Soft Nanoscience Letters, 2014, 4, 69-74
Published Online July 2014 in SciRes. http://www.scirp.org/journal/snl
http://dx.doi.org/10.4236/snl.2014.43010

Synthesis of Luminescent CdTe Nanorods on Anodized Aluminum Oxide Template and Their Utility in Divalent Heavy Metal Ion Sensing

Gyanan[1*], Jayakrishna Khatei[2,3]
[1]Department of Physics, Birla Institute of Technology and Science, Pilani, India
[2]Department of Physics, Indian Institute of Science, Bangalore, India
[3]Present Address: Solid State Institute and Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel
Email: *gyanan2007@gmail.com

Received 17 May 2014; revised 17 June 2014; accepted 17 July 2014

Abstract

A simple one-pot hydrothermal method to grow luminescent CdTe nanorods on porous anodized aluminum oxide (AAO) template is described. These CdTe nanorods on the AAO template were further applied as an optical probe to detect divalent heavy metal ions such as Hg, Pb, Mg and Zn, by examining its photoluminescence (PL) responses. The presence of Pb and Hg ions quenched the photoluminescence (PL) of the CdTe nanorods where as Zn and Mg ions enhanced it with the effect of red shift in the peak position respectively. These PL enhancements/quenching of the nanorods after exposing to the divalent ions were explained on the basis of the active surface related recombination, which depends on the direction of carrier transfer mechanism *i.e.* from nanorods to the surface adsorbed metal ions or vice-versa and is attributed to the alignment of bands thus formed. The luminescent CdTe nanorods grown on AAO template was found to be effective in sensing metal ions (Pb, Hg, Zn and Mg) up to a micro-molar concentration.

Keywords

CdTe, Hydrothermal, Nanorods, Luminescence, Divalent Ion Sensing

1. Introduction

Nanomaterials as sensor are given a prime focus as it has enhanced the responsiveness, selectivity, reproducibil-

*Corresponding author.

How to cite this paper: Gyanan and Khatei, J. (2014) Synthesis of Luminescent CdTe Nanorods on Anodized Aluminum Oxide Template and Their Utility in Divalent Heavy Metal Ion Sensing. *Soft Nanoscience Letters*, **4**, 69-74.
http://dx.doi.org/10.4236/snl.2014.43010

ity and detection limit of the sensors [1] [2]. Among them, 1D and 2D semiconducting nanostructures like nanorods, nanowires etc are particularly attractive as sensors as it has high surface-to-volume ratio, which leads to higher sensitivity [3] [4]. Divalent heavy metal ions play an important role in the biological activities such as O_2 movement, carbon fixation, methylation, phosphorylation, electron transfer mechanism as well as in the stabilization of bio molecules [5]. Also it is evident that uncontrolled human practice has modified the natural cycle of heavy divalent metals including the toxic non-essential elements like Pb, Hg etc. These modifications have become a serious concern for global sustainability. Consequently many efforts have been carried out by the research community to develop different kinds of sensors for monitoring and detecting heavy metal ions in food, drinking water, and other biophysical system in nature [6]-[8].

Till today, many kinds of novel 1D nanostructured materials have been successfully synthesized, such as III - V [9], II - VI semiconductors [10] [11], elemental and oxide nanowires/Nanorods [12] [13]. To fabricate nanowires of various material, diverse experimental procedure have been reported by a variety of nanofabrication techniques [14] [15] and crystal growth methods. Among these techniques, arc discharge [16], laser ablation [17] and catalytic CVD [18] growth are few prominent ones. Apart from these, the other most important methods of preparation of 1D structures are the catalyst- and template-based methods in which the catalysts provide the energetically favoured sites for the adsorption of gas reactants, while the templates/substrates are used to control and direct the growth of the 1D structure. The size and shape of the formed 1D structures therefore depends greatly on the selection of suitable catalysts as well as templates, which apparently involves complications [19]. The anodic alumina membrane (AAM) is among the several templates used generally for growing 1D structures; it is hard with uniform, nearly parallel and ordered pore structure [20]. Among various groups, the growth of MnS rods on the AAO template using Al (99.999%) via a two-step anodization [21], growth of metal telluride/carbon nanocables via Te/carbon nanocables [22], the fabrication of a coaxial silica shell on the surface of CdTe nanowires via the base-catalyzed hydrolysis of tetraethyl orthosilicate [23] are few examples of template assisted 1D structure growth.

