Indian Journal of Biochemistry & Biophysics
Vol. 58, February 2021, pp. 56-61

Greener synthesis and characterization of cadmium-tellurium quantum dots using aqueous extract of waste orange peel

A Mahalakhsmi[1] & G Baskar[2,]*

[1]Department of Physics; & [2]Department of Biotechnology, St. Joseph's College of Engineering, Chennai-600 119, Tamil Nadu, India

Received 28 August 2020; *revised 29 January 2021*

Cadmium-Tellurium quantum dots are inorganic semiconductor material. In the present study, highly stable Cadmium-Tellurium (CdTe) quantum dots with good optical properties were successfully synthesized by using waste orange peel extract. Fourier-transform infrared spectroscopy (FTIR) identified the presence of hydroxyl, carboxyl and amine groups. Multifunctional X-ray Photoelectron Spectroscopy (XPS) confirmed the presence of cadmium and tellurium. The average size of the quantum dots was found to be 6nm using Transmission Electron Microscopy (TEM). The cubic zinc blende type crystalline structure of quantum dots was confirmed by X-ray powder diffraction (XRD). Thermal stability was studied using thermo-gravimetric analysis (TGA). The influence of temperature with respect to mass change of 8% was observed at 200°C. The high luminescence property exhibits at the wavelength of 502 nm were investigated using photoluminescence analysis (PL) and the blue shift is confirmed by UV-Visible spectroscopy.

Keywords: Cadmium-Tellurium, Greener Synthesis, Optical properties, Photoluminescence, Quantum dots

Today developing the materials in nano scale is the most prominent advanced technology. The uniqueness of nano scale materials have become a new challenge for various applications[1-4]. In periodic table group II and VI or group III and V semiconductors are usually luminescent semiconductor. Quantum dots (QDs) have great attention due to their superior properties such as surface to volume ratio, size-dependent optical and electronic properties caused by quantum confinement, high photo stability, controllable and narrow emission bands, high photoluminescence quantum yield, strong photo stability, high quantum yield and biocompatibility[1-11,12]. For many practical applications QDs of different sizes, shapes and compositions were studied for solar batteries, optoelectronic transistor components, biological fluorescence markers, biological and biomedical studies in past two decades[2-4,9]. Cadmium Telluride (CdTe) nanocrystal, it's an inorganic semiconductor has unique attention for energy, electronics and biomedical applications because of their emission within the whole visible range which have attracted the worldwide researches[2,8]. CdTe is the most successful photoactive material for the solar cells due to its high efficiency and low cost applications.

*Correspondence:
E-mail: basg2004@gmail.com

For the past few years biosynthesis of nanoparticles getting more and more attention. To synthesis QD, mostly natural, efficiently biological system is employed. Usually in the biosynthesis of CdTe, bacteria, yeast, fungi is used[4,8]. This highlights that Plant extract mediated CdTeQDs can be biocompatible, less toxic and cost effective. Orange is natural chemical factory. It is a natural non hybrid citrus fruit. Orange fruit is an energy source that brings nutrition and refreshment; break the skin of an orange, its sweet-tangy scent fills the air, but lot of peels will be thrown in the trash. Discarded Orange peel waste is left for biodegradation and end up in pollution. Orange peels are known for air freshening, effective mosquito repellent, but second life usage of orange peels into value added products by cost effective approaches needs serious concern. Normally biological thiol and glutathione are used as reducing and capping agent, which is so expensive method[8,10]. In the present work waste orange peel extract was used as citrus source for the synthesis of CdTeQDs which makes the whole process is environmentally friendly.

Materials and Methods

Materials

Cadmium chloride and potassium telluride were purchased from LOBA Chemie Pvt. Ltd., Mumbai, India. The waste are orange peel was collected from

local market in Thanjavur, Tamil Nadu, India. All reagents were in analytical grade and used without further purification.

