



Research Article

TGA-capped CdTe quantum dots: synthesis, characterization and stabilization in polymer matrix by using a water dispersible polymer

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Quantum dots, water dispersible polymers, synthesis, photoluminescence spectroscopy

Thioglycolic acid (TGA) coated CdTe quantum dots (QDs) in several particle sizes having red and blue colors were stabilized in solid phase by a water dispersible polymer (wdp). Absorption and fluorescence spectra showed that the as-prepared CdTe QDs had good photoluminescence property. A kind of self-assembly aggregation of the prepared CdTe-wdp nanoparticles was observed as the first time in solid phase. The QDs were characterized by Fourier transform infrared spectroscopy (FTIR), Atomic force microscopy (AFM), Scanning electron microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDS), Steady state fluorescence spectroscopy and fluorescent imaging using BAB Image Analysis System®, Transmission-electron microscopy (TEM) and X-ray powder diffraction (XRD).

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TGA-kaplı CdTe Kuantum tanecikleri: Sentez, karakterizasyon ve suda dağılabilen bir polimer kullanımı ile stabilizasyonları

ÖZET**Keywords:**

Kuantum noktalar, suda dağılabilir polimerler, sentez, fotoluminesans spektroskopisi

Kırmızı ve mavi renklere sahip olan çeşitli parçacık boyutlarında tiyoglikolik asit (TGA) kaplanmış CdTe kuantum noktaları (QD'ler), katı fazda suda dağılıbilir bir polimer (wdp) ile stabilize edildi. Absorpsiyon ve floresan spektrumları, hazırlanan CdTe QD'lerin iyi bir fotoluminesans özelliğine sahip olduğunu gösterdi. Hazırlanan CdTe-wdp nanopartiküllerinin bir tür kendiliğinden toplanma agregasyonu, katı fazda ilk kez gözlenmiştir. QD'ler, Fourier transform infrared spektroskopisi (FTIR), Atomik kuvvet mikroskopisi (AFM), Taramalı elektron mikroskobu (SEM), Enerji Dağılımlı X-ışını spektroskopisi (EDS), Sabit durum flüoresans spektroskopisi ve BAB Görüntü Analiz Sistemi® kullanılarak floresan görüntüleme, Transmisyon-elektron mikroskobu (TEM) ve X-ışını toz kırınımı (XRD) ile karakterize edildi.

1. Introduction

CdTe quantum dots (QDs) are one of the most promising and interesting developments in the rapid growing world of nanotechnology. CdTe QDs shows narrow and tunable emission spectrum, photo stability, high luminescence quantum efficiency and extended absorption spectrum over conventional fluorescent organic dyes. In last few years, CdTe QDs have been applied for quantitative determination of ionic species such as Ag[I], Pb[II], Cu[II], Zn[II] and Cd[II], Hg[II], and As[III] [1-8]. Several analytical methods applying CdTe quantum dots have been used to investigate some important molecules like dopamine, ATP, Folic acid, L-Cysteine, glucose, L-Proline, melamine, Prion protein, S-fenvalerate, DNA, Vitamin B₆ and Vitamin B₁₂ [9-18].

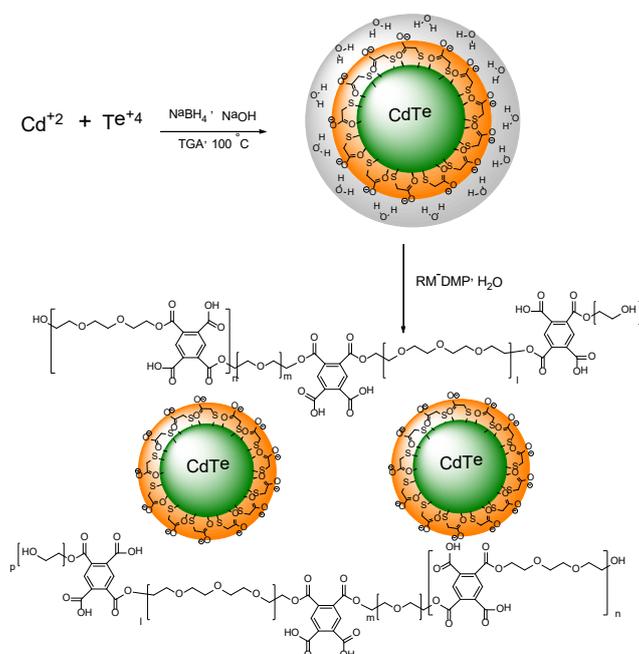
Recently, certain device applications of CdTe quantum dots have been reported as an excellent choice for proton sensor, delta-methrin sensor, sensing, latent fingerprint development and solar cells [19-23]. CdTe quantum dots also have attracted much attention in different cancer cells imaging and therapy [24-28].

