\text{CH}_3)_2\text{CH(OH)} + \text{OH•} \rightarrow (\text{CH}_3)_2(\text{OH})\text{C}• + \text{H}_2\text{O}
\]

Being a reducing radical, (CH3)2(OH)C• reacts with S2O32− rapidly to form S2− ions:

\[
2 (\text{CH}_3)_2(\text{OH})\text{C}• + \text{S}_2\text{O}_3^{2−} \rightarrow \text{S}^{2−} + 2 \text{H}^+ + \text{SO}_3^{2−} + 2 (\text{CH}_3)_2\text{CO}
\]

The presence of (CH3)2CH(OH) has a great influence on the structure and particle sizes of CdS nanocrystallites. It is known that kinetic factors are important in defining the crystal structure. (CH3)2CH(OH) can influence the dissolution and transmission of ions in the solutions, and might lead to the different kinetic factors.

The sonochemical reaction of volatile organometallics in organic solvents was discovered to be a novel approach to nanophase metal chalcogenides. Mleleni et al. [51] reported that nanophase MoS2 could be synthesized by irradiating a slurry of molybdenum hexacarbonyl and sulfur in 1,2,3,5-tetramethylbenzene (isodurene) with high-intensity ultrasound (20 kHz) under Ar. The as-prepared high-surface-area nanostructured MoS2 was distinct from its conventional counterpart (Fig. 4) and catalyzed thiophene HDS with higher activities than those of the most active materials. Amorphous WS2 has been prepared by ultrasound.
irradiation of W(CO)_6 solution in diphenylmethane (DPhM) in the presence of a slight excess of sulfur at 90 °C under Ar [52]. Heating the amorphous powder at 800 °C under argon yields WS_2 nanorods and their packing. The average size of WS_2 nanorods was found to be 3–10 nm in thickness and 1–5 μm in length.

Lelieur and co-workers [53] and Parkin and co-workers [54, 55] have developed a room-temperature liquid-ammonia route to prepare metal chalcogenides. Reaction of sulfur, selenium, or tellurium with elemental metals in liquid ammonia at room temperature in a pressure vessel produces a series of binary and ternary metal chalcogenides. They pointed out that in sulfur-ammonia solutions, there were various sulfur imido anions (S_xN^- x = 1–8) as well as sulfur polyamions (S_xN^+ x = 1–8). Sulfur could also dissolve in organo-amine to produce colored N,N'-diamine-polysulfide solution and hydrosulfuric acid [56]. Ethylenediamine plays an important role in generating the active sulfur species, such as S^2-. Meanwhile, ethylenediamine as a strong bidentate ligand can coordinate with metal ions to give stable complexes in the form of chelate compounds \([M(en)]^+\). These chelate compounds would then react with the active sulfur species, leading to the formation of metal sulfides. Metal selenides and metal tellurides would also be produced in a similar way. The whole process can be described as follows:

\[
M^{x+} + xen \rightleftharpoons [M(en)x]^x+ \\
S_N + en \rightarrow H_2S + N \\
yH_2S + 2[M(en)x]^x+ \rightarrow M_Sy + 2xen + 2yH^+ 
\]

In most cases, the as-prepared chalcogenides were X-ray amorphous or poorly crystalline, and needed to be annealed to get crystalline products. Ultrasound has the ability to greatly accelerate such reactions, and the products obtained are nanocrystalline. Gedanken and co-workers [57] employed ultrasound irradiation to induce such liquid-ammonia reactions in ethylenediamine and managed to obtain nanocrystalline spherical HgS and rectangular PbS particles. Later, they extended this method [58] and prepared nanospherical Ag_2S/PVA and nanoneedles of CuS/PVA composites by sonication of a 10% ethylenediamine-water solution of elemental sulfur, silver nitrate, or copper acetate in the presence of polyvinyl alcohol (PVA). This method can also be used to prepare other metal sulfides coated with polymers. Qian and Xie’s group has synthesized a variety of selenide and telluride nanoparticles sonochemically based on the room-temperature liquid ammonia routes, such as Ag_2Se, CuSe, PbSe [59], Cu_7Te_4, Cu_4Te_3 [60], and Ag_8Te [61]. Ag_2Se, CuSe, PbSe could be prepared by irradiating the mixtures of AgNO_3, CuI, or PbCl_2 with Se in ethylenediamine (en) with ultrasound at 18 kHz, using a commercial ultrasonic cleaner. The products were orthorhombic Ag_2Se, hexagonal CuSe, and cubic PbSe, respectively, and all are well crystallized in nanometers. They have also reported a simple and clean method of producing nanocrystalline silver tellurides in organic solvent systems by high-intensity ultrasound irradiation at room temperature. Ag_2Te and Ag_7Te_4 were prepared in an ethylenediamine system and an ethanol system, respectively. Sonication of CuCl_2 and Ag_2Te_4 were prepared in a pure ethylenediamine system and an ethanol system, respectively. The use of ultrasound irradiation facilitates the reduction of tellurium to an active form that can react with copper cations at room temperature. In ethylenediamine, which has N-chelating ligands, CuCl_2 can dissolve and form a complex. The system where the reaction is conducted is a heterogeneous system. In liquid-solid solution, the presence of ultrasound can enhance the reactions between metal cations and Te. The effects of interparticle collisions, microjets, and shockwaves can drive high-speed jets of liquid to impinge upon the surface which act to create a localized erosion to produce a newly exposed and highly active surface. Meanwhile, the ultrasound improves mass transport, and causes particle fragmentation that substantially increases the surface activity of the solid products that have a large number of dangling bonds, defects, or traps on their surface. All these factors are favorable to the activation of the reactions and the formation of copper telluride nanoparticles.

Ultrasound irradiation has also been used to induce the polyl process, through which nanocrystalline metal chalcogenides can be produced. Gedanken’s group [29] applied high-intensity ultrasound irradiation to induce the reaction between Pb(Ac)_2 and Se or Te in ethylene glycol. The as-prepared PbSe and PbTe were composed of monodisperse rectangular nanoparticles. The conditions resulting from the adiabatic implosion show that the final temperature is inversely proportional to the vapor pressure inside the collapsing bubbles. In the case of nonvolatile solutions the only gas inside the collapsing bubbles will be the solvent vapor. Taking this into consideration will make ethylene glycol an
excellent solvent for sonochemistry. On the other hand, the development of a bubble to its full size is strongly dependent on the viscosity of the solvent. Ethylene glycol is a favorable solvent for sonochemistry. Nano-crystalline silver chalcogenides Ag_{x}E (E = Se, Te) can also be synthesized by such a polyol reduction method under sonochemical irradiation [62]. Recently, Zhu and co-workers [63] found that monodisperse PbSe nanocrystals could also be fabricated via ultrasound-induced polyol reduction when polyethylene glycol (PEG)-400 was used as the solvent. The final product was characterized to be PbSe/PEG-400 composite nanocrystals. It was found that PEG played an important role in the formation of PbSe nanocrystals. On the one hand, PEG, like some other polyol solvent, such as ethylene glycol and triethylene glycol, can act as a reducing agent, and on the other hand, it is a dispersion stabilizer which prevents the generated nanocrystals from agglomerating together.