Extraction of orange juice

Orange peel was collected from juice stall in Chennai, India. Orange peel was washed with deionised water to remove dust adhered. 100 g of orange peel was cut in to small pieces, crushed by a blender and mixed with 200 mL of double distilled water in a beaker. The mixture was boiled for 10 min at 80°C. The solution was cooled to room temperature and filtered using Buchner funnel[9].

Green synthesis of cadmium tellurium quantum dots

Cadmium chloride solution (16 mL, 25 mM) and aqueous orange peel extract (36. 4 mL) were mixed in flask and mixed vigorously and allowed to settle at room temperature for 10 min. Potassium telluride solution (14. 3 mL, 7 mM) was added slowly to cadmium chloride-orange peel extract solution using micropipette. The final ratio of cadmium chloride:potassium telluride in the mixture was maintained at 4:1. The reaction flask was placed in a 90°C hot water bath to initiate nucleation. Synthesized QDs was precipitated with 2 volume of ethanol and separated by centrifugation at 15000 rpm for 30 min. The separated QDs was washed with deionised water for several times, and CdTeQDs powder was obtained by drying in oven for 24 h[10].

Characterization of cadmium tellurium quantum dots

Optical properties of CdTeQDs were measured using UV-Visible spectrophotometer (Systronics, India, Double Beam spectrophotometer-2202. The crystal structure was of the synthesized QDs was examined by powder X-ray Diffraction analysis (XRD). The morphology of resultant CdTeQDs was examined by the High Resolution Transmission Electron Microscopy (HR-TEM, JEOL). For the binding characteristics and functional group were analysed using Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer System). X-ray photoelectron spectroscopy (XPS) used to study the oxidation states of solids. XPS were recorded by Multilab 2000 Base system with Twin Anode Mg/Al (300/400 W) X-ray, Auger and ISS attachments. Thermal stability was determined by thermogravimetric analysis (TGA). TGA was carried out by NETZSCHSTA 449 F3 Jupiter at the temperature range of 25 to 1400°C.

Results and discussion

Structural characterization of cadmium tellurium quantum dots using x-ray diffraction analysis

The internal atomic structure of crystal system can be clearly explained by XRD. In CdTeQDs sample the prominent peaks are at 23, 27, 38 correspond to the plane indexed as (111), (200), (220) thus the sample has cubic zinc blende structure from (Fig. 1). It has Face centred cubic lattice structure with respect to the reference JCPDS card: 75-2083 respectively. By using Debye –Scherer's formula, $D=k\lambda/\beta\cos\theta$, where λ is the wavelength of the X-ray used, β is the full width at half maximum of the XRD peak and θ is the Bragg angle, the average size of the CdTeQDS is about 3-7 nm and the lattice spacing 'a' is calculated by $a^2=(h^2+k^2+l^2)d^2$, a is approximately equal to 6.463 A° which agree with JCPDS card: 75-2083 where a =6. 4 A°. Thus the position and relative intensities of diffraction peaks matched well with cubic CdTe (JCPDS card: 75-2083). Thus XRD Pattern clearly shows that CdTe quantum dots were synthesised by green synthesis are crystalline in nature[13,14].

Surface morphology of synthesized cadmium tellurium quantum dots using high resolution transmission electron microscopic analysis

TEM images shows synthesized CdTeQDs are homogeneously distributed in the size range of 5 to 7 nm. Thus average size of mono disperse nanoparticles of 5-7 nm indicating a highly crystalline structure of CdTeQDs by the (Fig. 2A & B). Selected area electron diffraction (SAED) pattern (Fig. 3) clearly shows clear diffraction ring of Face Centred Cubic (FCC) structure. Well resolved lattice fringes in (Fig. 3) clearly confirmed the nanoparticles had good crystallinity, Thus