Meanwhile, in spite of having a variety of applications, QDs can become a source of the toxic compounds containing in their core [29]. The toxicity of CdTe QDs appears to be linked to the leaching of toxic heavy metals from the colloid form. It could also be derive from intrinsic properties of the size and surface chemistry of CdTe quantum dots (semi-conductors), which make them efficient energy donors as well [30]. They could transfer energy to nearby oxygen molecules and lead to the formation of reactive oxygen species, which drive to cell inflammation, damage and death. Some studies about cytotoxicity of CdTe quantum dots have been reported recently [31-34]. These properties of the CdTe QDs sometimes useful but at the same time, the potential toxicity of CdTe QDs on nerve-racking is being argued seriously. The preparation of QDs with low toxicity and satisfactory luminescence properties is thus currently one of the most challenging objectives in the field. The polymer coating on the QDs surface can effectively reduce the potential toxicity, enhanced their bio comp ability, stability and stimulated the endocytosis of the nanoparticles [35-37].

In general, surface functionalization is the key to fabricate QDs-based nanoparticles. Applying surface modification affords not only the excellent stability of QDs but also the desired surface binding sites and protect from toxicity. Multilayers of polystyrene nano spheres coated with CdTe QDs/polyelectrolyte to construct bio-functional QDs-labeled nano spheres and the stable colloidal CdTe/polystyrene composite nano spheres have been reported recently

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Scheme 1. Preparation of thiolglycolic acid functionalized-CdTe-water dispersed polymer containing nano-composites.

[38, 39]. Naturally polymer chitosan based film (QDs-Chitosan derivatives) found to be useful for tracking the cells and intercellular process through bio-signaling [40] and also an improvement of fluorescent intensity and photo stability of ordered-CdTe-polyamido amine (PAMAM) nano composites have been observed [35].

In this study, we report a simple method to stabilize CdTe quantum dots by a water dispersible polymer (wdp) in the both solution and solid phases in different particle sizes having different colors (red and blue) and sharp fluorescence intensities. In one of the closest application, the stretch biopolymers such as DNA and/or DNA chains have been used to decorate with Nanoparticles [41]. Similarly, our research suggests that the TGA-CdTe-wdp nano composite material might be a potential candidate for the biomedical/analytical applications having with the interesting ion-dipole interaction in their nanomaterial structure.

2. Experimental

2.1. Materials

All reagents and solvents obtained from commercial suppliers were of reagent grade quality. Industrial grade RM-DMP water dispersible polymer purchased from DyStar Colors Distributions GmbH, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and TeO_2 were purchased from E. Merck, NaBH_4 was purchased from Aldrich and TGA was purchased from Merck Schuchardt OHG, as well. Regularly distilled water was used in the experiments and the whole procedure was performed under open-air condition.

2.2. Synthesis

2.2.1. Synthesis of TGA-capped CdTe QDs

TGA-capped CdTe QDs were prepared according to the derived procedure from the literature [42]. Typically, 0.4027 g (2 mmol) $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ was dissolved in 100 mL of deionized water in a 250 mL three-neck flask, and 0.2781 μL (4 mmol) thiolglycolic acid was added while stirring. The solution was adjusted to pH 10.0 with 1.0 mol.L⁻¹ NaOH solution. After 5 minutes 0.1011 g NaBH_4 and 0.0168 g (0.1 mmol) TeO_2 were added successively into the above solution. The molar ratio of $\text{Cd}^{2+}/\text{Te}^{2-}/\text{TGA}$ was fixed to 1:0.05:2. The solution was then refluxed at 100 °C for different time to control the size of the CdTe QDs. The particle sizes of the CdTe QDs increase with the reflux period. Three different particles sized CdTe QDs were prepared by refluxing the above solution for 18h, 8h and 4h, respectively.