One of the most advanced and intriguing developments in the area of nanoparticles is the coating of semiconductor clusters on a solid support. This can be exploited to synthesize core/shell type materials with unusual optical, electronic, magnetic, and catalytic properties that are more than the sum of their individual components. Although the technology for coating the nanoparticles on rather large substrates is well established, coating on very small substrates, such as submicron-sized particles, still remains a technical challenge. Arul Dhas et al. [64] reported the surface synthesis of ZnS semiconductor nanoparticles coated on submicron-sized SiO_{2} by the ultrasound irradiation of a slurry of SiO_{2}, zinc acetate, and thioacetamide in water at near room temperature. They paid special attention to the reaction mechanism of the zinc sulfide-silica (ZSS) formation under the given sonochemical conditions. It was noteworthy that in contrast to the use of Zn(Ac)_{2}, zinc nitrate, zinc chloride, or zinc perchlorate solutions did not show the coating behavior of the resulting ZnS on silica. Therefore, the choice of Zn^{2+} ion source was a particular factor for the sonochemical surface synthesis of ZnS. The formation of \textit{CH}_{2}COO radicals ([\textit{Ac}) in various transition metal acetates, in an appropriate liquid medium, has been known in the literature. Accordingly, the formation of solute radicals under sonochemical conditions can be written as

\[
(CH_{2}COO)_{2}Zn + 2 \text{H}^{\bullet} (CH_{2}COO)_{2}Zn \text{ZnS nanoparticles homogeneously coated on the silica (SiO}_{2}) \text{carrier. Besides silica microspheres, ultrasound irradiation can also be used to induce the formation of semiconductor nanoparticles coated on the surface of some polymer microspheres. Breen et al. [66] reported that zinc sulfide films could be grown on carboxyl-modified polystyrene microspheres (PS-CO_{2}) through sonochemical deposition in an aqueous bath containing zinc acetate and sulfide, released through the hydrolysis of thioacetamide. The resulting particles were “optically hollow,” due to a large refractive index contrast between the core and shell materials. Continuous uniform films were obtained after 3–4 h and reached a maximum thickness of 70–80 nm after 13 h of growth. Aggregation was minimized by subsequent modification of the core-shell particles with mercaptoacetic acid to increase their surface charge and produce good colloidal suspensions. Oscillations in the optical spectra of dilute suspensions of the particles were indicative of interference patterns as expected from Mie light scattering calculations. X-ray diffraction patterns match the zinc blende structure of ZnS and indicate compression in the crystal lattice (\alpha = 5.305 \pm 0.037 \text{ Å}), as compared to the bulk material (\alpha = 5.406 \text{ Å}). Hollow ZnS shells were formed by annealing the core-shell particles in a thermal gravimetric analysis (TGA) oven, at 400 °C. A 34% weight loss was observed upon heating, a value approximately equal to that of the polystyrene core. The hollow shells remained intact and readily resuspended in water. Both core-shell and hollow ZnS particles self-assemble to form well-ordered, hexagonal close-packed layers.

In summary, the sonochemical method has been established as a powerful tool to prepare nanosized metal chalcogenides with various morphologies and structures. It shows great prospect in its application in materials science and will play a more and more important role in the preparation of nanostructural materials with desirable properties.

### 2.3. Sonoelectrochemical Synthesis

The sonochemical method has been widely used in chemistry for some time now. It was discovered as early as 1934 that the application of ultrasound irradiation can increase the rate of electrolytic water cleavage. The effects of ultrasound irradiation on chemical reactions are due to the very high temperatures and pressures developing in and around the collapsing bubbles. Meanwhile, electrodeposition has been proven to be a simple and low-cost method with many advantages to prepare various novel materials with special properties. The electrodeposition process can be controlled more accurately, and the reactions involved are closer to equilibrium than in many gas-phase methods. However, only quite recently have the potential benefits of combining sonochemistry and electrochemistry (sonoelectrochemistry) in the preparation of nanosized materials been studied increasingly. The beneficial effects of sonoelectrochemical method include acceleration of mass transport, cleaning and degassing of the electrode surface, and increased reaction rate [67, 68]. Generally speaking, sonoelectrochemical formation of nanoparticle powders is accomplished by applying an electric current pulse to nucleate the electrodeposition, followed by a burst of ultrasonic vibration that removes...
the newly formed particles from the sonic probe cathode. By adjusting the various electrodeposition and ultrasonic parameters, control over the size and morphology of the products can be realized.

Reisse and co-workers [69–73] have described a novel device for the fabrication of metals, alloys, and semiconductors using pulse sonoelectrochemical reduction. This device exposes only the flat circular area at the end of the ultrasonic tip to the electrodeposition solution. The exposed area acts as both the cathode and the ultrasound emitter. A pulse of electric current produces a high density of fine nuclei. This is followed by a burst of ultrasonic energy, which removes the particles from the cathode, cleans the surface, and replenishes the double layer with metal cations by stirring the solution. The metals and metallic alloys were obtained as chemically pure, fine crystalline powders with high surface areas. Reference [73] gives a list of powders prepared by this method, with particle size varying from 10 to 1000 nm depending on the deposition conditions. Reference [73] also reports the first sonoelectrochemical reaction in which a chalcogenide, CdTe, was successfully prepared, by sonoelectrodeposition from an aqueous solution of TeO2 and CdSO4.

Gedanken's group has carried out systematic research work on the sonoelectrochemical preparation of metal chalcogenide nanoparticles. They have prepared several nanocrystalline metal chalcogenides including CdSe [74], PbSe [75], and MoS2 [76] by using a sonoelectrochemical device that is similar to the one described by Reisse and co-workers. The schematics of the experimental setup assembled for the experiments are presented in Figure 5. A titanium horn acts as both the cathode and the ultrasound emitter. The electroactive part of the sonoelectrode is the planar circular surface at the bottom of the horn. The immersed cylindrical part is covered by an isolating plastic jacket. The sonoelectrode produces a sonic pulse that is triggered immediately following a current pulse, which is shown in Figure 9. One pulse driver is used to control a potentiostat and a second one controls the ultrasonic processor, which is adapted to work in the pulse mode. The potentiostat is operating in the constant current regime, without using a reference electrode.

By employing such a device, Mastai et al. [74] synthesized CdSe nanoparticles sonoelectrochemically from an aqueous solution containing Na2SeSO3 and CdSO4 in the presence of nitrilotriacetate (NTA) as the complexing agent. The crystal size could be varied from X-ray amorphous up to 9 nm by controlling the various electrodeposition and ultrasonic parameters. The details about the effect of various deposition parameters on CdSe nanoparticles are listed in Table 1. PbSe nanoparticles 10–16 nm in size have also been prepared in a similar way by a pulse sonoelectrochemical technique from an aqueous solution containing Pb(Ac)2 and Na2SeSO3 [75]. Several factors that influence the particle size, such as the reaction temperature, ultrasonic intensity, deposition current pulse width, and current density are discussed in detail. It is found that decreasing temperature, shorter pulse duration, higher sonic intensity, and lower current density all lead to a decrease of PbSe particle size.

Since the discovery of the original fullerenes, C60, C70, and multishell closed carbon structures, a wide range of

<table>
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<th>Nanodimensional chalcogenides</th>
<th>Ref.</th>
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<tr>
<td>Microwave assisted heating</td>
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<td></td>
<td>ZnS</td>
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<td></td>
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<td>[95]</td>
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<td></td>
<td>PbS/polycaronitrile</td>
<td>[98, 103]</td>
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continued
related fullerene-like structures, have been identified. Mastai et al. [76] reported the sonoelectrochemical synthesis of MoS$_2$ fullerene-like nanoparticles (Fig. 5). They have exploited ultrasonic excitation, involving a local burst of very high temperature in and around the collapsing bubbles, to synthesize closed fullerene-like structure of MoS$_2$ by electrodeposition from thiomolybdate solutions onto an ultrasonic probe at room temperature. Either electrodeposition or ultrasonic irradiation alone results in X-ray amorphous Mo-S products, but the combination of both gives well-crystalline closed structure of MoS$_2$.

