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TOPICAL REVIEW

Cadmium selenide nanowires from growth to applications

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Abstract

This review article deals with the synthetic strategies of cadmium selenide nanowires via electrodeposition, solution liquid solid methods, vapor liquid solid methods and template wet methods. Applications of these nanowires in solar cells, photodetectors, field effect transistors, and field emission have been presented. A comparative account of cadmium selenide nanowires with other cadmium selenide morphologies (ribbons, rods, belts etc) and cadmium compounds has been discussed.

1. Introduction

Modification of semiconducting nanomaterials into well defined mono or multilayer morphologies is the basic requirement for their use in various devices such as light emitting diodes [1], light emitting films [2, 3], biosensors [4, 5], light harvesting devices [6], solar cells [7], photodetectors [8], forster resonance energy transfer sensing [9] etc. Properties of semiconducting nanomaterials are dependent not only on size but also on the type of nanostructure as well therefore; all these properties can be tuned with proper size and structure orientations. Extensive work has been carried out in the last two decades on inorganic semiconducting chalcogenides materials for all the above mentioned applications [10–12]. Carbon free energy demand of the world is the motivational force behind all these research efforts. Noble metals have shown good results (in solar cells [13, 14] and water splitting [15–17]) but their availability in the Earth crust along with economic concerns limit their market applications. Chalcogenides of those metals which are easily available in the Earth crust are considered to be an alternate option. In this regard transition metal oxides [18], sulfides [19, 20], selenides [21, 22] and tellurides [23, 24] have been deeply investigated and their properties and applications have been compared curiously.

Cadmium selenide (CdSe) is a semiconducting chalcogenide material which exists in hexagonal (wurtzite), cubic/zinc blende (sphalerite) and cubic (rock-salt) crystal structures [25]. CdSe nanostructures (Ns) have been investigated extensively owing to their direct band gap which is tunable with size and morphology. As the size of CdSe quantum dots (QDs) decreases their band gap increases e.g. band gap of 2.4 nm QDs is 2.4 eV and 0.9 nm QDs have a band gap of 2.7 eV [26]. This band gap management is important for optical and electronic properties of any material which in turn determines its use in device applications.

After the discovery of carbon nanotubes (CNTs) [27], one dimensional (1D) inorganic nanowires (NWs) [28], nanorods (NRs) [29] and nanotubes (NTs) [30] have been explored comprehensively due to their specialized physical and chemical properties. NWs particularly have quantum confinement in two directions and one direction is unconfined for electrical conduction which makes them useful for applications depending upon electrical conduction as compared to tunneling. This unidirectional electron mobility in length provides the possibility to tailor the physical properties by confinement effect. Keeping this in view CdSe NWs have been synthesized by top down and bottom up approaches with success via electrodeposition [31–39], solution-liquid solid methods (SLS) [40–44], vapor liquid solid methods (VLS) [45–47] and template wet methods [48, 49]. Because of the bitter fact that we are far behind the technical mass production, nanoscience is the most
appropriate term for the field. In this review article we have covered all these synthetic routes and applications of CdSe NWs.

2. Growth of cadmium selenide nanowires

2.1. Electrodeposition

Electrodeposition is a widely used technique for metal chalcogenide thin films preparation. It has advantages of low cost, good thickness control, deposition on any shape and working under ambient conditions. First report of CdSe NWs is attributed to the first attempt number of other workers [32–39] have used electrodeposition with different modifications. Details of deposition parameters in terms of precursors, bath composition, electrode system and templates have been presented in table 1. For all the different parameters in table 1, pH of the deposition solution is maintained between 1–3 by the addition of sulfuric acid or hydrochloric acid in aqueous media. In most of the cases films deposited are annealed between 300–400 °C.

For the growth of NW, nuclear growth should occur with high linear density denoted by \( \delta \) (units of \( \mu m^{-1} \)) at the step edge of template. This phenomenon is known as electrostatic step edge decoration (ESED). Li et al [38] have used this technique with \( \delta \) value of 30 \( \mu m^{-1} \) for the growth of CdSe NWs. This \( \delta \) value should be greater than 1 NW diameter for hemispherical nuclei and this higher value was only achieved when supporting electrolyte was not used. Having a close look at cyclic voltammetry (CV) profile in the absence and presence of sodium sulfate (supporting electrolyte) it is evident that both the reactions provide a reversible oxidation and reduction maxima (figure 1). Dwarf type peak in figure 1 is attributed to high ohmic resistance in the absence of sodium sulfate. Another difference between the two CV profiles is the onset of cathodic current for supporting electrolyte free CV at \(-0.1\) V and second faradic process starts at \(-0.62\) V. Cathodic processes between \(-0.1\) V to \(-0.65\) V in the starvation of CdSe nuclei due to ohmic resistance yield NWs at step edge of template (highly oriented pyrolytic graphite, HOPG). Cathodic reaction for the production of CdSe is direct 6e⁻ reduction process according to following reaction

\[
H_2SeO_3 + Cd^{2+} + 6e^- + 4H^+ \rightarrow CdSe + 3H_2O
\] (1)

Mechanism of CdSe NWs growth can be explained according to following steps. In the first step from \(-0.45\) V to \(-0.65\) V \( H_2SeO_3 \) is reduced to elemental Se via following reactions

\[
H_2SeO_3 + 6e^- + 4H^+ \rightarrow H_2Se + 3H_2O
\] (2)

\[
H_2Se \rightarrow Se + 2H^+ + 2e^- 
\] (3)