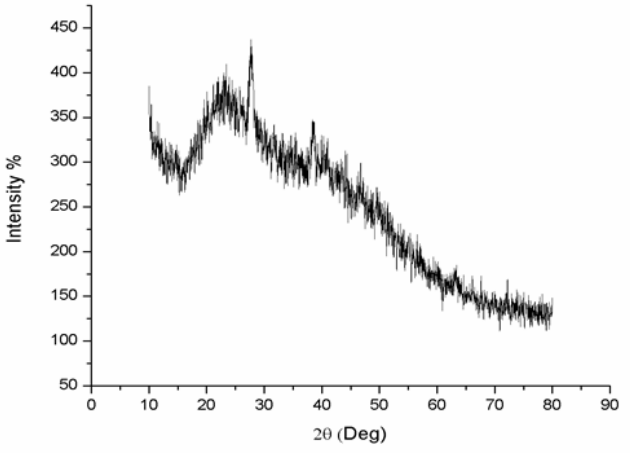

Fig. 1 — XRD image of synthesized cadmium tellurium quantum dots

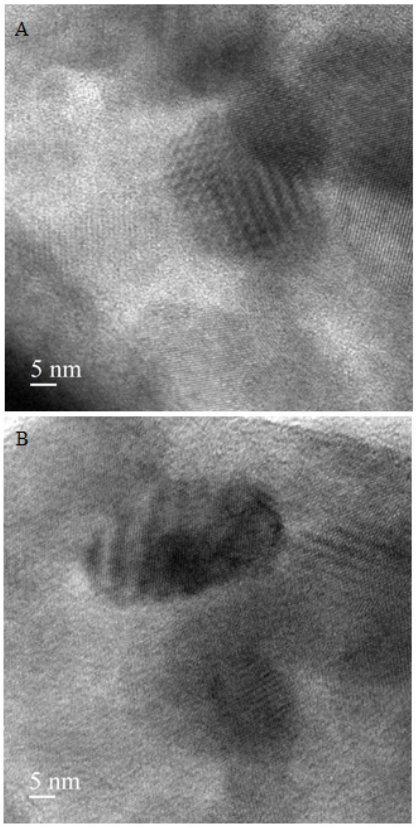

Fig. 2 — TEM image synthesized cadmium tellurium quantum dots (A) and (B) are different view at 5 nm

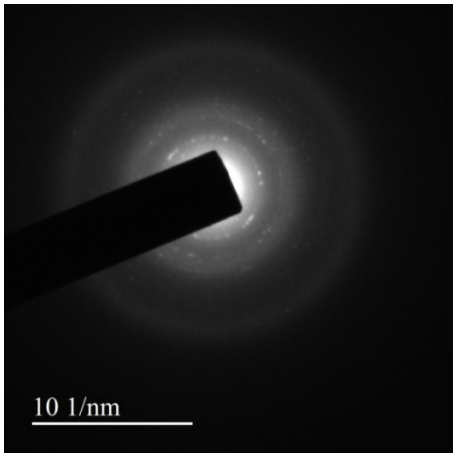

Fig. 3 — SAED pattern of cadmium tellurium quantum dots

in the greener synthesized of CdTeQDs are homogenous in shape and highly stable[14,15].

FTIR analysis of synthesized cadmium tellurium quantum dots

FTIR spectrum is used to characterize the surface chemistry of green synthesis CdTeQDs and various functional groups were identified from multiple