In summary, sonoelectrochemical processes provide a promising method for the preparation of metal chalcogenides and some other nanoparticles with experimental variables which allow control over particle size, morphology, and size distribution. The application of sonoelectrochemical method in nanoscience and nanotechnology has been increasing and will keep increasing in the future due to the advantages of combining electrochemical and sonochemical processes.

### 2.4. Photochemical Synthesis

It has been known that absorption of photoenergy can change the structure of molecules and induce a variety of photochemical reactions. During recent years, a photochemical technique has emerged as an effective synthetic technique for the preparation of nanosized metal chalcogenides with various morphologies. This method has the advantages of mild reaction conditions and convenient operations, and the equipments involved are simple and cheap. Generally speaking, a low-pressure mercury pillar lamp ($\lambda = 253.7$ nm) and a high-pressure column-like indium lamp ($\lambda = 420–450$ nm) are most commonly used as the ultraviolet irradiation and visible photoirradiation source, respectively.

![TEM image of the sonoelectrochemically prepared MoS$_2$ powder. The inset in the top left-hand corner shows part of the image at ×2 magnification. Reprinted with permission from [76], Y. Mastai et al., Adv. Mater. 11, 1010 (1999). © 1999, Wiley-VCH, Weinheim.](image)
Zhu’s group reported the photochemical synthesis of CdSe [77] and PbSe [78] nanoparticles by employing a high-pressure indium lamp as the visible photorradiation source. Exposing aqueous solutions containing CdCl₂ (or Pb(Ac)₂) and Na₂SeSO₃ in the presence of complexing agents to photorradiation for several hours at room temperature would lead to the formation of 7-nm CdSe (or 25-nm PbSe) spherical nanoparticles. The mechanism of the photochemical formation of CdSe and PbSe nanoparticles can be summarized as below:

\[
\begin{align*}
\text{SeSO}_3^- + e^- & \rightarrow \text{Se}^- + \text{SO}_3^- \\
\text{Se}^- + e^- & \rightarrow \text{Se}^{2-} \\
\text{Cd}^{2+} + \text{Se}^{2-} & \rightarrow \text{CdSe} \\
\text{or} \\
\text{Pb}^{2+} + \text{Se}^{2-} & \rightarrow \text{PbSe}
\end{align*}
\]

The formation of CdSe or PbSe nanoparticles may include the above-given three steps through photorradiation: first, \(\text{SeSO}_3^-\) is reduced to \(\text{Se}^-\); then \(\text{Se}^-\) is further reduced to \(\text{Se}^{2-}\); finally, \(\text{Se}^{2-}\) reacts with metal cations to form metal selenide nanoparticles. The first reaction may be a slow reaction, and the second reaction may be a fast reaction. Both light intensity and irradiation time have influence on the size of the final products. The complexing agents also play an important role: they can retard the rate of the reactions and cause the particle size to be small. The reactions conducted without complexing agents were unsuccessful.

Chen and co-workers [79] established an ultraviolet irradiation method for in situ synthesis of nanocrystalline CdS particles. CdS nanocrystallites with cubic or hexagonal phase structures were prepared at room temperature via precipitation of \(\text{Cd}^{2+}\) ions with homogeneously released \(\text{S}^{2-}\) ions, generated from the decomposition of thioacetamide by ultraviolet irradiation reduction. It was found that the solvent has a great influence on the phase structure, the product composition, and the mean size of the CdS nanocrystals. This technique may be extended to prepare other sulfide semiconductor nanoparticles, including ZnS, Ag₂S, PbS, NiS, and CuS. Based on this approach, Chen’s group extended this method to the preparation of nanocrystalline CdS with different morphologies. Mo et al. [80] established a morphology-controlled synthesis of CdS nanocrystallites by introducing poly(vinyl alcohol) (PVA) as the protecting agent, which self-assemble into desirable shapes. CdS spherical nanoparticles, nanodisks, and nanowires were obtained conveniently, and there were some CdS nanotubes that appeared in the CdS nanodisk sample. It is found that the concentrations of \(\text{Cd}^{2+}\) and thioacetamide have significant effects on the morphologies of products. Hao et al. [81] prepared CdS nanocrystals in selective \(\text{C}_2\text{H}_5\text{OH}\) and \(\text{H}_2\text{O}\) solvents using sodium dodecyl sulphate (SDS) as capping material by ultraviolet irradiation technique. The capping material SDS in the solvents with different volume proportions of \(\text{C}_2\text{H}_5\text{OH}\) and \(\text{H}_2\text{O}\) has much influence on the morphology of the produced CdS nanocrystals, and the solvent with the volume proportion of \(\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O} = 9:1\) containing 0.2 mol/L SDS was the favorite medium for the formation of CdS nanorods. While the volume proportion of \(\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}\) was changed up to 9.5:1, the dendritic supermolecular CdS nanostructures, known in short as diffusion-limited aggregation (DLA), were obtained. When the volume proportion of \(\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}\) was down to 6:1, only CdS nanocrystals with irregular morphologies could be formed. It has been demonstrated that surfactant could act as capping material in fabrication of low-dimensional nanocrystals. The physical chemical properties such as polarity (dielectric constants) and softness of different solvents are different according to various volume proportions of \(\text{C}_2\text{H}_5\text{OH}\) and \(\text{H}_2\text{O}\). The difference in properties of the solvents may influence the dissolution and transmission of ions in solution, which may lead to the different cap structures of SDS in the formation of CdS nanocrystals. The SDS in various solvents can produce patterns of the different structures. These different patterns may act as suitable nucleation sites or interact with special crystal planes of the growing CdS nanocrystals, leading to the formation of CdS nanorods and dendritic supermolecular CdS nanostructures. Wu and co-workers [82] synthesized CdS nanowires by a convenient ultraviolet irradiation method using hydroxyethyl cellulose as a soft template at room temperature. In this experiment, the hydroxyethyl cellulose (HEC) is a long-chain macromolecule with many hydroxy groups and the average molecular weight of HEC is approximately 123,000. When HEC is dissolved in water, the HEC is unfolded and the long chain can be easily formed by HEC molecules through hydrogen bonds. The long chains can act as soft templates. When Cd²⁺ ion meets with S²⁻ ions, CdS can grow along these long chains and the CdS nanowire may be formed. S²⁻ ions are from the decomposition of sodium thiosulfate (Na₂S₂O₃) by ultraviolet irradiation. HEC in solution is used as a soft template, which directs the one-dimensional growth of CdS nanowires. This method gives a norm mild chemical route to fabrication of semiconducting nanowires which may be applied in many fields.

### 2.5. \(\gamma\)-Irradiation Method

\(\gamma\)-irradiation is one of the new and effective methods for synthesis of nanometer materials. It has been extensively used in the preparation of nanocrystalline metals, alloys, oxides, and polymer/metal nanocomposites [83]. Over the past few years, the \(\gamma\)-irradiation method has been extended to the fabrication of chalcogenide nanoparticles.

In \(\gamma\)-irradiation processes, the detailed mechanisms of the formation of nanocrystalline chalcogenides are not very clear up to now. However, some probable reactions may be going under \(\gamma\)-irradiation. It has been known that as a result of \(\gamma\)-irradiation, some reducing radiolytic species, such as solvented electrons or free radicals, are generated. These transient intermediate radiolytic species may react with some chalcogen sources such as S₂O₂⁻, SeSO₂⁻, C₂S, thiourea, and thioacetamide, leading to the formation of active S²⁻ or Se²⁻ anions. So far, a variety of metal sulfide and selenide nanoparticles have been successfully synthesized by \(\gamma\)-irradiation method in aqueous or nonaqueous systems [84–97].