In this article we demonstrate a simple and convenient method for the growth of luminescent CdTe nanorods on the anodized aluminum oxide (AAO) template by the hydrothermal method at a temperature of 180˚C for 4 hours without any catalyst. Also the hydrothermal method in the present case is milder and less harmful to the environment because of the use of stable sodium tellurite (Na_2TeO_3) as the tellurite source. Thus obtained CdTe nanorods on the AAO templates were used as a fluorescence probe for the detection of divalent ions such as Pb, Hg, which has adverse effects on human health, environment and for some essential microelements such as Zn and Mg.

2. Materials and Methods

All analytical grade chemicals were purchased from sigma Aldrich and were utilized without further purification. The AAO templates were purchased from Whatman. The stock solution of Hg^{2+}, Pb^{2+}, Mg^{2+}, Zn^{2+} ions were prepared by dissolving suitable amount of compounds like $HgCl_2$, $MgCl_2$, Pb $(CH_3COO)_2$, and $ZnCl_2$, in deionized water. The molarities of the solution prepared were maintained at 1µM concentration.

The experimental procedure of CdTe nanorods on AAO template is depicted in **Figure 1**. In a typical synthesis, the commercially available AAO template having anodic circles of diameter 25 mm with pore size of 0.1 µm was first treated with organic solvents such as acetone, ethanol as well as deionized water before use. This AAO template was then placed into the 60 ml Teflon lined stainless steel autoclave and CdTe precursor solution is added to it. The CdTe precursor solutions were prepared by mixing 4 ml of cadmium chloride solution ($CdCl_2$, 0.04 mol/L) diluted to 42 ml with de-ionized water and sequentially adding, trisodium citrate dihydrate (100 mg), Na_2TeO_3 (0.01 mol/L, 4 ml), 3-mercaptopropanoic acid (MPA) (40.7 mg) and $NaBH_4$ (50 mg) under magnetic stirring. Then the autoclave was sealed and was kept inside an oven at 180˚C for 4 hours. The oven was programmed to switch off after 4 hours and was allowed to cool to room temperature naturally. The AAO template was taken out of the autoclave, cleaned with de-ionized water and dried with dry N_2 gas.

The luminescence measurements were done with TRIAX 550 monochromatic based Photoluminescence (PL) system with liquid nitrogen cooled InGaAs detector excited by Ar^+ laser (514.5 nm) with laser power of 10 mW. The topography of the template was taken by SEM. The XRD patterns were recorded on Philips X'pert SW having X'pert pro diffractometer with Cu Kα radiation (α = 1.5406 Å). The sample of AAO template containing CdTe nanorods was made into several pieces and their photoluminescence signature were recorded. These pieces of template with nanorods are then used for sensing different divalent heavy metal ions by physically placing

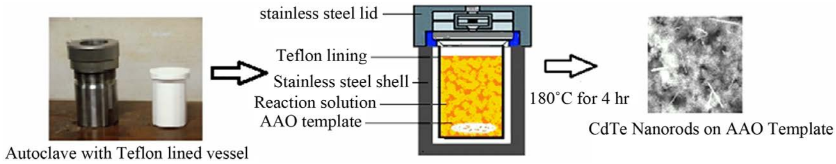

Figure 1. Schematic representation of growth of the CdTe nanorods on AAO template.

them in an ionic solution, approximately for 5 minutes and then dried at room temperature. The photoluminescence of these samples were recorded to understand the effect of different divalent ions on the luminescence property of CdTe nanorods. All the optical measurements were performed at room temperature.

3. Results and Discussion

Figure 2(a) shows the SEM image of the commercial AAO template after pre-treatment with organic solvents and deionized water used for the growth of CdTe nanorods. The image shows that the template has a precise honeycomb like pore structure with some spongy particulates adsorbed on the surface of the AAO template. The **Figure 2(b)** shows, the large number of highly distributed CdTe nanorods grown on the AAO template. The dimension of the rods ranges from 50 - 300 nm in diameter. **Figure 3** shows, the XRD of the nanorods grown on the commercial AAO template. The reflections of [111] and [220] planes of Cadmium telluride zinc blend structure are indexed here.