2.2.2. Synthesis of TGA-CdTe-wdp composites

For the synthesis of water dispersible polymer (wdp) stabilized TGA capped CdTe QDs composites, to a solution of 2 g of RM-DMP (wdp) in 20 mL water was added 20 mL of previously prepared CdTe QDs solution. The resulted mixture was stirred for 1h at room temperature and divided into two. One part was kept for the solution studies and the other part containing the prepared TGA capped CdTe QDs-wdp composites were precipitated by adding methanol (10 mL) and sufficient amount of chloroform drop wise. The precipitate was collected via centrifugation and dried under vacuum.

2.3. Characterization

Infrared spectra were recorded on a Perkin Elmer FT-IR spectrophotometer equipped with Perkin Elmer UATR-TWO diamond ATR and corrected by applying the ATR-correction function of Perkin Elmer Spectrum software. Electronic spectra were recorded on a Shimadzu UV-2600 spectrophotometer using a 1 cm quartz cell for solution and electronic spectra of solid samples were recorded by using the beam attached with the apparatus. Hitachi F-2710 fluorescence spectrophotometer was used to record the fluorescence spectra in solution and solid phases. The surface morphologies of the composites were observed with a scanning electron microscopy (SEM), JEOL, JSM 6060LV. The chemical composition of the prepared materials were determined by an energy disperse X-ray spectrometer (EDS) attached to the SEM. Morphologies of the composites were also investigated using a semi contact mode NTEGRA Aura atomic force microscopy (AFM) instrument (NT-MDT Co.), fluorescent imaging by BAB image analyzing system microscope, JEM3010 TEM instrument for tunneling electron microscopy and XRD pattern were derived using a Rigaku D/MAX series pc 2200 diffractometer with Cu K α 1 radiation ($\lambda = 1.54059 \text{ \AA}$).

3. Results and Discussion

The preparation rote of the TGA-capped CdTe QDs and its polymer stabilized nano composite, TGA capped CdTe QDs-wdp, have been shown at scheme 1. TGA acts as the ligand to form CdTe QDs combining via thio group of TGA. A kind of ion-dipole interaction between TGA surrounded QDs and wdp causes to stabilize the nanoparticles in the polymer matrices both in solution and solute phases.

