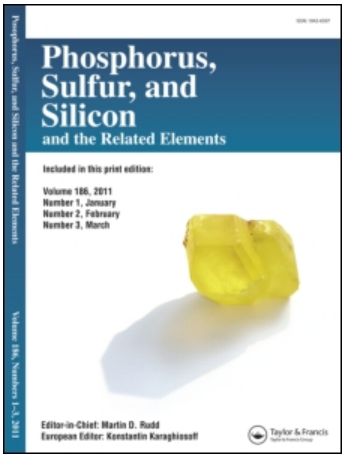

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NOVEL APPROACHES TO THE DEPOSITION OF SELENIUM CONTAINING MATERIALS

M. AZAD MALIK, PAUL O'BRIEN* AND DAVID J. OTWAY
Department of Chemistry, Imperial College of Science Technology and Medicine, South Kensington, London, SW7 2AZ, UK.

Selenium containing materials find wide ranging utility in a number of applications and some novel routes to such materials are discussed.

Keywords: selenium, selenide, MOCVD, CBD, precursors

INTRODUCTION

There is considerable contemporary interest in selenium containing materials. Group II-VI semiconducting materials such as zinc selenide, cadmium selenide or copper indium diselenide are materials which are, or have the potential to be, used in a variety of applications from solid state lasers to solar cells (see Table 1). Often the compounds are required as thin films of high quality and techniques such as metal organic chemical vapour deposition (MOCVD) are used for deposition. There has been considerable interest recently in the synthesis of materials such as CdSe as isolated nanometric particles which show quantum confinement effects. In this paper the uses, and potential uses, of such compounds will be briefly reviewed.

Table 1 : Metal Selenide Materials: Some Characteristics and Uses.

Material	Lattice Parameters Å	Band Gap eV	Applications
ZnSe(cubic)	a = 5.669	2.58	blue/green LED's and lasers, interference coating for optical components and switching devices
ZnSe (hexagonal)	a = 3.996, c = 6.626		
ZnSSe			alloy used to vary band gap or lattice match
ZnMgSSe			blue to short λ ὸptoelectronics, lattice matching
CdSe (cubic)	a = 6.084		solid state solar cells, photoconductors
CdSe (hexagonal)	a = 4.298, c = 7.010	1.74	solid state solar cells, photoconductors
$Zn_xCd_{1-x}Se$		1.74 - 2.67	phosphor material for colour television screens
Au-$Zn_xCd_{1-x}Se$		0.36 - 1.16	schottky diodes
As_xSe_{1-x}			IR transmitting glasses for lenses, IR optical system glass fibre for laser assisted surgery.
Bi_2Se_3 (hexagonal)	a = 9.84	0.15	thermoelectric refrigeration
$PbSe_xS_{1-x}$			infra-red photodetectors and lasers
PbSeTe			
In_2Se_3	Confused	1.5-2.0	
InSe	a = 4.005, c = 16.640	1.172	binary parent of $CuInSe_2$
CuSe			binary parent of $CuInSe_2$
α-Ga_2Se_3	a = 5.418	2.2	
β-GaSe	a = 3.755, c = 15.94	2.021	Insulator for MOSFET gates
γ-Ga_2Se_3	a = 5.17	------	
$CuInSe_2$		1.04	Lightweight, radiation resistant, solar cells

The deposition of selenium containing materials by chemical methods most often uses volatile and toxic sources, *e.g.*, in MOCVD, selenides are often deposited using a metal alkyl in combination with hydrogen selenide or an alkyl selenide. We and others have developed classes of precursors in which the selenium is delivered along with the metal in a single compound - so called a single source or single molecule precursor. Frequently the compounds used have been diseleno-carbamates. The use of diselenocarbamates has been a particular focus of our work.

Metal-Organic Chemical Vapour Deposition (MOCVD)

MOCVD is an important deposition technique for thin films. The technique has a number of advantages over conventional film deposition methods such as sputtering (line of sight only) and the "heat and bake" methods {grinding and sintering} (high temperatures, defects, stoichiometry problems *etc.*). MOCVD allows the use of low temperatures and is potentially a non-line of sight technique (*i.e.* it can be used to deposit films on curved and "unusual" surfaces). A simple low pressure (LP) MOCVD reactor as used in our laboratory, is shown in Figure 1.