In the second step CdSe NWs are formed at electrodeposited Se between \(-0.6\) V to \(-0.8\) V. In step 3, between \(-0.76\) V to \(-1.00\) V, elemental Cd is deposited according to following reaction

\[
Cd \rightarrow Cd^{2+} + 2e^- 
\] (4)

In step 4 and 5 between \(-1.0\) V to 0.6 V and 0.6 V to 0.8 V, excessive Cd and Se are stripped respectively. Diameter of CdSe NWs in all these experiments is directly proportional to scan cycles i.e. for \( n = 1, 2, 5 \) and 10, diameter is 32 nm, 102 nm, 210 nm and 278 nm respectively. This is because of the fact that with increasing number of cycles more time is available for the deposition of CdSe NWs. In a similar way at higher scan rates CdSe NWs of smaller diameter will be formed. This study also reveals that by increasing the pH crystallite size decreases. In another study [39] electrodeposition at 10 mV s⁻¹, 30 mV s⁻¹ and 90 mV s⁻¹ produced NW of 380 nm, 200 nm and 50 nm respectively.

Kung et al [37] have reported the synthesis of nanocrystalline cadmium selenide (nc-CdSe) NWs by lithographically patterned nanowires electrodeposition (LPNE) method on glass surfaces having a trench in which is embedded a vertical nickel nanoband electrode with a dimension of 20 × 50 nm at pH 1–2 and 25 °C according to the following equation
| Precursors     | Bath composition | Electrode system | Deposition time (min)/temperature (°C) | Scan rate (mV s\(^{-1}\)) | Template | References |
|---------------|------------------|------------------|----------------------------------------|-----------------------------|----------|------------|
| CdCl\(_2\)Se  | DMSO             | AAO cathode, Pt anode | 30–60/185                              | dc                          | AAO      | [50]       |
| Cd(SO\(_4\))\(_2\)SeO\(_2\) | H\(_2\)O, H\(_2\)SO\(_4\) | HOPG W, Pt C, SCE R | RT                                    |                             | HOPG     | [38]       |
| Cd(SO\(_4\))\(_2\)SeO\(_2\) | H\(_2\)O, H\(_2\)SO\(_4\) | PCM W, Pt C, Ag/AgCl R | 20/RT                                 | 10, 30, 90                  | PCM      | [39]       |
| CdCl\(_2\)Se  | DMF              | ITO glass W, Pt foil C | 147                                    | Nil                         | Nil      | [34,37]    |
| Cd(SO\(_4\))\(_2\)SeO\(_2\) | H\(_2\)O, H\(_2\)SO\(_4\) | Ni W, Pt C, SCE R | RT                                    |                             | Ni nanoband | [37]       |
| CdCl\(_2\)SeO\(_2\) | HCl, H\(_2\)O   | ITO glass W, Pt guaze C, Ag/AgCl R | 30 min/RT                             | 570 to 610 (deposition potential) | h-PDMS   | [33]       |
| CdCl\(_2\)SeO\(_2\) | HCl, H\(_2\)O   | SWCNTS W, Au C, Ag/AgCl R, | RT                                    | 10                          | SOCNTs   | [35]       |
| Cd(SO\(_4\))\(_2\)SeO\(_2\) | H\(_2\)O, H\(_2\)SO\(_4\) | Cu rod anode, PC cathode | 20/RT                                 | dc                          |          | [33]       |
In this method LPNE template was dipped in precursor plating solution containing 0.3 M CdSO₄ and 0.3 mM SeO₂ in 0.25 M aqueous H₂SO₄. Concise detail of the process is that CdSe was first deposited at −0.8 V versus saturated calomel electrode (SCE) on nickel during a negative scan and excessive Cd was stripped at −0.4 V during a positive scan. Excessive Se is removed by using optimized Cd:Se ratio of 43:1 and −0.4 V value was optimized in such a way that it should not strip deposited CdSe during removal of excessive Cd. LPNE (following reaction 5) provides nc-CdSe of 5 nm which can be increased to (i) 10 nm by thermal annealing, (ii) 20 nm by deposition from 75 °C hot plating solution and (iii) 100 nm by exposing it to methanolic CdCl₂ [36]. Moreover by increasing the number of scans, width of NWs increases i.e. 50 nm at 1 scan, 100 nm at 5 scans, 200 nm at ~20 scans [37].

For industrial overall acceptance of the process electrodeposition should be user friendly and high throughput fabrication method. In this regard electrodeposition on the templates prepared from soft nanoimprinting lithography (SNIL) has been used by Brucin Erenturk et al [33] for the fabrication of CdSe NWs of 100 nm in thickness, 300–500 nm width and several centimeter in length (figure 2(i)). Figures 2(a)–(h) shows schematic presentation of CdSe NW growth which involves the casting of polydimethyl siloxane (h-PDMS) mold from a master of patterned polycarbonate (PC). PC master has a height of 180 nm, width of 450 nm and spaces of 350 nm. Low adhesion force between PC master and PDMS supports easy separation after curing. Surface hydrophobic nature of daughter mold was confirmed by water contact angle of 113°. Norland optical adhesive 60 (NOA 60) was applied to O₂ plasma treated and washed ITO glass substrate. Curing was carried out by exposure to UV radiation (365 nm, 17 mWcm⁻²) for 15 s in air to improve pattern transfer. These daughter molds can be used for over 20 imprints. Details of electrodeposition have been given in table 1 which follow the chemistry of reaction 1. Color of CdSe deposited to ITO glass is yellow brown after 5 min and becomes dark brown after 30 min [33]. CdSe NWs produced with this technique are organized, ductile and crystalline with dimensions of 100 nm height × 500 nm width × 2.5 cm length reciprocating the dimensions of photoresist.