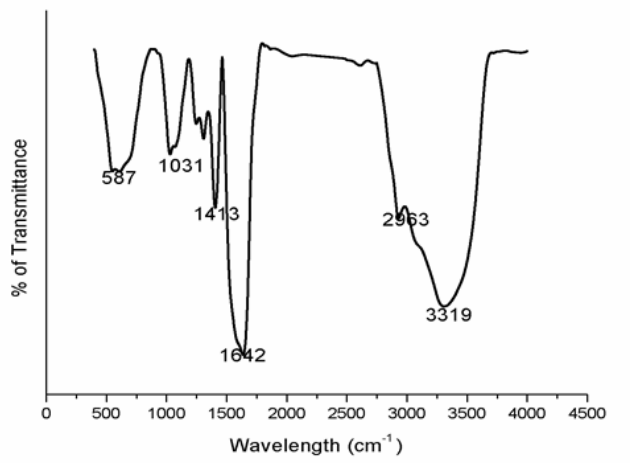

Fig. 4 — FT-IR spectrum of synthesized cadmium tellurium quantum dots

absorption peaks in (Fig. 4). The broad peak 3327 cm^{-1} was due to the –OH stretching of –COOH group. The absorption peak at 2933 cm^{-1} due to stretching vibration of CH_2,the strong absorption peak at 1641 cm^{-1} is due to the C=C group. Moreover the strong absorption peaks at 1396, 1020 and 553 cm^{-1} confirmed the formation of O-H and C-O groups and it can be used in bioimaging[12,13].

XPS Studies of synthesized cadmium tellurium quantum dots

Elemental composition of the synthesized cadmium tellurium quantum dots was recorded by XPS core level spectra. Figure 5A shows the overview spectra of CdTeQD. We focus to confirm the presence of cadmium and tellurium species in CdTeQDs. Cd 4d is near to the valence band thus it was less reliable to analyze. The binding energy of Cd ions were at 410, 403 and 398 eV which is similar to the core level binding energy of Cd as shown in (Fig. 5B). Similarly the peaks of Te 3d were at 572, and 582 eV was noted with characteristics metallic Te as shown in the (Fig. 5C). Thus XPS spectra confirm the presence of cadmium and tellurium in the greener synthesized CdTeQDs. This result is in good agreement with the literature[16].

Optical property of synthesized cadmium tellurium quantum dots

The optical property of QDs were characterised by UV-*vis* spectroscopy. Absorption spectrum was taken in the range of 200-800 nm shown in the (Fig. 6). In the CdTeQD sample the maximum strong optical absorption peak is at the wavelength of 450 nm. This is corresponds to approximately 2.75 eV band gap energy. This implies that CdTeQDs synthesised using

waste orange peel is approximately 1.25 eV higher than the bulk CdTeQD (1.5 eV), as the size is reduced the band gap energy increases. Due to quantum confinement, the band levels get quantized[14,17].