We have been interested in the deposition of thin films of various metal selenide materials, in particular, ZnSe, CdSe and CuSe, In_2Se_3, $CuInSe_2$. ZnSe is currently a potential material for use as a blue light emitter in, *e.g.*, blue lasers. CdSe and $CuInSe_2$ are starting to find use as photovoltaic materials, (*i.e.*, for clean power generation from solar energy) but, as yet, the radiation hard $CuInSe_2$ has not been reproducibly deposited as thin films by simple thermal MOCVD.

There are plans to include the material on one of NASA's space vehicles to test its suitability/reliability in space environments.[1]

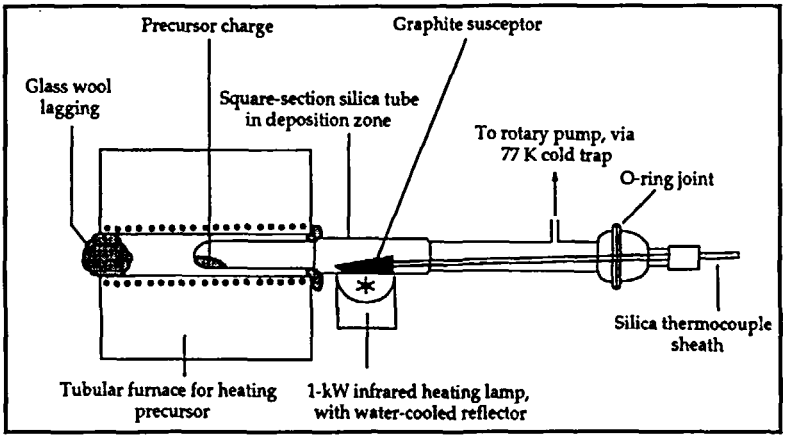
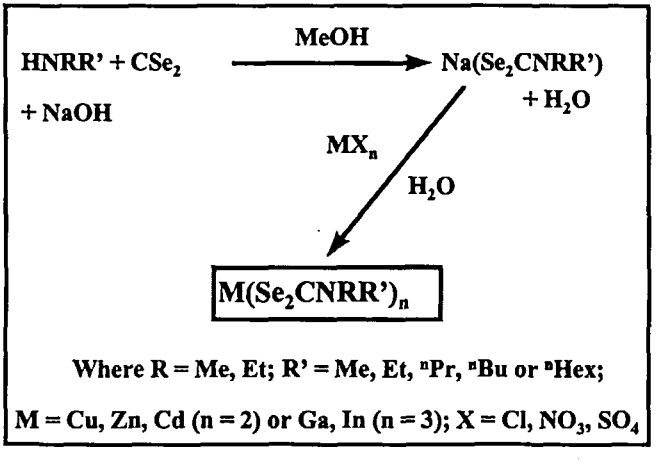


FIGURE 1 : The Low Pressure MOCVD Reactor as used at Imperial College for the Deposition of Thin films.

Usually in MOCVD a separate precursor for each of the elements to be deposited is required, *i.e.*, Me_2Cd and H_2Se for CdSe deposition. We have started to develop the area of "single source precursors", in particular, the deposition of thin films of ZnSe, CdSe, CuSe, In_2Se_3, and $CuInSe_2$, by MOCVD, from metal diselenocarbamate $(RR'NCSe_2)^-$ compounds has been studied along with some of the chemistry of the precursor compounds.[2] A typical general synthetic strategy to such metal diselenocarbamates is illustrated in Scheme 1.

The rational design of a MOCVD precursor is vital in order to control the film impurities, properties, contamination and the vapour pressure of the precursor. Single source precursors potentially exhibit many or all of the following advantages over conventional MOCVD precursors : a) Air and moisture stability, b) Low toxicity, c) No pre-

reaction, d) Control of stoichiometry, e) Good volatility, and f) Low temperature growth is often possible. Some compounds synthesised *via* the reactions shown in Scheme 1 have recently found utility as precursors in our laboratory as illustrated in Table 2.