Currently, inorganic/organic composites have been playing increasingly important roles in research and in numerous applications. They frequently have special properties, which are combinations of those of their original organic and inorganic components. Among these materials, semiconductive chalcogenide/polymer nanocomposites have aroused more
and more attention. 7-irradiation offers an applicable means by which the polymerization of monomers and formation of inorganic nanoparticles take place simultaneously, leading to the fabrication of inorganic/polymer nanocomposites. However, it is only quite recently that the 7-irradiation has been applied to the synthesis of chalcogenide/polymer nanocomposites. Liu et al. [98] developed a 7-irradiation method to synthesize PbS/polymer nanocomposites by using polymerized bicontinuous microemulsions. The as-prepared nanocomposite has large nonlinear optical response. Besides a polymeric nonionic surfactant, ω-methoxy poly(ethylene oxide)(40) undecyl-alpha-methacrylate (C-1-PEO-C-11-MA-40), a system consisting of methyl methacrylate (MMA), acrylonitrile (AN), ethylene glycol dimethacrylate (EGDMA), aqueous solutions of Pb(NO₃)₂/thioacetamide was selected. High-resolution transmission electron microscopy results indicated PbS nanocrystals with a width of 5 nm and a cubic structure is formed in water domains. A single-beam Z-scan measurement showed that the nanocomposite polymer has a nonresonant and negative nonlinear refractive index (γ) of 6.8 × 10⁻¹² cm²/W at 780 nm. The origin of the large nonlinear optical response is based on the contribution of surface recombination owing to high surface-to-volume ratios of PbS nanoparticles to the optical nonlinearity. In recent years, Qian’s group [99–103] has carried out some systematic work in this field and successfully employed 7-irradiation to prepare a series of sulfide/polymer nanocomposites including CdS/polyacrylonitrile composite nanoparticles [99], PbS/(polyvinyl acetate) nanocables [100], CdS/poly(styrene-alt-maleic anhydride) nanofibers [101], CdS/polyacrylamide [102], and PbS/polyacrylonitrile [103] composite nanoparticles.

In conclusion, 7-irradiation offers an attractive method for the preparation of nanodimensional chalcogenide particles and chalcogenide/polymer nanocomposites. The ease, reproducibility, and versatility of this synthetic approach will facilitate development of functional nanomaterials and the examination of their structure-property relationships.

2.6. Low-Temperature Solid-State Synthesis

Solid-state chemistry is a fast-developing science, enhanced by its numerous applications in high-technology industries [104]. Though solution-phase synthetic methods are most commonly used in the preparation of nanodimensional materials, solid-state reactions provide an alternative route to prepare nanoparticles. Solid-state reaction methods, especially low-temperature solid reactions, have been developed rapidly in recent years, and have shown their unique advantages in the preparation of nanodimensional chalcogenides, such as the simplicity, low energy cost, and mild conditions. However, up to now, the details about the formation of chalcogenide nanoparticles via low-temperature solid-state reactions are still unclear.

Though low-temperature solid-state synthesis has been long and widely used in a wide variety of fields in chemistry [105], it is only in recent years that considerable progress has been made in its extension to the synthesis of nanodimensional metal chalcogenides. Xin and his research group [106] reported an effective approach based on solid-state metathesis reaction of transition metal hydroxides and sodium sulfide at room temperature to produce nanocrystals of sulfides. It is known that the structures of the products by solid-state reactions depend on the rate of nucleation and growth of reaction products. The diffusion of solid particles of reactants at ambient temperature is often in short range, and thus helps yield nanosized products. Prompted by this study, Li and co-workers [107] developed a simple solid-state reaction of Cd(Ac)₂ · 2.5 H₂O and Na₂S · 9 H₂O in the presence of polyethylene glycol (PEG) 400 to synthesize CdS nanowires. During this solid-state reaction, the presence of coordinated water in Cd(Ac)₂ · 2.5 H₂O and Na₂S · 9 H₂O helps lower the activation energy and the reaction temperature, since most hydrated metal salts have structures with point defects and relatively lower lattice energies. The NaAc produced in the reactions may form the physical and spacious obstacle around the CdS particles to prevent them from aggregating to larger particles. PEG 400 also plays a critical role in the formation of CdS nanowires. It may interact with Cd(Ac)₂ · 2.5 H₂O or Na₂S · 9 H₂O during the first grinding. After absorbing free water and heat generating by this exothermal reaction, the structure of PEG 400 turns to loose and the PEG 400 molecules extend to form chain structures without any twist. Actually, PEG 400 acts as a soft template in the course of CdS nanowire formation. Similarly, ZnS nanoparticles have also been synthesized by solid-state reaction method at room temperature [108, 109]. It is found that the reaction is affected by the structures of reactants, crystal water, and defects. The as-prepared ZnS nanoparticles show a good sensitivity and selectivity to H₂S gas. Wang et al. [110] reported a novel and simple one-step method for the preparation of ca. 10- to 15-nm PbS nanoparticles by solid-state reaction in the presence of a suitable surfactant C₁₈H₃₇(CH₂CH₂O)₁₀. In the reaction of Pb(Ac)₂ · 3 H₂O and Na₂S · 9 H₂O the reaction product is PbS nanoparticles, free water and NaAc are produced. The surfactant C₁₈H₃₇(CH₂CH₂O)₁₀ dissolves in the free water to form a C₁₈H₃₇(CH₂CH₂O)₁₀ “shell” surrounding PbS particles, preventing them from aggregating to larger particles.

Though the solid-state synthesis of nanoparticles has been developing over the past few years, its application in nanomaterial synthesis still remains quite limited compared with gas-phase or liquid-phase methods. In the field of chalcogenide nanoparticle preparation, it is only restricted to sulfide synthesis at present. A continuous exploration for low-temperature solid-state method for the preparation of selenide and telluride nanoparticles is now under way.

2.7. Solvothermal Synthesis

One of the most promising techniques applicable to the synthesis of the nanocrystalline metal chalcogenides is the solvothermal method. Unlike some other conventional synthetic processes, the solvothermal synthesis involves much milder conditions and softer chemistry conducted at relatively low temperatures. This technique has been widely employed for the crystal growth of many inorganic compounds. An intriguing achievement of this synthetic technique includes the preparation of new phases, inaccessible at high temperatures, because of their thermodynamic metal stability. In recent years, a variety of reports have described the preparation of nanocrystalline metal chalcogenides with
different sizes and morphologies under solvothermal conditions. These reactions are conducted in sealed autoclaves, maintained at a certain range of temperatures (in most cases in the range of 100 °C to 300 °C) for a period of time (from few hours to several days), and requiring relatively high pressures. The solvothermal conditions provide a special environment for various chemical reactions and can induce the formation of nanocrystals with controllable sizes and morphologies.