The structure of AAO templates, believes to play an important role in controlling the localization of supersaturated CdTe solution in the pores of the template and have favoured anisotropic growth, which may have led to growth of the nanorods [21]. This can also be the reason that we have highly distributed rods on the AAO template. After a certain critical length, the nanorods might have been dislodged from the base plate to find randomly distributed ones on the template.

The growth procedure of CdTe nanorods can be described as follows. During synthesis, $NaBH_4$ reduces TeO_3^{2-} to Te^{2-}. These Te^{2-} first reacts with Cd^{2+} in the presence of MPA to forms CdTe clusters, which gets deposited in the pores of the AAO template and serves as nuclei for the growth of the nanorods. Increasing Te^{2-} concentration and supersaturation of CdTe in water gives the required kinetic force for anisotropic growth, which leads to the formation of nanorods similar to MnS [21]. The following reaction is proposed in the synthesis of CdTe nanorods on the AAO template [24].

$$4TeO_3^{2-} + 3BH_4^{-} \rightarrow 4Te^{2-} + 3BO_2^{-} + 6H_2O \quad (1)$$

$$CdCl_2 + Te^{2-} + MPA \rightarrow Cd^{-}(MPA)_x Te_y + 2Cl^{-} \quad (2)$$

$$Cd^{-}(MPA)_x Te_y \rightarrow CdTe \quad (3)$$

The template with CdTe nanorods looks brown in color after the reaction and found to exhibit nearly the same emission spectra. **Figure 4(a)** represents the PL spectra of CdTe nanorods prepared on the AAO template. The PL spectra of CdTe nanorods are broad and asymmetric, which indicated that it consists of more than one component. The CdTe nanorods do not exhibit strong quantum confinement and has an emission band around 759 nm, which is probably a band-to-band emission as the diameter of CdTe nanorods (50 - 300 nm) grown on AAO template is much larger than the diameter of the Bohr exciton in bulk CdTe (10 nm). **Figure 4(b)** shows the variations in the PL responses of the CdTe nanorods in the presence of 1 μM concentration of different divalent ions such as Pb, Hg, Mg, and Zn. In the presence of Mg^{2+} and Zn^{2+} ions, the PL intensity of the nanorods got enhanced and there was a change in the spectral features too. However, the presence of ions like Hg^{2+} and Pb^{2+} quenches the PL intensity without any change in the spectral features.

The PL quenching and enhancement of CdTe nanorods in the presence of different divalent ions can be due to the modification of surface states or the atoms and molecules located near the surface because of carrier transfer. If the carriers are transferred from the rods to the surrounding ions, the PL intensity decreases or else, if the carrier transfer is in the opposite direction, there is enhancement in PL intensity [25].

The enhancement and quenching of the photoluminescence can also be possible due to the band alignments of the respective interacting ions species with the rods [26]. The Hg^{2+} and Pb^{2+} ions activate the surface dangling bonds of CdTe and forms narrow band-gap material *i.e.* HgTe ($E_g = -0.3$ eV), PbTe ($E_g = 0.41$ eV) at the surface. It results in the opening of some non-radiative pathways due to band-alignment (**Figure 5**) between core-shell

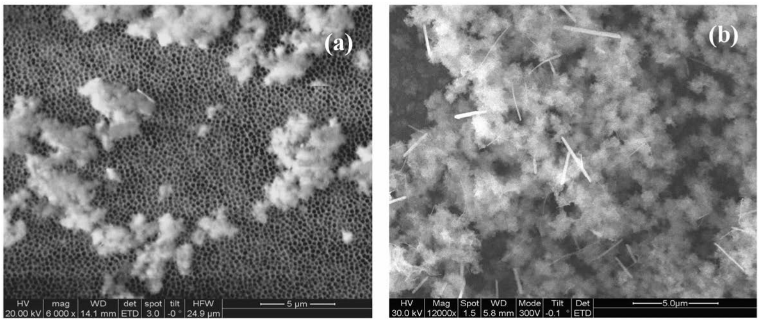

Figure 2. (a) The SEM image of the commercially purchased AAO template used for growth of CdTe nanorods; (b) highly distributed CdTe nanorods grown on the AAO template after hydrothermal procedure.