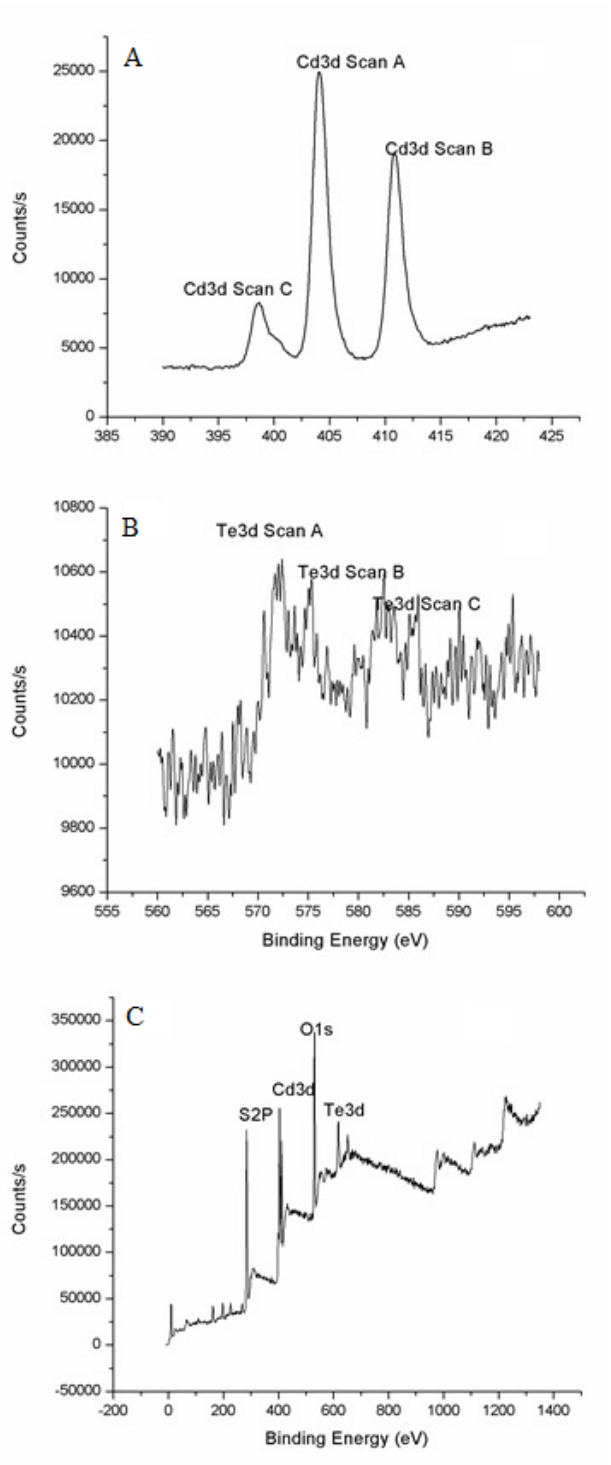

Fig. 5 — XPS spectrum for (A) Cd 3d; (B) Te 3d; and (C) CdTe quantum dots

Photoluminesence analysis of synthesized cadmium tellurium quantum dots

Photoluminesence spectrum of CdTeQD is shown in the (Fig. 7). The luminescent spectra of orange sample indicated maximum emission at 502 nm. Even though there was no much difference in the physical property of CdTeQD by green synthesis but there was a change in electro-optical property, which was observed. Figure 7 shows the photoluminescence result of CdTeQD by the green synthesis with orange peel extract. The graph shows the blue shift of maximum emission of wavelength at 502 nm. The results are in good agreement with CdTeQD synthesised by chemical and biological methods[16,17].

Thermogravimetric analysis of synthesized cadmium tellurium quantum dots

TGA was performed to the green synthesized CdTeQDs, there was a weight loss of approximately

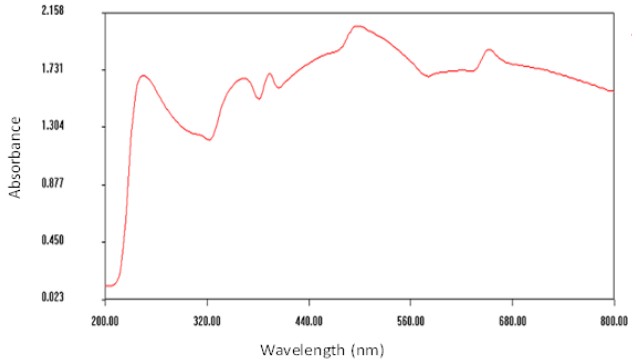

Fig. 6 — UV Spectrum of synthesized cadmium tellurium quantum dots

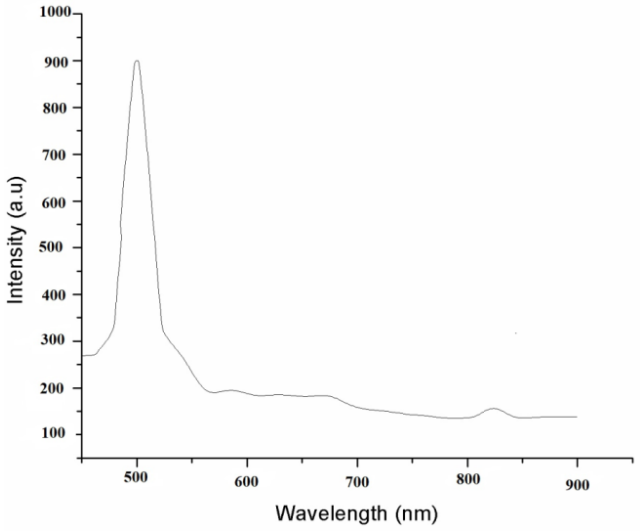

Fig. 7 — Photoluminescence analysis of synthesized cadmium tellurium quantum dots