The most straightforward way to synthesize binary metal chalcogenides is the direct combination of elemental metals and chalcogens (S, Se, or Te) at elevated temperatures, but the products formed via such high-temperature reactions are not nanosized. Li’s group has carried out systematic work and found that such elemental-direct reactions can be conducted under solvothermal or hydrothermal conditions at relatively low temperatures, and the products obtained are nanocrystalline. Solvothermal reactions between Cd powders and elemental S, Se, or Te in different organic solvents in the temperature range of 120 to 200 °C have been investigated systematically to prepare a series of cadmium chalcogenide CdE (E = S, Se, Te) nanocrystals [111]. It was found that the characteristics of the products, such as crystal size, shape, and structure, were strongly influenced by the solvent and temperature during the solvothermal processes. In case of CdE, one-dimensional nanorods of CdE with 10- to 40-nm diameters and several micrometers in length were obtained by choosing coordinating solvents such as ethylenediamine and 1,6-diaminohexane as the reaction solvent. When some noncoordinating solvents were used, only spherical nanoparticles could be obtained. The influence of different solvents on the morphologies of the products was systematically investigated, and a outline of the solvent coordination molecular template mechanism for the growth of the nanorods was proposed, though further studies on this mechanism are still in progress. Solvothermal reaction between Zn and Se powders in pyridine at 180 °C would give rise to ZnSe nanoparticles [112]. The formation of nanocrystalline ZnSe results from the combination of Zn and Se by electron transfers. Nanocrystalline ZnS could also be synthesized under similar conditions. Such elemental-direct reactions can also be conducted in aqueous systems under hydrothermal conditions. Li et al. [113] reported the preparation of ZnTe nanorods by a solvothermal process and a subsequent thermal treatment using Zn and Te as the reactants and hydrazine hydrate (N_2H_4·H_2O) as the solvent. Analysis of the result showed that the produced ZnTe was well crystallized with nanorod morphology, and the yield of this method is up to 80–90%. The hydrazine was found to play a very important role in this reaction process. It acted not only as an electron transfer medium but also as a strong electron provider. Peng et al. [114] reported a hydrothermal elemental-direct-reaction route to nanocrystalline CdSe and ZnSe particles. During the reactions, Zn or Cd powders can first react with water and generate metal oxide (or metal hydroxide) and H_2. At a temperature of about 180 °C, Se can partially dissolve in water and the dissolved ones may be reduced by the H_2 to produce Se^2-. The possible mechanism to produce ZnSe and CdSe under solvothermal conditions can be presented as follows:

\[ 3 \text{M} + 6 \text{H}_2\text{O} \rightarrow 3 \text{M(OH)}_2 + 3 \text{H}_2 \quad (\text{M} = \text{Zn or Cd}) \]
\[ 3 \text{Se} \rightarrow 3 \text{Se(sol)} \]
\[ 3 \text{M} + 3 \text{Se(sol)} + 3 \text{H}_2 \rightarrow 3 \text{MSe} + 6 \text{H}_2\text{O} \]

total reaction: \[ \text{M} + \text{Se} \rightarrow 3 \text{MSe} \]

On the basis of the mechanism presented above, this method is predicted to be applicable to other selenide nanoparticles.

Thermal degradation of metal complexes with sulfur-containing ligands seems to be an attractive method for the synthesis of metal sulfides. Several reports refer to thiolato, dithiocarbamate, and thiourea complexes [115]; however, such routes require the use of H_2S or H_2S/H_2 at high temperatures. It is well known that thiourea forms metal complex with metal ions in aqueous and alcoholic solutions. Such metal-thiourea complexes can be thermally decomposed to form metal sulfides in forms of thin films and ultrafine particles dispersed in glasses [116]. Yu and co-workers developed a novel one-step solvothermal decomposition process for fabrication of Bi_2S_3 [117] and Sb_2S_3 [118] nanowires. Bi-thiourea and Sb-thiourea complexes have the tendency to decompose under solvothermal conditions to produce Bi_2S_3 and Sb_2S_3 nanowires. The wirelike morphology of the products is possibly due to the inherent chain type structures of Bi_2S_3 and Sb_2S_3. The in situ generated nuclei could connect with each other and self-assemble into one-dimensional nanostructures. Solvothermal conditions, in which high temperatures are generated, are favorable for the self-assembly of the particles to form connections among them and a great number of such connections provide more opportunities for the formation of nanowires. Similarly, CdS nanowires could be successfully prepared via solvothermal reaction between cadmium salts and thiourea in polyamine solvents, such as ethylenediamine and diethylenetriamine [119]. The polyamines, which contain more than one N-chelating atom in each molecule, play a key role in the formation of the CdS nanowires.

Qian and co-workers [120–122] reported a novel solvothermal approach to prepare a series of metal chalcogenides by reactions between metal oxalates and chalcogens in organic solvents at temperatures ranging from 120 °C to 180 °C. Nanocrystalline Ag_2E [120], CdE [121], and PbE and Bi_2E_3 [122] (E = S, Se, Te) have been synthesized via this route. The reactions can be expressed as the following equations:

\[ \text{Ag}_2\text{C}_2\text{O}_4 + \text{E} \rightarrow \text{Ag}_2\text{E} + 2 \text{CO}_2 \quad \uparrow \]
\[ \text{CdC}_2\text{O}_4 + \text{E} \rightarrow \text{CdE} + 2 \text{CO}_2 \quad \uparrow \]
\[ \text{PbC}_2\text{O}_4 + \text{E} \rightarrow \text{PbE} + 2 \text{CO}_2 \quad \uparrow \]
\[ \text{Bi}_2(\text{C}_2\text{O}_4)_3 + 3 \text{E} \rightarrow \text{Bi}_2\text{E}_3 + 6 \text{CO}_2 \quad \uparrow \]

Both temperature and solvent have significant effects on the synthesis of the metal chalcogenides. By changing the preparation conditions, control over size and morphology of the products could be realized.
The magnetic and electric properties of many transition metal dichalcogenides have shown large varieties in behavior and have been studied in considerable detail. Typical substances such as ME₂ (M = Ni, Co, Fe; E = S, Se) are diamagnetic semiconductors, ferromagnetic and antiferromagnetic semiconductors. Meanwhile, transition metal dichalcogenides have extensive applications in energy areas such as electrochemistry and catalysis. The large surface areas and high activity of nanomaterials will enhance their applications in these fields. Yang et al. [123] synthesized transition metal diselenides (MSe₂, M = Ni, Co, Fe) through a simple solvothermal-reduction reaction at low temperatures. With increasing temperature, the obtained NiSe₂ transformed from initial filament nanocrystallites to final octahedral crystals. The studies on the thermal stability of the as-prepared NiSe₂ showed that NiSe acted in an intermediate role in the pyrolysis process. The as-prepared CoSe₂ at higher temperature had an orthorhombic structure similar to that of FeSe₂. At low temperature, this orthorhombic phase CoSe₂, which displayed rodlike shape with the growth direction along (121), coexisted with a trace of the cubic phase CoSe₂.