SCHEME 1 : Typical synthetic strategy for metal diselenocarbamates.

Compound	Melting Point (°C)	Precursor Temp (°C)	Growth Temp (°C)	Successful growth
$In[Se_2CNMe^nBu]_3$	146-147	250	450-470	Yes In_2Se_3
$In[Se_2CNMe^nHex]_3$	102-103	250	450-500	Yes In_2Se_3 [3]
$Cu[Se_2CNMe^nBu]_2$	78-79	250	450-480	Yes CuSe
$Cu[Se_2CNMe^nHex]_2$	47-48	250	450-480	Yes CuSe [4]
$Cu[Se_2CNMe^nHex]_2$ and $In[Se_2CNMe^nHex]_3$	____	Mixed together 250	450-470	Yes $CuInSe_2$ [5]

TABLE 2 : Some Typical Precursors and Growth conditions for In_2Se_3, CuSe and $CuInSe_2$.

Other groups working in this area include those of Barron,[6] Gysling,[7] Arnold,[8] Chichibu,[9] Cole-Hamilton,[10] Cowley,[11] Raston,[12] Atwood,[13] and Bochmann.[14] Thin films of, *e.g.*, InSe, In_2Se_3 and GaSe have been grown from several interesting single source precursors including $In[SeC(SiMe_3)_3]_3$,[7] and the cubane compounds $[(^tBu)GaSe]_4$ and $[(EtMe_2C)InSe]_4$.[6]

Some of the compounds used as precursors for MOCVD of metal selenide thin films are summarized in Table 3.

Table 3 : Some Se based Precursors utilized in MOCVD and Nanoparticle Deposition.

Precursor	m.p. / b.p. (°C)	Structure	Reference
$Cu(Se_2CNMeHex)_2$	47-48		[4]
$In(Se_2CNMe^nHex)_3$	102-103		[3]
$In(Se_2CNMe^nBu)_3$	146-147		[4]
$In_4Se_4[C(SiMe_3)_3]_4$	350	X-ray	[8]
$In[SeC(SiMe_3)_3]_3$	195	X-ray	[7]
$[Mesityl_2In(SeMe)]_2$	281		[15]
$[Mesityl_2In(SePh)]_2$	245	X-ray	[15]
$[Mesityl_2In(SeMesityl)]_2$	207-208	X-ray	[15]
$[MeIn(SePh)_2]_n$	127	X-ray	[15]
$[Me_2InSePh]$			[7]
$In(SePh)_3$			[7]
$[(^tBu)GaSe]_4$			[6]
$[(EtMe_2C)InSe]_4$			[6]
$Zn(Se_2CNMe_2)_2$	152-154		[16-18]
$Zn(Se_2CNEt_2)_2$	137-139	X-ray	[16]
$Zn(Se_2CN^iBu_2)_2$	129-130		[16]
$Zn(Se_2CNMe^nHex)_2$	81-83	X-ray	[19]
$Cd(Se_2CN^iBu_2)_2$	93-95		[16]
$Ni(Se_2CNEt_2)\ PEt_3Cl$	290		[16]
$Pd(Se_2CN^iBu_2)PPh_3Cl$	216-218		[16,20]
$Pd(Se_2CNEt_2)_2$	199-202	X-ray	[16,21]
$Pt(Se_2CNEt_2)$	300		[16]
$Pt(Se_2CNEt_2)\ PPh_3Cl$	205-208		[16]
$Pt(Se_2CNEt_2)\ PPh_3Cl$	167-169		[16]
$[Pt(Se_2CN^iBu_2)\ (PPh_3)_2]Cl$	224		[16]