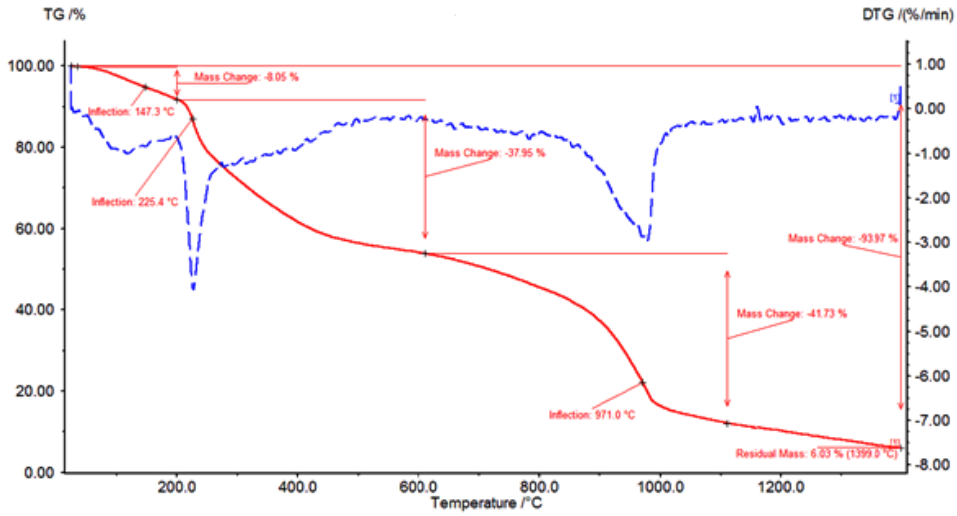

Fig 8 — Thermogravimetric analysis of synthesized cadmium tellurium quantum dots

8% against the temperature range of 200°C, this weight loss might be due to release of water vapour and bio molecules in the surface of QDs as shown in (Fig. 8). CdTeQDs are stabilized over a temperature range of 880-1200°C with 41% mass of QDs remain as it is[13].

Conclusion

CdTeQDs have been synthesised by greener method using aqueous extract of waste orange peel. The synthesised CdTeQD showed good crystalline structure with the average particle size of 5-7nm. The energy gap CdTeQD was found as 2. 75 eV due to quantum confinement. The O-H and C-O functional groups were found on the surface of CdTeQDs. A good stability CdTeQDs was confirmed by thermo gravimetric analysis. Experimental results suggest that the synthesised CdTeQDs were highly stable and homogeneous shaped. Thus the CdTeQDs synthesized using aqueous extract of orange peel can easily attach with biomolecules and can be used in biological applications like bioimaging and *in vitro* studies.

Conflict of interest

All authors declare no conflict of interest.

References

1 Stanisavljevic M, Krizkova S, Vaculovicova M, Kizek R & Adam V, Quantum dots-fluorescence resonance energy transfer-based nanosensors and their application. *Biosens Bioelectron*, 74 (2015) 562.

2 Bao H, Lu Z, Cui X, Qiao Y, Guo J, Anderson JM & Li CM, Extracellular microbial synthesis of biocompatible CdTe quantum dots. *Acta Biomater*, 6 (2010) 3534.

3 Chen N, He Y, Su S, Li X, Huang Q, Wang H, Zhang X, Tai R & Fan X, The cytotoxicity of cadmium-based quantum dots. *Biomater*, 33(2012) 1238.