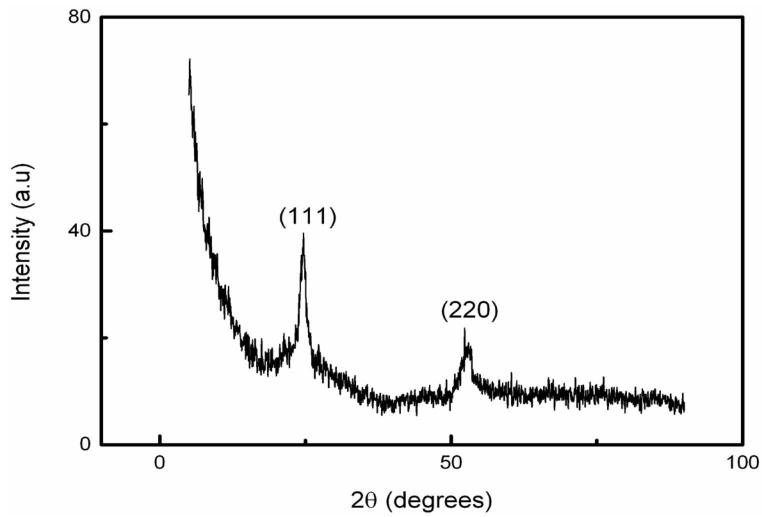

Figure 3. The XRD spectrograph of the nanorods grown on the commercial AAO template.

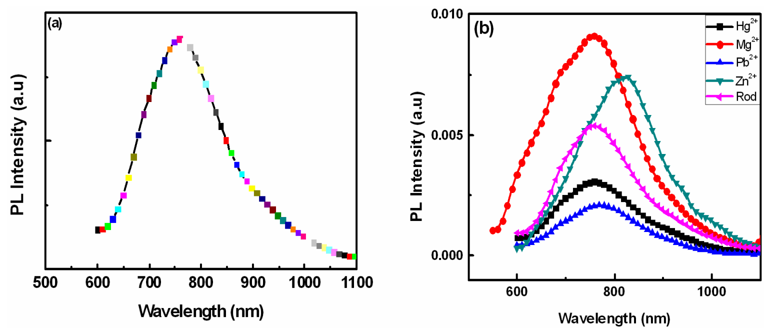

Figure 4. (a) Photoluminescence spectra of CdTe Nanorods grown on AAO template; (b) photoluminescence response of CdTe Nanorods grown on AAO inpresence of different heavy metal ions.

like (CdTe-HgTe, CdTe-PbTe) structures formed due to the presence of the respective ionic species. In this case the shell being low band gap material that results in quenching of PL in CdTe nanorods. The enhancement and red shift in the presence of Zn^{2+} and Mg^{2+} is attributed to the passivation of the surface states due to the similar core-shell structure formed with the higher band gap material as the shell structure CdTe-ZnTe (E_g = 2.26 eV), CdTe-MgTe (E_g = 3.5 eV). The resulting band-alignment is shown in Figure 5. In this case, it is expected that the excitons in CdTe nanorods are efficiently confined inside the large band gap materials (ZnTe and MgTe)

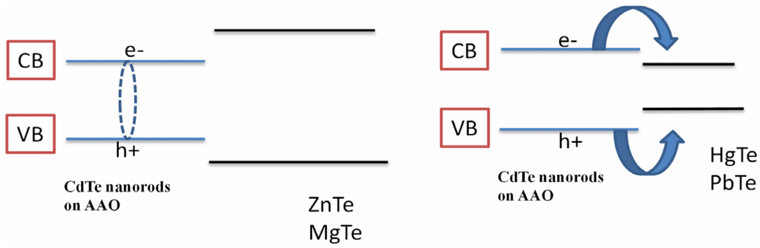

Figure 5. Energy-schemes of the photo physical processes in the presence of different metal ions.

which enhance the PL by preventing non-radiative pathways. Thus, the band alignment between core-shell like structures formed after exposing selective metal ions to the nanorods plays an important role in the luminescence mechanism that helps in understanding the detection of divalent ions here.

4. Conclusion

In summary, luminescent CdTe nanorods were grown on commercially available AAO (aluminum oxide template) via hydrothermal procedure at a relatively low temperature of 180˚C for 4 h. The structure of AAO templates, believed to participate in controlling the localization of supersaturated CdTe solution in the pores of the template and have favoured the nanorod growth. As obtained CdTe nanorods on the AAO template were used as sensitive and selective probes for the detection of hazardous metal ions like Pb^{2+}, Hg^{2+} and other microelements like Zn^{2+}, Mg^{2+}. The PL of the nanorods quenched in the presence of Hg^{2+} and Pb^{2+} ions however it got enhanced in the presence of Zn^{2+} and Mg^{2+} ions. The enhancement and quenching of PL were described on the basis of band alignments of the respective interacting ion-species. Further investigation is needed to understand the effect of different molar concentration of divalent salts and find out the detection limit.