cis- $Pt(Se_2CN^iBu_2)_2I_2$	178-182		[16]
$Zn(Se_2CNMe_2)_2$	236-239		[18]
$Cd(Se_2CNEt_2)_2$	225-226	X-ray	[21,22]
$Cu(Se_2CNEt_2)_2$	225-226	X-ray	[17,21]
$Co(Se_2CNEt_2)_2$	285		[21]
$Cr(Se_2CNEt_2)_2$	275		[21]
$Ni(Se_2CNEt_2)_2$	255-256	X-ray	[16,21]
$[MeZnSe_2CNEt_2]_2$	155	X-ray	[23]
$[EtZnSe_2CNEt_2]_2$	131	X-ray	[23]
$[NpZnSe_2CNEt_2]_2$	135	X-ray	[24]
$[MeCdSe_2CNEt_2]_2$	160		[23]
$[NpCdSe_2CNEt_2]_2$	145	X-ray	[25]
$[^tBuZnSe_2CNEt_2]_2$	163		[24]
$Me_2CdZn(Se_2CNEt_2)_2$	200	X-ray	[23]
$[CdSeCCPh)_2(TMEDA)_2]$	129	X-ray	[26]
$[Cd_4Br_4(SePh)_6$			[27]
$[NMe_4]_2[Cd(SePh)_4]$			[28]
$[NMe_4]_2[Cd_4(SePh)_{10}]$			[29]
$Cu(Se_2CNBu_2)_2$	82		[30]
$Ni(Se_2CNBu_2)_2$	93		[30]
$Pd(Se_2CNBu_2)_2$	108		[30]
$Pt(Se_2CNBu_2)_3$	261		[30]
$Ca(Se_2CNBu_2)_3$	175		[30]
$Fe(Se_2CNBu_2)_3$	121		[30]
$Co(Se_2CNBu_2)_3$	161		[30]
$Au(Se_2CNBu_2)_3$	177		[30]
$Ru(Se_2CNEt_2)_3$	218		[30]
$Os(Se_2CNEt_2)_3$	250		[30]
$Li(Se_2CNEt_2)_4$	112		[30]
$Zn[Se_2CN(Me)(CH_2)_3NMe_2]_2$	123-125	X-ray	[31]
$Cd[Se_2CN(Me)(CH_2)_3NMe_2]_2$	146-148		[31]
$[Cd_2(Se(C_6H_5)_4(DEPE)]_n$			[32]
$Zn(SePh)_2$	>300		[33]
$Zn(SePh)_2DEPE$	137-138		[33]
$Cd(SePh)_2$ DEPE	162-164	X-ray	[33]
$Zn(SePh_2)_2$ DEPE	205-207		[33]
$[Zn(SeC_6H_2{}^tBu_3)_2(p\text{-}OCHC_6H_4OMe)]_2$		X-ray	[34]
$[Cd(SeC_6H_2{}^tBu_3)_2]_2$		X-ray	[35]

$Zn(SeC_6H_2{}^tBu_3)_2$			[35]
$Hg(SeC_6H_2Me_3)_2$	200		[36]
$Hg(SeC_6H_2Et_3)_2$	133		[36]
$Hg(SeC_6H_2{}^tBu_3)_2$	150		[20]
$RZn(SeC_6H_2{}^iPr_3$ (R = Me, Et, ^{i}Pr, Pr)			[37]
$RCd(SeC_6H_2{}^iPr_3$ (R = Me, Et, ^{i}Pr, Pr)			[37]
$Zn(SeSi(SiMe_3)_3)_2$			[38]
$Cd(SeSi(SiMe_3)_3)_2$			[39]

Recently we have deposited $CuInSe_2$ by MOCVD (with conditions as described in Table 2). Figure 2 shows the XRD pattern and an SEM photograph of one of these films where the precursor ratio was 1:1 $Cu(Se_2CNMeHex)_2$: $In(Se_2CNMe^nHex)_3$.[5]