Synthesis and characterizations of inorganic-organic polymer nanocomposites have received much intensive research, owing to their optical, electrical, catalytic, and mechanical properties, and potential applications in microelectronics. The hybridization of organic and inorganic semiconductors is expected not only to permit wide-range selection of emitter and carrier transport materials, but to provide a new approach to construct high-performance electroluminescence devices, taking advantage of organic and inorganic semiconductor characteristics, such as high photoluminescent efficiency of organic materials and high carrier density and low resistivity of inorganic semiconductors. In addition, polymer is also expected to provide good mechanical properties, conferring high kinetic stability on nanometer-sized semiconductor particles. To organize the semiconductor nanoparticles in an orderly fashion in a polymer matrix may afford a potential application of their special properties. Chen and co-workers [124] reported a solvothermal in situ simultaneous copolymerization-decomposition (SCPD) technique for fabrication of poly(acrylamide-co-styrene)-semiconductor CdE (E = S, Se) nanorod composite. It is well known that the radical thermal initiator AIBN (2,2′-azobisisobutyronitrile) decomposes at about 45–65 °C, of which the decomposition reaction is described as

\[(\text{CH₃})₂\text{CN} \rightarrow \text{N} = \text{N} = \text{C}(\text{CN})(\text{CH₃})₂\]

\[\rightarrow 2 (\text{CH₃})₂\text{CN} \cdot + \text{N}_₂\]

In this system, the produced radicals will initiate the copolymerization of the acrylamide and the styrene monomers. The copolymerization process simultaneously accompanies the solvothermal formation of CdE nanorods. Therefore, it was found that the produced CdE nanorods were well dispersed homogeneously in the poly(acrylamide-co-styrene) matrix. Yoshimura and co-workers [125] developed a novel one-step soft solution processing route called the solvothermal-copolymerization technique for in situ fabrication of polystyrene/CdS nanocomposites embedded with CdS nanowires in ethylenediamine media at lower temperatures (80–140 °C). In this route, the polymerization of the monomers and the formation of the CdS nanocrystallites occur simultaneously in a certain temperature range. The embedded CdS nanowires, with diameters of 4 to 15 nm and lengths up to several micrometers, have (001) preferential orientation. Both temperature and solvent were found to play a key role in the synthesis of the nanocomposites. The produced novel hybrid nanocomposites display obvious quantum size effects and interesting fluorescence features. The spectroscopic properties of the polystyrene/CdS nanowire nanocomposites were found to be sensitive to synthetic conditions, including the concentrations of Cd²⁺ or the monomer, temperature, and reaction time.

One of the keys to semiconductor nanoparticle research is the ability to prepare stable (typically through surface passivation—also referred to as capping) monodisperse particles that have very few defects. Gautam et al. [126] presented a convenient and safe one-pot route to capped CdSe nanoparticles making use of common starting materials and inexpensive, low-boiling solvents under solvothermal conditions. The H₂Se required for the reaction was generated in situ through the aromatization of tetralin by Se. The addition of small amounts of dodecanethiol as a capping agent resulted in 3-nm monodisperse nanoparticles with a narrow size distribution. The dark solution obtained from the reaction precipitates solid products when the solvent polarity is increased through the addition of propan-2-ol. The precipitated solid easily redissolves in toluene forming bright orange solutions.

In recent years, the solvothermal technique has been extended to the synthesis of a variety of ternary metal chalcogenide nanoparticles. Among the ternary metal chalcogenides, I-III-VI₂ compounds have been most intensively investigated due to their important technical applications. I-III-VI₂ chalcopyrite semiconducting compounds, such as AgGaS₂, AgInS₂, CuInS₂, and CuInSe₂, have been shown to be useful linear and nonlinear optical materials. Nanocrystalline semiconductors AgGaS₂ and AgInS₂ with particle sizes ranging from 5 to 12 nm have been prepared by a solvothermal reaction of AgCl, Ga (or In), and S in the temperature range 180–230 °C [127]. The synthetic reaction can be represented as

\[3 \text{AgCl} + 4 \text{M} + 6 \text{S} \rightarrow 3 \text{AgMS}_2 + \text{MCl}_3 \quad (\text{M} = \text{Ga, In})\]

Jiang et al. [128] prepared CuInS₂ and CuInSe₂ nanorods via an elemental solvothermal reaction route. Cui et al. [129] also successfully prepared CuInS₂ and AgInS₂ nanorods from stoichiometric mixture of In(S₂CNEt₂)₃ and Cu(S₂CNEt₂)₃ or Ag(S₂CNEt₂)₃, by removal of the thione groups with ethylenediamine at 195 °C in a solvothermal process.

### 2.8. Electrochemical Template Synthesis

One-dimensional nanostructures, such as nanorods, nanowires, nanowhiskers, and nanotubes, represent the smallest dimensions for efficient transport of electrons and excitons and are ideal building blocks for hierarchical assembly of functional nanoscale electronic and photonic structures.
During the past decade, materials with one-dimensional nanostructures have been the focus of much attention due to their special properties and potential applications. Template synthesis is an elegant chemical approach for the fabrication of nanowires and has attracted more and more attention. Arrays of metal [130], semiconductor [131], conducting polymer nanowires [132], and carbon nanotubes [133] are obtained by electrodeposition or other methods in porous templates such as anodic aluminum oxide (AAO) films and nuclear track membranes. Nanophysics fabrication methods such as molecular beam epitaxy followed by nanolithography of ever-increasing resolution are usually considered to represent the ultimate limit for producing nanoscale materials. However, such nanoscale materials can also be fabricated using a different method, whose key ingredients are templates and electrodeposition. In this method, the desired materials are electrochemically synthesized within the voids of the template materials. The electrochemical synthesis in templates has been taken as one of the most efficient methods in controlling the growth of nanowires because the growth is controllable almost exclusively in the direction normal to the substrate surface. Though there are wide ranges of nanoporous materials, most studies have been performed using AAO membrane as the template.

Routkevitch et al. [131] have fabricated CdS nanowire arrays by a single-step alternating-current electrodeposition in an electrolyte containing Cd\(^{2+}\) and S in dimethylsulfoxide (DMSO). They reported that on average the thicker wires (with diameters larger than 12 nm) consisted of a large number of crystallites in the axial direction and rather few in the radial direction, while the thinner wires (with diameters less than 12 nm) were of single crystalline structure. Guo’s group [134–138] has prepared cadmium chalcogenide (CdS, CdSe, CdTe) nanowire arrays by direct-current electrochemical deposition in porous AAO templates. The as-prepared nanowires have uniform morphology and present single crystalline nature. TEM and HRTEM images of an individual CdSe nanowire prepared by this method are shown in Figure 6. The diameters of the nanowires can be controlled by the pore diameters of the template. This approach can also be used to fabricate other semiconductor (ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, GaAs, InP, etc.) nanowires both in aqueous solution and in nonaqueous solution systems.

### 2.9. Microemulsions Route

Surfactants provide several types of well-organized assemblies that provide specific sizes, geometrical control, and stabilization to particulate assemblies formed within the organized surfactant assemblies. Among the host surfactant assemblies that are available for the formation of nanoparticles are the following: the aqueous micellar solutions, reverse micelles, microemulsion, vesicles, monolayers, Langmuir–Blodgett films, and bilayer liquid membranes. The surfactant host assemblies not only provide favorable sites for the growth of the particular assemblies; they also influence the formation process as well as the chemical properties of the particulate guest, thus unfolding novel chemistries. Fendler [139] has reviewed these aspects in detail and coined a new term “membrane mimetic chemistry.”

![Figure 6. TEM (a) and HRTEM (b) images of an individual CdSe nanowire prepared by direct-current electrochemical deposition in porous AAO templates. Reprinted with permission from [136], D. S. Xu et al., J. Phys. Chem. B 104, 5061 (2000). © 2000, American Chemical Society.](image)

Among these surfactant host assemblies, microemulsions are most commonly used in the synthesis of chalcogenide nanoparticles. Microemulsions have been intensively used as spatially constrained microreactors for the controlled growth of inorganic materials. In the case of a microemulsion, the reactions take place in the core of the microemulsions and the hydrophilic head groups of the surfactant molecules. Microemulsions are thermodynamically stable, fluid, optical clear dispersions of immiscible liquids. They provide suitable reaction media for the synthesis of nanoparticles because the droplets of water or oil can be seen as nanoreactors, favoring the formation of small crystallites with a sufficiently narrow size distribution.