A new trend in material research is to synthesize the NWs of helical, saw like and zigzag shapes with an aim to use them as nano mechanical springs, nanoelectronics, nano lightening elements etc. Gu et al [35] have fabricated CdSe NWs serpentines and loops (figure 3). Conditions of electrodeposition have been presented in table 1 and chemistry of deposition was similar to previously reported reactions 1–4 in above paragraph. Increasing the number of cycles increases the size of deposit and keeps the composition same. This finding is in agreement with previously reported results [32]. This bottom up approach of designing CdSe NWs on the architecture of CNTs can be assumed to design semiconducting NWs on any available nano geometry.

Template methods explained above in electrodeposition have yielded very good results but they have disadvantages of multisteps, extensive experimentation and requirement of optimal conditions for the removal
of resist and detachment of mold. A one step template free method having facile and mild reaction conditions is highly beneficial. Feng et al [34] have reported nontemplated synthesis of CdSe by electrodeposition (table 1). It was observed in this study that NWs are only formed above 145 °C and below this temperature nanoparticles (NPs) are produced. Dimethyl formamide (DMF) was used as a solvent in this study which has a B.P of 152 °C.
This means that NWs were produced in a narrow temperature range of 145 °C–150 °C. At this high temperature, diameter of NWs and deposition rate increases which is controlled by current density, stirring rate and concentration of reactants. Increase in the current density has direct proportionality to deposition potential of working electrode which increases the diameter of CdSe NWs and Se-Cd ratios. Mass transfer to electrode is directly dependent on stirring rate and then deposition rate. Higher is the concentration higher is the deposition rate. Keeping in view all these mentioned details optimized current density was 0.22 mA cm$^{-2}$, temperature 147 °C, concentration 10 mM CdCl$_2$ and 5 mM Se and a stirring rate of 1000 rpm for perfectly single crystalline CdSe NWs. CdSe grows fast in three directions i.e. (000$I$), (0$I$ $Ī$0) and (2$Ī$Ī0). Surface of CdSe is polar and contains positively charged Cd-000$I$ and negatively charged Se-000 $Ī$. If equal growth occurs in all the three fast growing directions then NPs are formed but if negatively charged Se surface is made relatively inert as compared to positively charged Cd surface then chances of NW growth are high. Three parameters namely, crystallography, electrochemical nucleation and growth kinetics govern preferred growth in electrodeposition. Among these three, nucleation kinetics is the most important [34]. Relationship between nucleation rate ($I$) and nucleation energy $W_{hkl}$ is given by following equation

$$I = A \exp\left(-\frac{W_{hkl}}{kT}\right)$$  

(6)

Where $hkl$ is the crystal plane, $k$ is the Boltzmann constant and $A$ is the function of overpotential. At very low current density and low overpotential, $A$ is constant and rate of nucleation is directly proportional to $\exp(-W_{hkl}/kT)$. Under this condition growth of CdSe is parallel to the direction of current. Below 145 °C nucleation energy of nuclei may be close which favors NPs formation however; more work is still required to understand the exact mechanism of NWs formation. Template free electrodeposition seems to be very appealing but it is inferior to templated electrodeposition in terms of structural control, diversity of different NWs geometries and thin temperature range for the production of NWs and poor understanding of mechanism [34].

### 2.2. Solution based methods

Solution chemistry routes may be broadly classified as catalyzed and un-catalyzed. Among catalyzed methods, metallic and nonmetallic catalysts are used for tuning the structural parameters. These catalysts should have low melting points and temperature during the reaction is kept at a level that these catalyst particles are present in a molten form. Cd and Se precursors are then adsorbed or dissolved into these molten nano-droplets and support 1D growth via a so called solution liquid solid method (SLS) [40, 41].

First purely solution based attempt for straight and branched CdSe NWs was published by Grebinski et al [51]. This method utilizes the catalysis by Au/Bi NPs. Synthesis of straight and branched NWs takes place by following scheme 1. This method is advantageous over vapor liquid solid (VLS) in terms of low temperature requirement, higher yield of NWs and soluble product for easy functionalization. In this method molten Au/Bi NPs catalyst is saturated with Cd and Se precursor in the presence of reagents having long chain hydrocarbon functionalities which form the basis of NWs growth on the surface of NPs via a so called seeded mechanism. Different parameters which effect the morphology and aspect ratio of CdSe NWs include concentration of reaction mixture, temperature, initial Cd/Se ratio, Au/Bi volume and size and concentration of TOP (trioctyl phosphine). We will now discuss these parameters one by one [51].
Greater is the concentration of TOPO (trioctyl phosphine oxide) in the reaction mixture i.e. reaction mixture is dilute, greater are the chances of straight NWs formation. This happens due to decrease of Se contents in the immediate vicinity of catalyst which supports nucleation only in one direction. At dilute concentrations catalyzed growth of CdSe NWs is preferred over un-catalyzed self CdSe nucleation. At higher concentrations of Se self-nucleation dominates to form NPs. Optimized concentration for branched and straight NWs has to be determined experimentally [51].