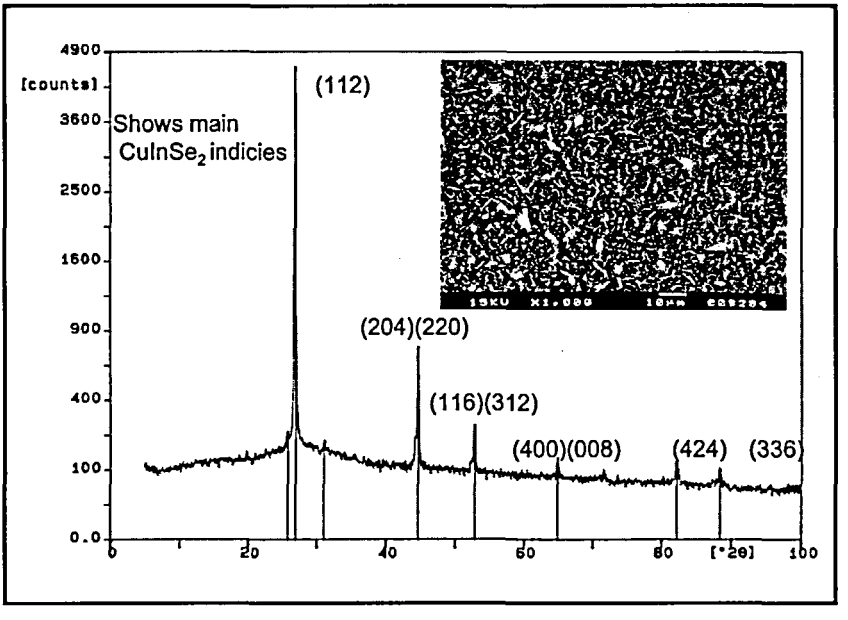


FIGURE 2 : XRD pattern and SEM photograph $CuInSe_2$ grown by MOCVD at T_s 450 and T_p 250 °C.

Nanoparticles

Nanoparticles, often referred to as Q-particles, quantum dots or nanocrystallites, have been recognized as suitable systems for studying the transition from the molecular to the macrocrystalline level (see Figure 3) and have been extensively studied in recent years.[40-50]

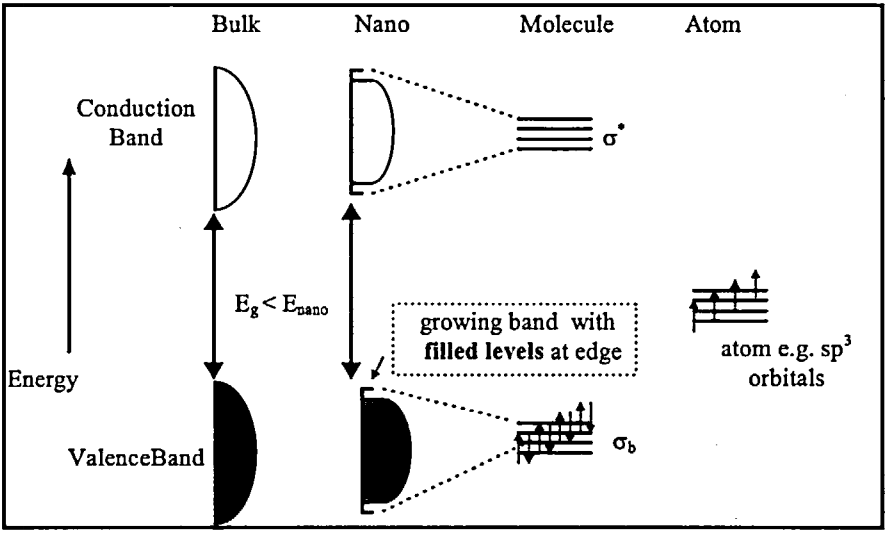


FIGURE 3 : Electronic Structure of a Semiconductor.

Interest in research into new synthetic routes for semiconductor nanocrystallites has been heightened as devices based upon such materials have been fabricated.[51-53] A number of synthetic methods including the use of aqueous solution, microemulsions, zeolites, gels, polymers and glasses have been reported for the preparation of a wide range of semiconductor nanoparticles.[40-46,54-63] High purity, monodispersity and ability to control the surface derivatization are the requirements for such systems.