In the past few years, a variety of chalcogenide nanoparticles, such as Ag\(_2\)Se [140], ZnS [141], Cu\(_2\)S [142], CdSe [143], and so on were prepared. Among all chalcogenides, microemulsion synthesis of CdS nanoparticles has been most intensively investigated. Suzuki et al. [144] reported preparation of cadmium sulfide nanoparticles with sharp size-distribution using cadmium dioleylphosphosphate microemulsion. Cadmium dioleylphosphosphate (CDOLP) and sodium dioleylphosphosphate (SDOLP) are expected to form rigid microemulsion droplets; they were used as surfactants in place of sodium bis(2-ethylhexyl) sulfosuccinate(AOT), which has been often used for the preparation of CdS nanoparticles in microemulsion. CdS nanoparticles were prepared by mixing hydrogen sulfide solution with the microemulsion composed of CDOLP and SDOLP. The growth process of the particles through their coagulation is restricted more strongly, and the size distribution of the obtained particles was sharper than those in AOT-microemulsion. Furthermore, in CDOLP/SDOLP microemulsion, the average number of cadmium ions per microemulsion droplet is larger and the number of contaminating “empty” RIE droplets, which contain no particle,
is much smaller than in AOT microemulsion systems. Dioleylphosphates are proper surfactants for the preparation of nanoparticles with sharp size-distribution, because particle coagulation is restricted in the system. The restriction of the coagulation between larger particles is attributed to two mechanisms: (1) It is hard for larger particles to be exchanged between two fusing microemulsion droplets through the “open channel” between them. (2) The microemulsion droplets with the larger particles can hardly coalesce with the other microemulsion droplets. Agostiano and co-workers [145] prepared CdS nanoclusters in a quaterternary cetyltrimethylammonium bromide (CTAB)/n-pentanol/n-hexane/water microemulsion. The presence of cosurfactant (n-pentanol), in additional to water, allows the simultaneous modulation of the water droplets dimensions and their exchange dynamics. Moreover, n-pentanol has an influence on the stability of CdS clusters, behaving as a capping agent at high concentrations. Recently, CdS nanorods have also been prepared by microemulsion route. Simmons et al. [146] prepared high aspect ratio CdS quantum rods at room temperature in the environment of water-in-oil microemulsions using a combination of two surfactants: the anionic bis(2-ethylhexyl) sulfosuccinate (AOT) and the zwitterionic phospholipid L-alpha-phosphatidylcholine (lecithin). These highly acicular particles, obtained from a water-in-oil microemulsion containing an equimolar mixture of AOT and lecithin, possess an average width of 4.1 nm ± 0.6 nm, with lengths ranging from 50 to 150 nm. In contrast, conventional spherical CdS quantum dots are obtained from the AOT water-in-oil microemulsion system, with an average particle diameter of 5.0 nm ± 0.6 nm. Mo et al. [147] developed a convenient microemulsion route at room temperature to produce star-shaped CdS patterns, which were composed of rodlike nanoparticles with diameters of 4 to 7 nm and lengths ranging from 150 to 200 nm. It is found that long hydrophobic carbon chain of surfactant molecule is favorable for the formation of fibrillar or dendritic morphology. When surfactant with shorter carbon chain was employed, only spherical CdS nanocrystallites were obtained.

Recent progress shows that the microemulsions can also be employed to prepare chalcogenide nanocomposites. Up to now, a number of chalcogenide nanocomposites have been successfully synthesized in microemulsions, including PbS/polymer [148], PbS-coated CdS [149], Ag2S/CdS [150] nanocomposites, CdS/CdSe core/shell type nanoparticles [143], and so on.

Over the past few years, the combination of microemulsion with some other synthetic techniques to prepare chalcogenide nanoparticles has been reported. For example, the combination of sonochemistry and microemulsions or micelles provides a promising way to produce different types of nanostructures. The cavitation behavior of ultrasound irradiation can lead to extraction, mixed phase reactions, and emulsification in a liquid-liquid heterogeneous system. Thus, under ultrasound irradiation it is possible that liquid-liquid heterogeneous systems could be emulsified to form microemulsions. Huang et al. [151] described the formation of spherical assemblies of nanocrystalline primary particles of CdS in a CS2-water-ethylenediamine microemulsion induced by ultrasonic irradiation. CS2 was employed as the sulfur source and also as the oil phase in the microemulsion. Under ultrasonic irradiation, the CdS nanoparticles formed in situ at the surface of CS2 droplets can be dragged inside by the oil surface movement motivated by the surrounding turbulent water flow, which might result in the final spherical nanostructure. Chen and co-workers [152] prepared CdS and CdSe nanorods via the reactions between cadmium chloride and sodium sulfate or sodium selenide in a micellar solution in the presence of sonication. The micellar solution was prepared by introducing appropriate amount of cyclohexane and CTAB into distilled water. The aspect ratios of the nanorods could be changed by changing the amount of cyclohexane. In this case, vigorous sonication could induce the formation of bilayer vesicles, and the formation of CdS or CdSe nanorods in a microemulsion might be attributed to the formation of these rodlike bilayer vesicles. Wang et al. [153] prepared PbS nanoparticles sonochemically in an oil-in-water (o/w) microemulsion system. Sulfur-toluene solution (STS) was chosen as the sulfur source. When STS was mixed with water in the presence of sodium lauryl sulfate (SLS) as the surfactant, a liquid-liquid heterogeneous system was formed. The cavitation behavior of ultrasound irradiation can lead to the formation of an o/w microemulsion of toluene-in-water. This synthetic design was motivated by the known simple interaction between sulfur and ethylenediamine, but it provides special conditions for the formation and growth of the PbS nanocrystals in such a microemulsion system in the presence of high-intensity ultrasound irradiation. Recently, hydrothermal microemulsion synthesis of CdS nanoclusters has also been reported [154]. The reaction of Cd2+ ions with S2− ions generated from the decomposition of thiaoacetamide proceeded in water microdroplets. The mean diameter of the CdS nanoclusters can be varied from 20 to 80 nm by increasing the reaction temperature from 30 to 120 °C. Two intense luminescence bands, that is, green and red, were observed to coexist in the CdS nanoclusters. Their peak positions and relative intensities were found to be sensitive to the size and structure of nanoclusters. These emissions are attributed to surface defects (green emission) and the Cd–Cl composite vacancies (red emission).

2.10. Sol–Gel Synthesis

Sol–gel processing is a promising method for the preparation of nanodimensional materials. The reaction product of the sol–gel synthesis could be either colloidal powders or films. One of the advantages of this method is the ability to control the microstructure of final product by controlling chemical reaction parameters. It was demonstrated that modification of the reaction conditions could significantly affect the structure of the sol–gel product. The connection between the sol–gel process kinetics and the sol–gel product microstructures can be illustrated by the following sequence [155]:

Solvolyis (hydrolysis, thiolysis)

→ condensation → nucleation → growth → aggregation

The prevalent application of sol–gel processing is in the production of metal oxides by one of the two synthetic
routes. The first route involves the hydrolysis of an alcohol solution of metal alkoxides. This reaction is catalyzed by acid and is very sensitive to the ratio of acid, alcohol, and water in the solution [156]. The second route involves the use of diols and metal salts to form the bridging bonds on the polymer and does not require water or acid [157]. Up to now, most publications related to the sol–gel synthesis have been confined to the preparation of ultrafine oxide powders or thin films. Reports on the sol–gel synthesis of nanosized sulfides, selenides, or tellurides are relatively much scarcer. There are two sol–gel routes that are used most commonly in preparation of metal sulfides. The first one involves a modified sol–gel route in which the conventional alcohol sol is exposed to a stream of H2S or some other sulfur sources [158]. The other one is the use of thiol in place of alcohol for the formation of sulfides by a modification of the first sol–gel route [159]. In the past few years, by using these two routes, a variety of nanocrystalline sulfides, either in powder form or films, have been successfully prepared by sol–gel method.