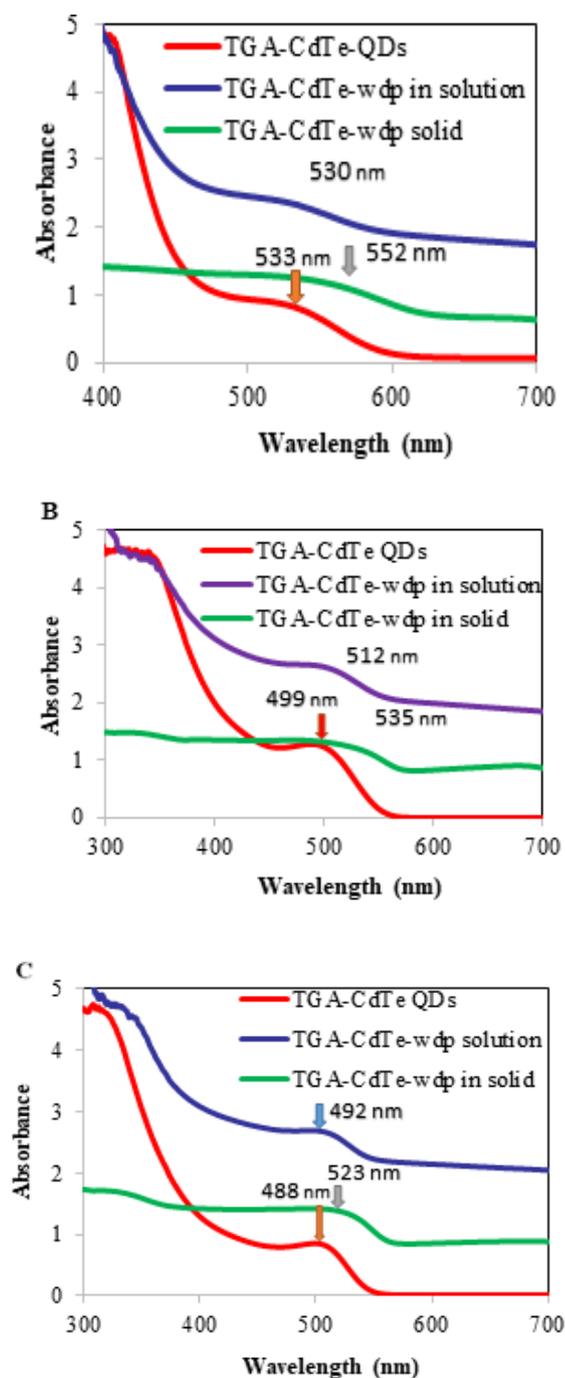


Fig. 1. UV-vis absorption spectra of TGA-coated CdTe QDs and TGA-coated CdTe QDs with wdp for nanoparticles with refluxing time (A) 18h, (B) 8h and (C) 4h at pH 10.0.

3.1. UV-Vis spectroscopy

The UV-Vis absorption spectra of as prepared TGA-CdTe QDs and TGA-CdTe-wdp composites are shown in Figure 1. A red shift in absorption spectrum of TGA-CdTe is observed with the increase in the reaction time shown as in Figure 1. Based on the above UV-Vis absorption spectra, the particle sizes of the TGA-QDs were calculated as 1.98 nm ($\lambda_{\max} = 488$ nm), 2.32 nm ($\lambda_{\max} = 499$ nm) and 3.03 nm ($\lambda_{\max} = 533$ nm) by using the following equation depending on the reflux time 4h, 8h, and 18h respectively.

$$D = (9.8127 \times 10^{-7}) \lambda^3 - (1.7147 \times 10^{-3}) \lambda^2 + 1.0064 \lambda - 194.84$$

Where D (nm) is the diameter of a given QD and λ (nm) is the wavelength of the first excitonic absorption peak of the UV-Vis absorption spectrum [43]. The diameters of the QDs in the polymer matrices in solution and solute phases were also determined by

considering the absorption bands at 492 nm and 523 nm for 4h reaction period, 512 nm and 535 nm for 8h reaction period, 530 nm and 552 nm for 18h reaction period, respectively (Table 1.). From the obtained results it is obviously seen that, the size of the nanoparticles increases gradually in polymer matrices when they transfer from solution to solute phase.

3.2. Photoluminescence (PL) spectroscopy

The photoluminescence spectra of the prepared TGA-CdTe QDs and their wdp composites in solution and solid phases are shown in Figure 2. It can be seen that the line width (full width at half maximum) values of the fluorescence spectrum are narrow (in the range of 10-11 nm, 5-6 nm and 5-6 nm wideness). Figure 2, which reveals that the prepared CdTe QDs and CdTe-wdp composites are nearly homogeneous in their corresponding phases. For TGA-QDs and TGA-QDs-wdp, emission maximums located close to their absorptions indicated the emission rose from the direct recombination between conduction and valence band charge carriers [44]. The fluorescence colors of the corresponding TGA-CdTe QDs are bright and change from orange to yellowish green, yellow to green and reddish to shiny reddish under the visible light with different wave length, respectively. This refers to the particle size increment with the increasing of the reflux time, as well [42].