4 Chena G, Yia B, Zenga G, Niua Q, Yana M, Chena A, Dua J, Huanga J & Zhanga Q, Facile green extracellular biosynthesis of CdS quantum dots by white rot fungus *Phanerochaete chrysosporium*. *Colloids Surf B Biointerfaces*, 117 (2014) 199.

5 Liu J, Shi Z, Yu Y, Yang R & Zuo Z, Water-soluble multicolored fluorescent CdTe quantum dots: Synthesis and application for fingerprint developing. *J Colloid Interface Sci*, 342 (2010) 278.

6 Kulkarnia P, Rondiyaa S, Pawbakea A, Waykara R, Jadhavara A, Jadkara V, Bhordea A, Datec A, Pathand A & Jadkard S, Structural and optical properties of CdTe thin films deposited using RF magnetron sputtering. *EnergProcedia,* 110 (2017) 188.

7 Morales-Saavedraa OG, Gutiérrez-Lazosb CD, Ortega-Lópezc M & Rodriguez-Rosalesaa AA, Original Fabrication and photophysical studies of CdTe quantum-dots dispersed in SiO_2sonogel optical-glasses. *J Appl Res Technol*, 13 (2015) 566.

8 Shivaji K, Mani S, Ponmurugan P, De Castro CS, Davies ML, Balasubramanian MG & Pitchaimuthu S, Green synthesis-derived CdS quantum dots using tea leaf extract: Antimicrobial, bioimaging, and therapeutic applications in lung cancer cells. *ACS Appl Nano Mater*, 1 (2018) 1683.

9 Wansapura PT, Díaz-Vásquez WA, Vásquez CC, Pérez-Donoso JM & Chasteen TG, Synthesis of CdTe quantum dots and study of their photostability and thermal-stability. *J Appl Biomater Funct Mater*, 13 (2015) 248.

10 Bichpuria P & Oudhia A, Effective size control through solvents in microwave aided synthesis of GSH-CdTe quantum dots. *J Appl Phy*, 8 (2016) 1.

11 Samadi-Maybodi A & Sadeghi-Maleki MR, *In situ* synthesis of high stable CdS quantum dots and their application for photocatalytic degradation of dyes. *Spectrochim Acta A Mol Biomol Spectrosc*, 152 (2016) 156.

12 Le W, Zheng-zhong L, Hui-ping Z, Ai-hong P, Xiao-mei C & Zhiyong H, Rapid detection of malachite green in fish

based on CdTe quantum dots coated with molecularly imprinted silica. *Sens Actuators B Chem*, 239 (2017) 69.

13 Liu F, Li S, Huo R & Shao N, Core–shell structured CdTe/CdS@SiO_2@CdTe@SiO_2composite fluorescent spheres: Synthesis and application for Cd^{2+} detection. *Luminescence*, 32 (2017)723.

14 Baruah JM & Narayan J, Development of greener methodology for the synthesis of CdSe quantum dots and characterization of their thin films. *J Opt*, 47 (2017) 202.

15 Kumar GN, Pandey SD, Mallick, Ghosh SK, Pramanik P & Ghosh AS Kumar GN, Pandey SD, Mallick, Ghosh SK, Pramanik P & Ghosh AS, Thiol stabilized copper nanoparticles exert antimicrobial properties by preventing cell division in *Escherichia coli*. *Indian J Biochem Biophys*, 57 (2020) 151.

16 Shen M, Jia W, You Y, Hu Y, Li F, Tian S, Li J, Jin Y & Han D, Luminescent properties of CdTe quantum dots synthesized using 3-mercaptopropionic acid reduction of tellurium dioxide directly. *Nanoscale Res Lett*, 8 (2013) 253.

17 Shamsipur M, Farzin L, Tabrizi MA & Shanehsaz M, CdTe amplification nanoplatforms capped with thioglycolic acid for electrochemical aptasensing of ultra-traces of ATP. *Mater Sci Eng C Mater Biol Appl*, 69 (2016) 1354.