Stanic et al. [160] reported a sol–gel method for the preparation of metal sulfides. Synthesis of sulfides was demonstrated by the example of monolithic germanium disulfide produced by reaction of the sol–gel product with sulfur. The elemental sulfur, in turn, was obtained as the result of oxidation of H2S in the presence of concentrated sulfuric acid. This sulfur was transported into a toluene solution at room temperature. The sol–gel product yielded single-phase GeS2. A chemical kinetics study of such a sol–gel processing of GeS2 from hydrolysis-condensation mechanism that operates in the lowing a thiolysis-condensation mechanism similar to the following reaction mechanism:

\[ 2n\text{ZnCl}_2 + \text{HSCH}_2\text{CH}_2\text{SH} \rightarrow (\text{ZnSCH}_2\text{CH}_2\text{S})_n + 2n\text{HCl} \uparrow \]

Cao et al. [168] reported sol–gel template synthesis of an array of single-crystal CdS nanowires on a porous alumina template. It shows that sol–gel technique can also be used in template synthesis and the extension of this sol–gel template method to the preparation of some other one-dimensional nanostructural materials is still underway. Though much progress has been made in the sol–gel synthesis of nanosized sulfides, available reports on the sol–gel synthesis of nanosized selenides and tellurides are still limited. Up to now, only a few selenides and tellurides such as CdTe zirconia films [169] and Cu2Se in silica glasses [170] have been synthesized via sol–gel process. Exploring new sol–gel routes to produce selenides and tellurides still remains a great challenge.

3. CHARACTERIZATIONS

In the past two decades, a wide variety of techniques have been used in the characterizations of chalcogenide nanoparticles. Herein, we briefly mention some of these techniques that are most commonly used.

(1) Crystallinity and crystallography analysis:
- X-ray powder diffraction (XPRD), selected area electron diffraction (SAED), low energy electron diffraction (LEED), …

(2) Observation of dimensions and morphologies:
- Transmission electron microscopy (TEM), atomic force microscopy (AFM), scanning electron microscopy (SEM), …

(3) Evaluation of composition and purity:
- X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), energy-dispersive X-ray analysis (EDAX), inductively coupled plasma (ICP) element analysis, …

(4) Methods used in estimation of crystal size [6]:
- XPRD (using Debye–Scherrer formula), direct TEM observations, calculation according to the relation between bandgap and particle size, Raman spectroscopy, surface area measurements, …

(5) Fine structures:
- High-resolution transmission electron microscopy (HRTEM), scanning tunnel microscopy (STM), extended X-ray absorption fine structure (EXAFS), …

(6) Spectroscopy characterizations:
- Ultraviolet-visible absorbance spectroscopy, ultraviolet-visible reflection spectroscopy, photoluminescence (PL) spectroscopy, …
4. PROPERTIES AND APPLICATIONS

Metal chalcogenides represent a class of compounds that have a wide range of applications owing to their important nonlinear properties, luminescent properties, quantum size effects, and other important physical and chemical properties [171].

In the past two decades, a growth in publications related to the properties and applications of chalcogenides is accounted. For example, the interest in PbSe, which is a typical narrow-bandgap chalcogenide, can be employed to produce photoresistors, photodetectors, and photoemitters in the IR range, as well as injection lasers [172]. PbSe has also been the object of an inquiry into nanosized effects [173]. The wide-bandgap II-VI chalcogenide semiconductors are of current interest for optoelectronic application light-emitting diodes and optical devices [174]. Among these materials, CdS is the most interesting material because of its high photosensitivity and attractive application in photocatalytic decomposition of water [175], particularly in the observation of the dependence of these properties on size.

Transition metal dichalcogenides crystallizing in the pyrite structure is another interesting material from both fundamental and technological points of view. For example, ruthenium disulfide has potential applications in energy-related technologies and it is a promising material for thermal catalytic processing as an effective catalyst in petroleum refining and also for photoelectrochemical energy conversion [176]. Ruthenium disulfide is highly stable against photocorrosion and absorbs visible light, and these properties have been exploited in photoelectrochemical energy conversion [177]. It is also used in the photocatalytic decomposition of water [178].

V-VI main-group metal chalcogenides $A_2B_3$ ($A$ = Sb, Bi, As; $B$ = S, Se, Te) are a group of important semiconductors, and have applications in television cameras with photoconducting targets, thermoelectric devices, and electronic and optoelectronic devices and in IR spectroscopy [179]. Bismuth sulfide (Bi$_2$S$_3$) is a representative V-VI semiconductive material with a lamellar structure whose direct bandgap Eg is 1.3 eV and is useful for photodiode arrays or photovoltaics [180]. It also belongs to a family of solid-state materials with applications in cooling technologies based on the Peltier effect [181]. Antimony sulfide and selenide (Sb$_2$S$_3$ and Sb$_2$Se$_3$) have also received a great deal of attention due to their good photoconductivity and are regarded as prospective materials for solar energy [182].

Chalcogenide nanoparticles promise to play a major role in a variety of new technologies. The intense interest in this area derives from their unique chemical and physical properties, which give rise to their potential uses in the fields of nonlinear optics, luminescence, electronics, catalysis, solar energy conversion, optoelectronics, and so on. The small dimensions of these chalcogenide nanoparticles result in different physical properties from those observed in the corresponding macrocrystalline bulk materials. As particle sizes become smaller, the ratio of surface atoms to those in the interior increases, leading to the surface properties playing an important role in the properties of the materials [183]. Chalcogenide nanoparticles also exhibit a change in their electronic properties relative to those of the bulk materials; as the dimensions of the solids get smaller, the bandgap becomes larger. This allows chemists and materials scientists to change the electronic properties of the materials simply by controlling their sizes. Progress in the synthesis of chalcogenide nanoparticles will promote the research on their applications. Meanwhile, advances in the applications will bring new challenges in the synthesis of these materials to both synthetic chemists and materials scientists.

5. CONCLUSION

Metal chalcogenides have attracted considerable interest due to their intriguing properties and structural diversity. In recent years, emphasis has been devoted to their preparation in the nanophased form with two aspects of consideration: one is the modern trend of miniaturization, and the other is the unique property associated with the nanostructures. Herein, several novel synthetic methods for nanocrystalline metal chalcogenides have been reviewed, including microwave assisted heating, sonochemical synthesis, photochemical synthesis, $\gamma$-irradiation method, low-temperature solid-state synthesis, solvothermal synthesis, electrochemical template synthesis, microemulsion route, and sol–gel synthesis. Though this review cannot cover all the methods for the preparation of metal chalcogenide nanoparticles ever reported in the literature, to some extent, these methods included represent the latest progress in this field. Compared with conventional methods, these novel methods have a variety of advantages and will play an increasingly important role in materials science in the future. However, there is still a long way to go. Exploring new methods that are mild, convenient, efficient, and environmentally friendly to prepare nanosized materials with desirable size, morphology, and properties is still a great challenge to us.

GLOSSARY

Chalcogenide A class of compounds including sulfides, selenides, and tellurides.

Sonochemistry The formation, growth, and implosive collapse of bubbles in liquids.

Sonoelectrochemical synthesis Combination of sonochemistry and electrochemistry in the preparation of nanosized materials.

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