Synthesis of straight NWs requires a temperature between 330 °C and 350 °C whereas branched NWs are formed between 280 °C and 300 °C. Although synthesis of NWs is a kinetically driven process but branching occurs at low temperature due to some un-identified thermodynamic parameters. At higher Cd concentrations (Cd/Se ratio = ~7:1) straight NWs are formed and if this ratio is increased more, then diameter of NWs increases. These findings of straight NWs formation at higher Cd/Se ratio (7:1) and high temperature (330 °C) have been confirmed by Zhen Li et al by using a novel Bi based nano catalyst [42]. Temperature dependence of NWs formation is important because melting point of nanocatalyst is size dependent. Bulk Bi NPs melt at 272 °C but nano sized Bi particles melt even at 150 °C. So, at the reaction temperature (330 °C) all catalyst particles are essentially present in molten state. Although a generalization is difficult to draw because other factors including precursor type (CdO, CdMe₂) and ratios are also important but wires can be generated even at 150 °C but will disappear to QDS after only one minute of reaction. If the reaction is carried out for 10 min then some NWs of 12 nm diameter and 0.8 μm length are obtained. This supports the hypothesis that QDs are intermediate products of NWs formation. Increasing the temperature from 150 °C to 180 °C, diameter of NWs increases from 12 nm to 22 nm and length increases from 0.8 μm to 6 μm. A further increase in temperature to 250 °C gives a diameter of 21 nm and length of 7 μm. Previously no NWs have been reported for Au/Bi catalysis below 240 °C. Melting point of Bi NPs is low and their reactivities are high that’s why their presence in molten form supports the formation of NWs [42, 43].

At higher Se ratios (Cd/Se 1.7:1) branching is favored. This condition can be achieved by two ways; firstly, by increasing the TOPSe concentration and keeping the volume same and secondly by adding more volume of TOPSe without considering the dilution effect however, after a certain dilution branching will not occur and diameter of NWs will increase. In addition, higher contents of Se in the reaction mixture decrease the length of NWs. This happens because of high reactivity of Se and low monomer concentration which yield magic sized NPs [43].

Increasing the size of catalyst NPs (Au/Bi and Au) increases the diameter of NWs [42, 51]. Smaller catalyst NPs (~1.4–2.2 nm) introduce more branching then larger catalyst NPs (2.5–2.7 nm). At very low volumes of the catalyst (Au/Bi NPs), QDs formation is favored relative to NWs [51] and this is true for Bi NPs catalyst as well [43]. Optimum value of volume for NWs formation is between 175 μl and 350 μl for either straight or branched NWs using bimetallic Au/Bi catalyst whereas 25 μl is the optimized value for monometallic Bi NPs which produces CdSe NWs of 18 nm diameter and 3 μm length. In a similar way amount of catalyst has to be optimized for length of NWs. Addition of small amount of TOP supports the formation of branched NWs dramatically [51, 52].

If we compare Au/Bi and pure Bi NPs, diameter of CdSe NWs is larger for pure Bi NPs catalyst and this pure catalyst produces straight NWs even at low Cd/Se ratios (1:1 and 1:7). These differences are due to slow release of Bi from Au cores (1.5 nm in diameter) which retards the formation of large Bi particles. As a result, thinner CdSe NWs are generated [43]. Surface modification of bimetallic catalyst (Au/Bi) and CdSe NWs with TOP or oleic acid always produces NWs of larger diameter than initial catalyst size however effect of TOP for monometallic catalyst (Bi NPs) is the production of thinner and shorter NWs. Using a polymer (poly(1-hexadecene)₀₋₁₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋˓→content removed to maintain length limits→...
NWs after formation [43]. In another attempt electrodeposited Bi NPs have been used for direct growth of CdSe NWs on ITO glass using the above mentioned details with success [44].

2.2.1. Solvothermal reactions

In solvothermal reactions, reactants are mixed in a particular solvent in a reaction vessel (mostly autoclave) and reaction is carried out at a temperature which is above the boiling point of the solvent [53–55]. This simple and easy to handle methodology has been adopted via scheme 2 for the fabrication of NWs of >50 nm diameter and 10–30 µm length [56]. As reported above, low temperature synthesis creates branching in the CdSe NWs. In fact when CdS combine in a particular direction to form NRs of less than 50 nm size, branching along the axis has been reported [51,57]. This approach has been further modified for the fabrication of CdSe NWs with diameters of 1.5–6 nm by using alkyl amines of different chain lengths as surface modifiers and solvents, between 100 °C–180 °C [58]. In the first step CdSe clusters are formed which act as an initiator for prewire aggregates and heating of these prewire aggregates produces solid NWs. By keeping the temperature same diameter of CdSe NWs increase by increasing the length of alkyl chain of amine and if the length of carbon chain is more than 14 carbons, formation of NWs is completely inhibited. For mixtures of small chain alkyl amines and long chain amines in which small chain proportion was high, diameters of NWs produced were small relative to higher proportion of long chain amines. For exactly 50% mixtures of short chain and long chain, both thinner and thicker CdSe NWs are produced [58]. Exact mechanism is not clear so far but it seems that amines having higher lengths of alkyl chains keep the nucleation centers separate from each other to favor NDs (nanodots) formation and when small chain amines are available in the mixture, they support the nucleation in a particular direction to support the NWs formation. At lower temperature, time is available for nuclei to form the branching but at high temperature growth only in one direction is favored by collision of nuclei along one axis only.