Acknowledgements

One of the authors (Gyanan) acknowledges Prof. K. S. R. Koteswara Rao, Department of Physics, IISc for his valuable support in carrying out research work in the laboratory. Also we would like to thank Institute Nanoscience Initiative, IISc, for electron microscopy measurements.

References

[1] Aragay, G., Pino, F. and Merkoçi, A. (2012) Nanomaterials for Sensing and Destroying Pesticides. *Chemical Reviews*, **112**, 5317-5338.

[2] Huang, X.J. and Choi, Y.K. (2007) Chemical Sensors Based on Nanostructured Materials. *Sensors and Actuators B*, **122**, 659-671. http://dx.doi.org /10.1016/j.snb.2006.06.022

[3] Luo, L., Jie, J., Zhang, W., He, Z., Wang, J., Yuan, G., Zhang, W., Wu, L.C.M. and Lee, S.T. (2009) Silicon Nanowire Sensors for Hg^{2+} and Cd^{2+} Ions. *Applied Physics Letters*, **94**, 193101. http://dx.doi.org/10.1063/1.3120281

[4] Sudibya, H.G., He, Q., Zhang, H. and Chen, P. (2011) Electrical Detection of Metal Ions Using Field-Effect Transistors Based on Micropatterned Reduced Graphene Oxide Films. *ACS Nano*., **5**, 1990-1994. http://dx.doi.org/10.1021/nn103043v

[5] González, B.M., Christie, G., Davidson, C.A.B., Blyth, J. and Lowe, C.R. (2005) Divalent Metal Ion-Sensitive Holographic Sensors. *Analytica Chimica Acta*, **528**, 219-228. http://dx.doi.org/10.1016/j.aca.2004.03.029

[6] Duffus, J.H. (2002) Heavy Metal-A Meaningless Term? *Pure and Applied Chemistry*, **74**, 793-807. http://dx.doi.org/10.1351/pac200274050793

[7] Aragay, G., Pons, J. and Merkoçi, A. (2011) Recent Trends in Macro-, Micro-, and Nanomaterials-Based Tools and Strategies for Heavy-Metal Detection. *Chemical Reviews*, **111**, 3433-3458.

[8] Li., M., Gou, H.L., Al-Ogaidi., I. and Wu, N.Q. (2013) Nanostructured Sensors dor Detection of Heavy Metals: A Review. *ACS Sustainable Chemistry Engineering*, **1**, 713-723.

[9] Li, Y.D., Duan, X.F., Qian, Y.T., Yang, L., Ji, M.R. and Li, C.W. (1997) Solvothermal Co-Reduction Route to the Nanocrystalline III-V Semiconductor InAs. *Journal of the American Chemical Society*, **119**, 7869-7870. http://dx.doi.org/10.1021/ja9707670

[10] Peng, Q., Dong, Y.J., Deng, Z.X. and Li, Y.D. (2002) Selective Synthesis and Characterization of CdSe Nanorods and Fractal Nanocrystals. *Inorganic Chemistry*, **41**, 5249. http://dx.doi.org/10.1021/ic0257266

[11] Duan, X.F. and Lieber, C.M. (2000) General Synthesis of Compound Semiconductor Nanowires. *Advanced Materials*, **12**, 298-302. http://dx.doi.org/10.1002/chin.200020229

[12] Gates, B., Yin, Y.D. and Xia, Y.N. (2000) A Solution-Phase Approach to the Synthesis of Uniform Nanowires of Crystalline Selenium with Lateral Dimensions in the Range of 10-30 nm. *Journal of the American Chemical Society*, **122**, 12582. http://dx.doi.org/10.1021/ja002608d

[13] Huang, M.H., Mao, S., Feick, H., Yan, H.Q., Wu, Y.Y., Kind, H., Weber, E., Russo, R. and Yang, P.D. (2001) Room-Temperature Ultraviolet Nanowire Nanolasers. *Science*, **292**, 897. http://dx.doi.org/10.1126/science.1060367

[14] Anderson, M., Iline, A., Stietz, F. and Trager, F. (1999) Formation of Gold Nanowires through Self Assembly during Scanning Force Microscopy. *Applied Physics A*, **68**, 609.