We observed an increase in separation of emission and excitation wavelength when TGA-CdTe QDs mixed with wdp in solution and further more separation when they isolated as solids. Since QDs are quantum confined "boxes" for electrons, when the size or shape of the "box" changes, the confined wavelength and emission wavelength can also change [45]. Thus, if a spherical QDs becomes compressed (ovoid) near another surface by binding or any kind of physical deformation of the QDs even a nanometer or less, it could dramatically influence the emission wavelength. We also believe that the interaction of wdp with the TGA-CdTe QDs made the surface of the particles changed, which induced the increase and shift of emission and excitation wavelength separation. The wdp made the particle size of TGA-CdTe QDs more uniform, increased the stability and decreased aggregation of TGA-CdTe nanoparticles.

Table 1. Calculated diameter (nm) of TGA-CdTe and TGA-CdTe-wdp in solution and solute phases

Synthesis time	TGA-CdTe	TGA-CdTe-wdp in solution phase	TGA-CdTe-wdp in solute phase
4h	0,963	2,701	1,372
	(488 nm)	(492 nm)	(523 nm)
8h	1,243	2,546	1,176
	(499 nm)	(512 nm)	(535 nm)
18h	0,318	2,44	1,018
	(533 nm)	(530 nm)	(552 nm)

*Maximum absorpsiton vs wavelength (nm) of TGA-CdTe and TGA-CdTe-wdp in solution and solute phases.

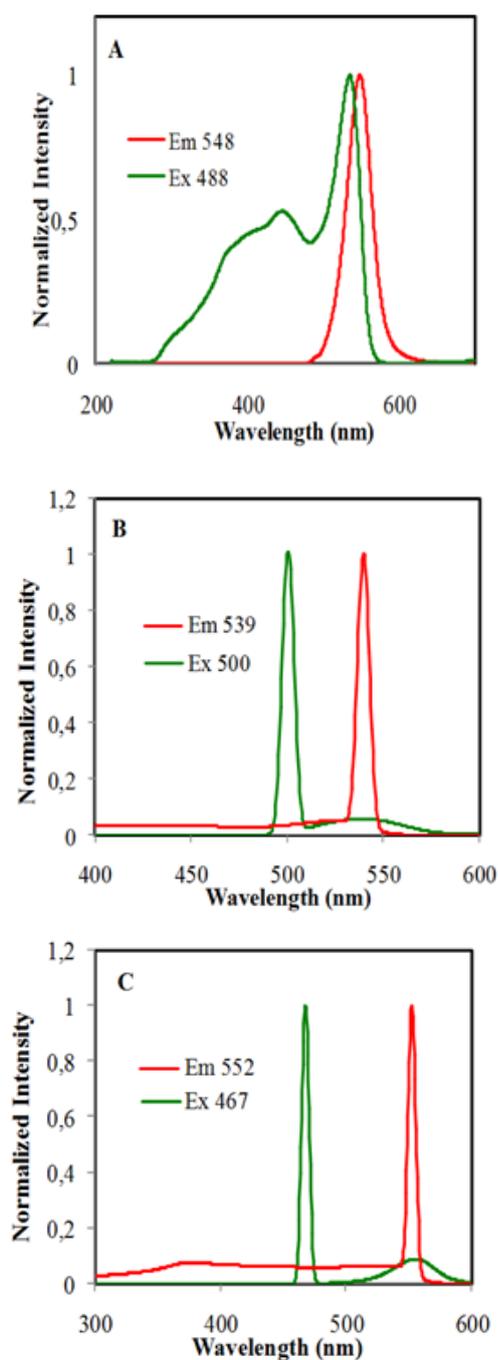


Fig. 2. Photoluminescence spectra of, (A) TGA-coated CdTe QDs, (B) TGA-coated CdTe QDs with wdp in aqueous solution and (C) TGA-CdTe-wdp as solid.