Use of metallic catalyst is not always necessary and synthesis of mono-dispersed CdSe NWs can be achieved by using dodecyl phosphonic acid (DDPA), octadecyl phosphonic acid (ODPA) and hexyl phosphonic acid (HPA) as complexing ligands for Cd and TOP as a ligand for Se [59]. Better control over morphology is achievable by using long alkyl chain phosphonic acids i.e. ODPA and DDPA rather than using HPA. Morphological results for DDPA are even better than ODPA. This is a contradiction with previously reported results [60] according to which cleavage of P = S bond governs the nucleation and growth allowing the low reactive complexes to position perfectly on the surface of NWs before the start of binding. If it is so then Cd-ODPA should provide a better aspect ratio than Cd-DDPA. These findings are also contradictory with the results of long chain amines in which long chain amines only, do not provide better aspect ratios until short chain amines are mixed with them [58]. However these result may be explained in terms of easy cleavage of P = Se bond relative to P = S bond in these two cases. TBP (tributyl phosphine) provides smaller sized NWs in terms of diameter and length than TOP. It has been proposed that this is because of strong binding of TBP with NWs. This result is also a contradiction with previously reported studies [61] which were based on the idea of stearic factors for low reactivity of TOP than TBP. Contrary to the previous experimental observations, decrease in temperature decreases the highest aspect ratio, in this study [59]. According to the authors, lowering in temperature decreases both the cleavage rate and monomer concentration in reaction mixture which in turn ceases the anisotropic growth. At higher temperature monomers find less time for adjustment so control over morphology becomes possible. Keeping total amount of reactants constant and doubling precursor’s concentration provides a length of 220 nm with a diameter of 8 nm but a further increase in precursor concentration effects distribution of size badly. This observation is in accordance with previous findings in which higher concentration of reactants favors NCs formation instead of NWs [51]. Continuous and multiple
injections do not effect morphology but increasing the injection time decreases the length of NWs with constant diameter. In fact large injection time decreases the monomer concentration in reaction medium which effects anisotropic growth. Time dependent studies provide a match with previous studies \[51\] i.e. generally with increase in reaction time, both diameter and length of the NWs increase \[51\].

2.3. Vapor based methods
Vapor based methods include chemical vapor deposition (CVD) and vapor liquid solid (VLS) methods \[12, 62–71\]. In a traditional VLS method a source material is evaporated inside a tube furnace and is transported with the help of a carrier gas to the catalyst coated substrates (figure 4). At reaction temperature, evaporated gaseous source material is deposited on liquid catalyst droplets, supersaturates them and is precipitated at solid liquid interface. VLS method requires higher temperature treatments than solution based methods. First ever attempt for morphologically controlled synthesis of CdSe from commercial CdSe via VLS method was reported by Christopher Ma et al \[45\]. According to this study, temperatures of the source, temperature of substrate and gas pressure inside tube are important parameters which determine the morphologies of resultant CdSe. Source temperature is important for the vaporization of source material but substrate temperature governs the actual growth of different CdSe morphologies. At 600 mbar and 575 ± 5 °C substrate temperature, nanosaws and nanocombs are produced whereas at 4 mbar and 575 ± 8 °C substrate temperature produces high percentage of nanobelts (figure 4). Synthesis of NWs is not conspicuously dependent on pressure however high percentage of NWs was observed in the region of high pressures and high temperatures \[45\]. This may be because of energy constraints at higher temperature for the production of teeth of nanosaws and nanobelts via secondary growth following so called spontaneous polarization induced asymmetric growth. Exact mechanism for the production of NWs has not been reported yet.

In a series of publications Shan et al have used a typical MOCVD setup for the preparation of CdSe nano needles and CdSe NWs \[72–75\]. Dimethyl cadmium and diisopropyl selenide were used as precursors for Cd and Se respectively in the presence of hydrogen as a carrier gas at 500 torr using varying temperatures. GaAs was used as a substrate and the reaction was catalyzed by gold for NWs production. Crystallographic surface of substrate and temperature governs the orientation of NWs according to these experimental efforts \[72–75\]. VLS method clearly shows inferior control of CdSe NWs morphologies and diameter of CdSe NWs is thicker in this case (~100 nm) \[46\]. This VLS method is important for the synthesis of thick CdSe NWs for application studies \[47, 76, 77\].

2.4. Template wetting method
Template wetting is a simple chemical method which involves the wetting of porous template with precursor and then subsequent temperature treatment firstly for insertion/infiltration of precursor into the pores and

\[\text{Figure 4. Schematic diagram of tube furnace used for VLS deposition of CdSe NWs (right). SEM images (top), TEM images (bottom right) and electron diffraction patterns (bottom left). (a) Nanosaws/nanocombs, (b) nanobelts, and (c) nanowires. Modified from [45]. Copyright Wiley 2005.}\]
secondly for the decomposition of precursor to semiconductor chalcogenide materials [48]. Using this method Lili Zhao et al [49] have coated porous alumina substrate (pore size 25 nm, pore depth 100 μm) with single source precursor Cd(SePh)₂ and TMEDA (TMEDA = tetramethylethylenediamine) powder according to Scheme 3. NPs, NRs, NRs with high aspect ratio and NWs after one (5 h), two (11 h), three (35 h) and four (83 h) wetting and crystallization cycles respectively have been generated. It has been proposed that these nanostructures are formed in two steps. In the first step small grains are formed from molecular precursors which combine with each other to form small NPs. These small NPs further grow to form larger NPs at the expense of smaller particles via Ostwald ripening process [78]. In the second step anisotropic growth of particles takes place for NRs and NWs formation. In this process mobility of NPs is hindered as compared to wet chemical processes (which have been extensively used by successors) for good anisotropic growth but this process requires much longer times for reaction completion [25, 48, 49].