[15] Palasantzas, G., Ilge, B., de Nijs, J. and Geerligs, L.J. (1999) Fabrication of Co/Si Nanowires by Ultrahigh-Vacuum Scanning Tunneling Microscopy on Hydrogen-Passivated Si (100) Surfaces. *Journal of Applied Physics*, **85**, 1907. http://dx.doi.org/10.1063/1.369171

[16] Iijima, S. (1991) Helical Microtubules of Graphitic Carbon. *Nature*, **56**, 354. http://dx.doi.org/10.1038/354056a0

[17] Yu, D.P., Lee, C.S., Bello, I., Sun, X.S., Tang, Y.H., Zhou, G., Bai, Z.G. and Feng, S.Q. (1998) Synthesis of Nano-scale Silicon Wires by Excimer Laser Ablation at High Temperature. *Solid State Communication*, **105**, 403. http://dx.doi.org /10.1016/S0038-1098(97)10143-0

[18] Martin, C.R. (1994) Nanomaterials: A Membrane-Based Synthetic Approach. *Science*, **266**, 1961. http://dx.doi.org/10.1126/science.266.5193.1961

[19] Yang J., Li., G.G., Peng, C., Li., C.X., Zhang, C.M., Fan., Y., Xu., Z.H., Cheng, Z.Y. and Lin, J. (2010) Homogeneous one-Dimensional Structured Tb(OH)3:Eu^{3+} Nanorods: Hydrothermal Synthesis, Energy Transfer, and Tunable Luminescence Properties. *Journal of Solid State Chemistry*, **183**, 451-457. http://dx.doi.org/10.1016/j.jssc.2009.12.005

[20] Riveros, G., Vásquez, J., Gómez, H., Makarova, T., Silva, D., Marotti, R.E. and Dalchiele, E.A. (2008) Single-Step Electrodeposition of Polycrystalline CdSe Microwire Array: Structural and Optical Properties. *Applied Physics A*, **90**, 423-430. http://dx.doi.org/10.1007/s00339-007-4318-9

[21] Zhang, C., Tao, F., Liu, G.Q., Yao, L.Z. and Cai, W.L. (2008) Hydrothermal Synthesis of Oriented MnS Nanorods on Anodized Aluminum Oxide Template. *Materials Letters*, **62**, 246-248.

[22] Xi, G.C., Wang, C., Wang, X., Qian, Y.T. and Xiao, H.Q. (2008) Te/Carbon and Se/Carbon Nanocables: Size-Controlled in Situ Hydrothermal Synthesis and Applications in Preparing Metal M/Carbon Nanocables (M = Tellurides and Selenides). *The Journal of Physical Chemistry C*, **112**, 965-971. http://dx.doi.org/10.1021/jp0764539

[23] Liang, X.R., Tan, S.S., Tang, Y.Z. and Kotov, N.A. (2004) Investigation of Transversal Conductance in Semiconductor CdTe Nanowires with and without a Coaxial Silica Shell. *Langmuir*, **20**, 1016-1020. http://dx.doi.org/10.1021/la035908s

[24] Duan, J., Song, L.X. and Zhan, J.H. (2009) One-Pot Synthesis of Highly Luminescent CdTe Quantum Dots by Microwave Irradiation Reduction and Their Hg^{2+}-Sensitive Properties. *Nano Research*, **2**, 61-68. http://dx.doi.org/10.1007/s12274-009-9004-0

[25] Pendyala, N.B. and Koteswara Rao, K.S.R. (2009) Efficient Hg and Ag Ion Detection with Luminescent PbS Quantum Dots Grown in Poly Vinyl Alcohol and Capped with Mercaptoethanol. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **339**, 43-47.

[26] Xie, H.Y., Liang, J.G., Zhang. Z,L., Liu, Y., He, Z.K. and Pang, D.W. (2004) Luminescent CdSe-ZnS Quantum Dots as Selective Cu^{2+} Probe. *Spectrochimica Acta Part A*: *Molecular and Biomolecular Spectroscopy*, **60**, 2527-2530. http://dx.doi.org/10.1016/j.saa.2003.12.039