Many nanocrystallites containing selenium have been prepared and characterized. In fact CdSe nanocrystallites are the most extensively studied. Nanocrystalline CdSe has been prepared by arrested precipitation in micelles[60,61] or by the reaction of molecular species at high temperature in organic solvents[62,64,65] and by using single molecular precursors such as $NpCdSe_2CNEt_2$ (see Figure 4).[63,66-69]

The latter method is particularly useful because it replaces the use

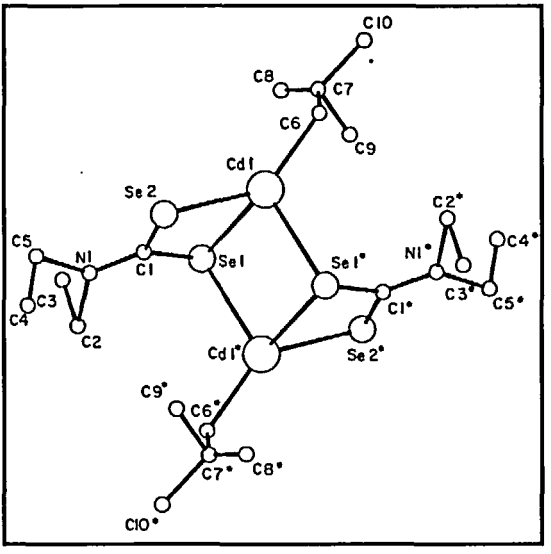


FIGURE 4 : Crystal Structure of $NpCdSe_2CNEt_2$

of hazardous compounds such as $CdMe_2$[51,52] or H_2Se[53] for the synthesis of CdSe. Steigerwald *et. al.*,[70] prepared CdSe nanoparticles using solution phase thermolysis of $Cd[Se(C_6H_5)]_2$. The method involved refluxing the precursor in 4-ethylpyridine, a high boiling solvent, to give optically clear solutions containing the nanoparticles. Composites containing CdSe nanoparticles have been prepared and characterized (see Figures 5 and 6). Semiconductor quantum-dot

composites have potential applications in optoelectronics, *e.g.*, in light emitting devices and optical switches. Composites are the materials which incorporate semiconductor nanocrystals in a thin film semiconductor matrix. These composites can be more easily integrated into electronic and optoelectronic devices and the conductivity of the matrix can be controlled by doping. A hybrid organic/inorganic electroluminescent device has been constructed by the recombination of holes injected into a layer of semiconducting p-paraphenylenevinylene(PPV)[71-73] with electrons injected into a multilayer film of cadmium selenide nanocrystals. Because of the quantum size effects[74-79] the colour of the emission can be varied from red to yellow by changing the nanocrystal size. At higher voltages green emission from the polymer layer predominates.[80]

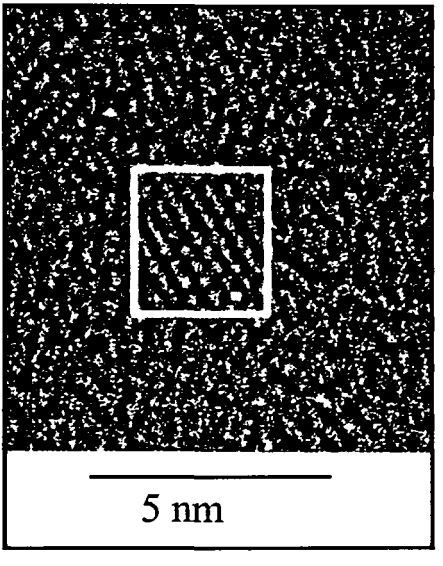


FIGURE 5 : HRTEM of CdSe Nanoparticles.

Charge separation and transport was studied in composites formed by cadmium selenide nanocrystals with the conjugated polymer poly(2-methoxy,5-(2'-ethyl)-hexyloxy-p-phenylenevinylene)(MEH-PPV).[81] The preparation and isolation of a linked homodimer of cadmium selenide has been carried out by using wet-chemical methods.[82] CdSe-TOPO was treated with thiols (or acyl hydrazides) with polar end groups at elevated temperature to

give a uniform surface coverage of ligands on CdSe nanoparticles. These particles were than cross-linked by the addition of a bis(acyl hydrazide) at elevated temperature and high PH to obtain a homodimer powder.[82] Cadmium selenide composites were also prepared with phosphine or phosphine oxide norborenene derivatives.[83]