3. Applications of CdSe nanowires

3.1. Solar cells
Energy crisis and pollution are two problems which endanger the existence of human race on the globe. Solar cells are a green solution to this problem because they can convert the Sunlight to electricity without any harmful effluents such as oxides of C, N and S which are generated by fossil fuels. Considering CdSe NWs as carrier transport material in solar cells their incident-photon-to-carrier conversion efficiency (IPCE) is 13% at 500 nm with concomitant 1 sun PCE of 0.007%. This low efficiency has been attributed to the presence of voids in irregularly oriented NWs which reduces the conductivity of charge carriers to the respective electrodes. Filling of these voids with colloidal CdSe QDs improves the efficiency of this hybrid architecture to 25% at 500 nm (figure 5) [79].

Blending of CdSe NWs with organic conjugated polymers is an interesting strategy for tuning the electronic and optical properties. In this domain Zhou and coworkers have reported short-circuit current density (Jsc) of 8.08 mAcm⁻², open circuit voltage (Voc) of 642 mV and fill factor (FF) of 0.69. This provided an overall energy conversion efficiency of 3.6% [34].

3.2. Photodetectors
Semiconductors can sense the light that has photon energy greater than their bandgap. This property of semiconductor materials makes them important in photon detection which has applications for light-wave communication, environmental and biological research and sensors etc. CdSe is important in photodetectors research because of its direct bandgap. Two important outcomes of research on single crystalline NWs [80], SnO₂ [81], GaN [82] and CdS are higher photoconductive gain than thin films of same materials [83] and delayed (approaching seconds) photorecurrent rise and decay [36]. It has been proposed that this difference is because of a barrier for electron hole recombination due to surface electric field. Source of this electric field is

\[
\text{Cd(SePh)}_2 \text{TMEDA} \rightarrow 30\% \text{ KOH at 70 °C} \\
\text{Porous Alumina Template} \rightarrow 160 °C, 2 °C/min \\
\text{Melting and infiltration of P} \rightarrow 500 °C, 2 °C/min \\
\text{to pores} \rightarrow 160 °C, 2 °C/min \\
\text{maintained for 2h} \rightarrow \text{P decomposition to nanostructures on template} \\
\text{Sonication} \rightarrow \text{Cooling to RT, 5 °C/min}
\]
material dependent and for CdS, CdS is trapped by surface states. For single crystalline NWs, photoconductive performance depend upon diameter, crystallographic orientation of long axis, dopant concentration and surface modification however photoconductive performance of polycrystalline NWs is also dependent on mean grain diameter \( d_{\text{avg}} \). Photoconduction bandwidth of 45 kHz has been provided by nanocrystalline CdSe (nc-CdSe) NWs having a \( d_{\text{avg}} \) of \( \sim 10 \) nm which was the best of all the NWs types till that time however, photoconductive gain was the lowest \( 0.032 – 0.050 \) among all the NWs types. Increasing the \( d_{\text{avg}} \) to 100 nm increases the photosensitivity by a factor of 375 which means that photoconductive properties of nc-CdSe NWs can be adjusted with mean grain diameter \( d_{\text{avg}} \). Table 2 presents the comparative photoconductive responses of nc-CdSe NWs with other cadmium based chalcogenides having different morphologies (figure 6). Figure 5. (a) CdSe nanowires (NWs) IPCE values (solid lines) and absorption (dashed lines) in the visible region of electromagnetic radiations. (b) I-V plots of optimized solar cell between 1.5 mW cm\(^{-2}\) and 330 mW cm\(^{-2}\) under halogen light illumination. (c) Comparative plots of open circuit voltage versus time of CdSe NWs, CdSe quantum dots (QDs) and CdSe NWs/QDs. Dashed line show the ~1/e lifetime of each trace. Modified with permission from [79]. Copyright Wiley 2010.

3.3. Field effect transistors (FETs)
CdSe is a promising candidate for research in the domain of inorganic field effect transistors due to its high Hall and field effect mobilities \( 800 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) relative to Si [98]. In this regard Lee and his fellows have doped CdSe NWs with indium to generate CdSe:In NWs hybrid which increases conductivity of NWs enormously especially at high doping [99].

Talin Ayvazian et al. have used lithographic patterning to produce pc-CdSe NWs arrays on SiO\(_2\)/Si substrates with and without exposure to methanolic solution of CdCl\(_2\) (growth promoter) [100]. These arrays of pc-CdSe NWs were used to prepare FETs via back gate configuration. Field effect mobility \( \mu_{\text{eff}} \) of sample exposed to CdCl\(_2\) increases from \( 1.94 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) to \( 23.4 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) with a decrease in threshold voltage of 75% and subthreshold slope by 35%. With increase in the channel length from 5 to 25 \( \mu \) a decrease in \( \mu_{\text{eff}} \) is observed because of the defects in the individual CdSe NWs. These inferior performances have been attributed to depressed electronic mobilities in the defects (figure 7) [100]. Same group has reported nc-CdSe NWs with lithographic patterning for electroluminescent studies [101]. Although the quantum yield is low \( (10^{-6}) \) but it is similar to devices having single crystalline CdSe NWs [102]. Table 3 presents the comparative device metrics for CdSe thin films and NWs samples.

3.4. Field emission properties
Emission of electrons under the influence of applied electric field from material surface into vacuum is called field emission (FE). This is a physical phenomenon and FE properties of CdSe have been uncommon. FE of CdSe NWs were first reported by H Li et al. [112] in which hybrid nanostructure consisting of branched and ordered
CdSe branches were present. This array was used as cathode and rod like copper probe single crystalline morphologies has been evaluated. This structure consisted of nano stem on which wurtzite anode under a direct current sweep from 100 to 1100 V to record the PL at room temperature. Hybrid CdSe NWs patterned on glass (5 μm pitch) and red is the photoluminescence spectrum recorded with excitation at 514.5 nm. (b) SEM image with 5 μm gap containing ~350 NWs of nc-CdSe. (c) Plot of photocurrent versus time as a result of chopped illumination (532 nm, 59 mW cm⁻²) at a frequency of 3940 Hz and biased at 2 V (black spectrum below) with silicon photodiode. (d) Plot of normalized photocurrent versus time presenting exponential fits and time constants for response (τresp) and recovery (τrec,fast,slow). (e) Schematic presentation of the apparatus used for measurement of photoconductive properties. Reproduced with permission from [36, 37]. Copyright ACS 2010 and 2011.

Table 2. Photoconductive responses of Cd based chalcogenides.

| Products          | Response, recovery | Photosensitivity | Dimensions                      | References |
|-------------------|--------------------|------------------|---------------------------------|------------|
| CdSe film         | 1.0 ms, 1.5 ms     | 10−10⁶           | 40 μm (gap) × 2.2 mm (w) × 700 nm (h) | [86]       |
| CdSe film         | 1.6 ms, 1.6 ms     | 11               | 0.3 cm (gap) × 2.0 cm (w) × 750 nm (h) | [67]       |
| CdSe film         | 1.0 ms, 0.2 ms     | 1 × 10⁶          | 35 μm (gap) × 10 μm (w) × 300 nm (h) | [88]       |
| CdSe film         | 1.3 ms, 0.2 ms     | NA               | 1 cm² (A) × 300 nm (h)           | [69]       |
| CdSe film         | 200 ms, 200 ms     | 10⁻⁴⁻¹⁰⁷         | 5 mm (gap) × 5 mm (w) × 170 nm (h) | [90]       |
| CdSe rods         | 1 s, 200 μs        | 15               | 350 nm (diameter)               | [91]       |
| CdS NWs           | 15 ms, 15 ms       | 39               | 20 μm (gap) × 200 nm (diam.) array | [92]       |
| CdS belt          | 1 s, 3 s          | 1.5 × 10³       | 200 nm (w)                      | [93]       |
| CdS ribbon        | 200 ms, 500 ms     | 2                | 25 μm (gap) × 640 nm (w) × 50 nm (h) | [94]       |
| CdS ribbon        | 746 μs, 794 μs     | 9.2 × 10³       | 18 μm (gap) × 10–60 μm (w) × 2–40 nm (h) | [95]       |
| CdS ribbon        | 551 μs, 1.09 ms    | 3.3 × 10⁶       | 50 nm (gap) × 5–10 μm (w) × 65 nm (h) | [96]       |
| CdSe ribbon       | 1.7 ms, 6.7 ms     | NA               | 5 μm (gap) × 5 μm (w) × 60 nm (h) | [85]       |
| CdSe NWs          | 700 ms, 700 ms     | 40               | 3 μm (gap) × 60 nm (diam.)       | [97]       |
| CdTe rods         | > 1 s, > 3 s      | 10               | 2 μm (gap) × 300 nm (diam.) vertical array | [86]       |
| CdSe NWs          | 20, 30 μs         | 10–100           | 5 μm (gap) × 200 nm (w) × 60 nm (h) array | [36, 37] |
| CdSe NWs          | 49 μs, 42 μs      | 8                | 5 nm cubic, (average crystallite size) | [36]       |
| CdSe NWs          | 8 μs, 30 μs       | 20               | 10 nm cubic (average crystallite size) | [36]       |
| CdSe NWs          | 200 μs, 6 × 10⁷ μs | 10               | 20 nm cubic (average crystallite size) | [36]       |
| CdSe NWs          | 8 μs, 2.7 × 10⁸ μs | 300              | 100 nm hex (average crystallite size) | [36]       |

single crystalline morphologies has been evaluated. This structure consisted of nano stem on which wurtzite CdSe branches were present. This array was used as cathode and rod like copper probe (1 mm²) was used as an anode under a direct current sweep from 100 to 1100 V to record the PL at room temperature. Hybrid CdSe nano array showed a turn on field at 4.3 ± 0.2 V μm⁻¹ for current densities of 10 μAcm⁻² [112]. This system
also showed high field enhancement factor (1160 ± 50) and long emission stability. CdSe NWs branched array also showed red lasing in the range of 700–720 nm (figure 8). These results are comparable to the result obtained for CNTs (5.4 V/μm) [113], zinc sulfide nanostructures (2.39 [114], 3.55 [115], and 3.8 V/μm [116]), zinc oxide nanostructures (11 V/μm [117], Si nanostructures (13 V/μm [118]) and CdS nanostructures (12.2 [119] and 1.4 [120] V/μm).