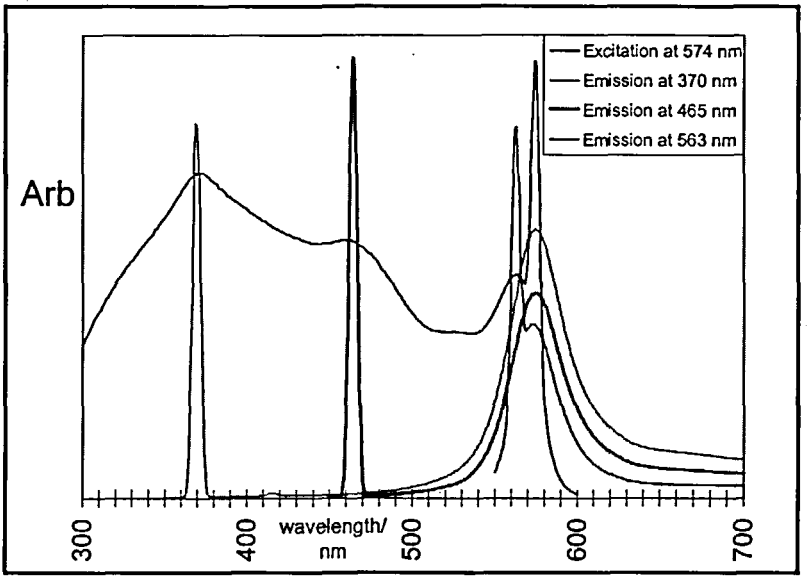


FIGURE 6 : Typical Band Edge Emission from CdSe *ca.* 5 nm Dots.

CdS_xSe_{1-x} doped glasses have promising use in optical communications and optical signal processing because of their large optical nonlinearity and fast response time.[84-86] Absorption and photoluminescence properties of this material with regard to the size of the particles have been studied.[87] Coupled composite CdS-CdSe nanoparticles were prepared by addition of H_2S and H_2Se in different proportions to aqueous $Cd(ClO_4)_2$ solutions containing $(NaPO_3)_6$.[88] Other size-quantized composite semiconductors containing selenium include $CdS_x/CdSe_{1-x}$,[89] $CdSe_x/Te_{1-x}$,[89] ZnS/CdSe,[90] and ZnSe

/CdSe.[91,92] Quantum dot/conducting polymer structures, *e.g.*, electrochemical cells, allow for direct electrical connection and excitation of the dots. Electroluminescent properties of a solid state assembly of nearly monodispersed nanocrystallites of CdSe embedded in a matrix of polyvinylcarbazole (PVK) and the oxadiazole derivative (^{t}Bu-PBD)[93] and CdSe/PPV[82,94] have been investigated. Thin film composites consisting of a ZnSe matrix and CdSe nanocrystals have been prepared by the combined methods of electrospray and metalorganic chemical vapour deposition (MOCVD).[95]

Indium selenide (InSe) and Gallium selenide (GaSe) nanoparticles have been prepared by vapour phase thermolysis of heterocubanes $[EtMe_2C)InSe]_4$ and $[^tBuGaSe]_4$ respectively.[6] The indium selenide particles consisted of spheres with a mean diameter of 88 nm whereas the gallium selenide particles were pseudo-spherical with a mean diameter of 42nm. Colloidal In_2Se_3 have been prepared in aqueous medium in the presence of sodium metaphosphate and the absorption properties and growth kinetics of the colloidal particles have been reported.[96] Copper selenide nanoparticles have also been prepared and XPS spectra, valence bands and Auger transitions are reported for the molecular cluster $Cu_{146}Se_{73}(PPh_3)_{30}$ and Cu_2Se.[97] Photoemission features are reported for both species.

Conclusions

Whilst significant progress has been made in the area of deposition of selenium containing materials, there is still a need for more, and many interesting materials remain to be studied. Nanoparticle formation and MOCVD appear to be two very useful routes to such materials.

Acknowledgements

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