**Table 3.** Device metrics comparison for FETs of CdSe thin films and NWs samples.

| Description | L x (W) (μm) | μμeff(cm²(Vs)−1) | Vth(V) | S(mV(dec)−1) | References |
|------------|--------------|------------------|--------|--------------|------------|
| pc-CdSe thin films | 8 × (293) | 1 | 6.7 | 7000–10 000 | [103] |
| 100 × (500) | 1–6.7 | 2.5–30 | 260–5000 | [104] |
| 20 × (200) | 15 | 3.5 | 500 | [105] |
| 200–200 | 0.2–0.6 | 60 | | [106] |
| (×1–2 mm) | | | | |
| sc-CdSe NRs | 3.2 | 9.6 | 20.9 | [99] |
| sc-Cd-doped CdSe NWs | | 0.5 | 2 | 5 × 10⁴ | [107] |
| | 18.3 | 0.77 | | [108] |
| | 2 | 0.1–6.7 | | [109] |
| sc-In-doped CdSe NWs | 2 | 0.1–6.7 | | [109] |
| sc-Cd-doped CdSe NRs | 20 | 800 | −4.1 | 65 | [110] |
| sc-In-doped CdSe NWs | 5 | 3.2–166 | −1.7 | 508–10⁸ | [111] |
| pc-CdSe NWs (annealed) | 5 | 1.9 (±0.2) × 10⁻⁴ | 18–25 | 3600 | [100, 101] |
| pc-CdSe NWs (annealed and CdCl₂ treated) | 5 | 23 (±5) × 10⁻⁴ | 4–8 | 2300 | [100, 101] |

![Figure 7. Relationship between the channel length and transfer characteristics of CdCl₂ treated and annealed pc-CdSe nanowires field effect transistors (NWFETs) (a) Plot of I沟 versus V门 at 2 V for indicated channel lengths, (b) Plot of log I沟 versus V门 for indicated channel lengths, (c) Plot of linear range carrier mobility (μμeff) versus channel length for untreated (with CdCl₂) pc-CdSe NWFETs before (green) and after (red) correction, (d) Plot of μμeff versus channel length for CdCl₂ treated pc-CdSe NWFETs. Reprinted with permission from Ref [100]. Copyright ACS 2012.]
4. Conclusions

Top-down approach generally follows conventional lithographic methods which have the advantages of tackling most of the physical and technological difficulties but with a very slow production rate, making them incompatible with industrial production. Nanoscale physicochemical phenomena are used to fabricate nanostructures in a spontaneous manner with high yield using bottom-up approach. Main advantages of bottom-up approach are reduced cost and control over crystal growth for better reproducibility. Shortcomings of bottom-up approach are the practical incompatibility between spontaneous growth and their use in transistors, memory cells and other electronic devices [121].

Electrodeposition (ED) is the pioneering technique for the production of CdSe NWs. In templated ED, length of CdSe NWs is dependent on deposition time and diameter of NWs depends on pore diameter of template, scan rate (time), thermal annealing, temperature assisted deposition and reaction medium. Non templated ED produces CdSe NWs only above 145 °C and this method is inferior to templated method in terms of structural control, diversity of NWs morphologies and workable temperature range.

Solution based synthesis of CdSe NWs is carried out by catalyzed and un-catalyzed methods. Au/Bi NPs and Bi NPs have been used as a catalyst for the growth of CdSe NWs. Among these two, Bi NPs can generate CdSe NWs at a temperature as low as 150 °C but Au/Bi NPs require at least 240 °C for NWs formation because of low melting point of Bi catalyst relative to Au/Bi catalyst. Bi NPs produce straight NWs of larger diameter than Au/Bi NPs, possibly due to slow release of Bi from Au cores. Chemistry of solution based synthesis is too much complicated but concentration of reaction mixture, temperature, Cd/Se ratio, volume of catalyst and concentration of surface modifiers (phosphines and amines) govern the tuning of structural parameters for a competition between catalyzed and un-catalyzed growth of CdSe NWs.

Vapor based synthetic methods (CVD and VLS) show inferior control of morphology relative to solution based methods and ED methods. VLS is important for thick NWs used in application studies. Among all the synthetic methods i.e. templated ED, non templated ED, catalyzed and un-catalyzed solution based methods, solvothermal method, VLS methods and template wetting method, templated ED has given the best control over size, morphology and phase. However, nano-science is the appropriate term when we discuss CdSe NWs because we are far behind technical mass production.
CdSe NWs are in research phase for their device applications and no product (to the best of our knowledge) has been marketed consisting of CdSe NWs. Solar cell applications of CdSe NWs are inferior due to the presence of voids and can be enhanced by filling the voids with CdSe QDs. Filling of these voids with other chalcogenide semiconductor quantum dots is the future horizon of research. Photoconduction band width of 45 KHz for CdSe NWs is the best of all NW types but photoconductive gain is the lowest. Applications of CdSe NWs in field effect transistors are not very promising due to defects in the wires. Improvement of these applications by enhancement of electronic conduction via doping and/or removal of defects is the future goal of research.

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