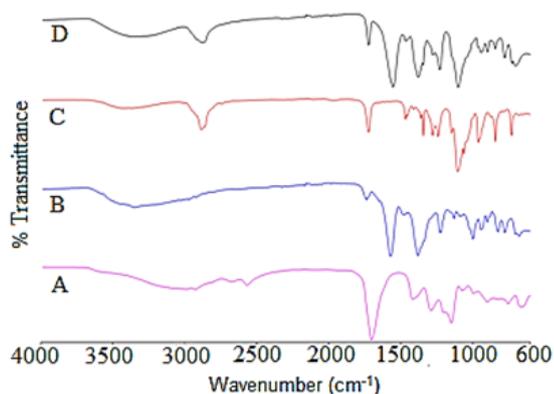


Fig. 3. FTIR spectra of (A) Thioglycolic acid, (B) TGA-CdTe QDs, (C) wdp, and (D) TGA-CdTe QDs-wdp.

3.3. Fourier transform infrared spectroscopy (FTIR)

The FTIR absorption spectra of thioglycolic acid, TGA-CdTe QDs, wdp, and TGA-CdTe QDs-wdp are depicted in Figure 3. The FTIR spectrum of TGA has a characteristic absorption band at about 2570 cm^{-1} , which belongs to $-\text{SH}$ stretching vibration. This absorption band disappeared and a significant shift in the asymmetric stretching vibration of the carboxyl group

($\nu_{\text{C=O}}=1702$ to $\nu_{\text{COO}^-}^{\text{as}}=1568$ cm^{-1} and $\nu_{\text{COO}^-}^{\text{s}}=1381$ cm^{-1}) was also observed in the TGA capped CdTe QDs. The differences between the FTIR spectra indicate that the formation of the complexes via cadmium ions with $-\text{SH}$ groups of TGAs contribute to the passivation of the surface of CdTe nanoparticles and inhibit the agglomeration of these small particles in water habitat. Furthermore, after mixing with wdp which behaves as bi-dentate ligand, the FTIR spectra of the sample change significantly.

In the FTIR spectrum of bare polymer (Figure 3C), the peak at 3400 cm^{-1} belongs to the free $-\text{OH}$ vibration of the carboxylic groups of the polymer chain shift to 3342 cm^{-1} and become broader. The peak at 1100 cm^{-1} also shifts to 1130 cm^{-1} . These evidences indicated that some kind of ion-dipole interactions occur between carboxylate groups of TGA and carboxylic hydrogen of polymer chain e.g. $\text{COO}^- \dots \text{HOOC}$ that might be the driving force to facilitate the combination of QDs with wdp.

3.4. Morphology Study

3.4.1. Atomic force Microscopy (AFM)

Figure 4 shows the AFM micrographs of the TGA-CdTe, TGA-CdTe-wdp QDs and self-assembling of TGA-CdTe-wdp QDs. The images confirm the formation of small agglomerated nanoparticles. For the TGA-CdTe QDs, the formed nanoparticles are random (Figure 4A) and become ordered when self-assembled with wdp (Figure 4B and C). They are observed both isolated particles and cross-linked chains structure. However, upon treatment of the TGA-CdTe QDs with wdp, much brighter nanoparticles were observed suggesting that the wdp is susceptible to forming composites with the TGA-CdTe QDs and enhancing the aggregation. The combination of the thioglycolic acid capped QDs with the applied polymer can be proposed by the ionic interaction of the species. This is the reason for the extra stability of the prepared nanoparticles.

3.4.2. Scanning electron microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS)

Topography dependent information of the surfaces of the prepared samples was obtained by this method. Typical SEM and EDS spectra depicting TGA-CdTe-wdp QDs were shown in Figure 5. From the SEM results, the surfaces do not contain any tellurium for all the composites and nano-aggregate formation was observed as expected. For larger nanoparticles containing QDs were found to contain higher Cd and Te mass ratio which is consistent with previous reported work [46]. The EDS spectra gave the information for all the expected elements in the prepared composites (except hydrogen as for instruments detection limit of elements) and are shown in Table 2. The EDS spectra of the prepared nano composites are depicted in Figure 5 inset.

Table 2. Mass ratio (% - norm.) of the elements in QDs

	Cd	Te	S	O	C
Sample-A	22.13	2.17	12.45	36.07	27.17
Sample-B	7.47	0.56	6.18	48.57	37.22
Sample-C	5.87	0.04	3.99	54.08	36.01

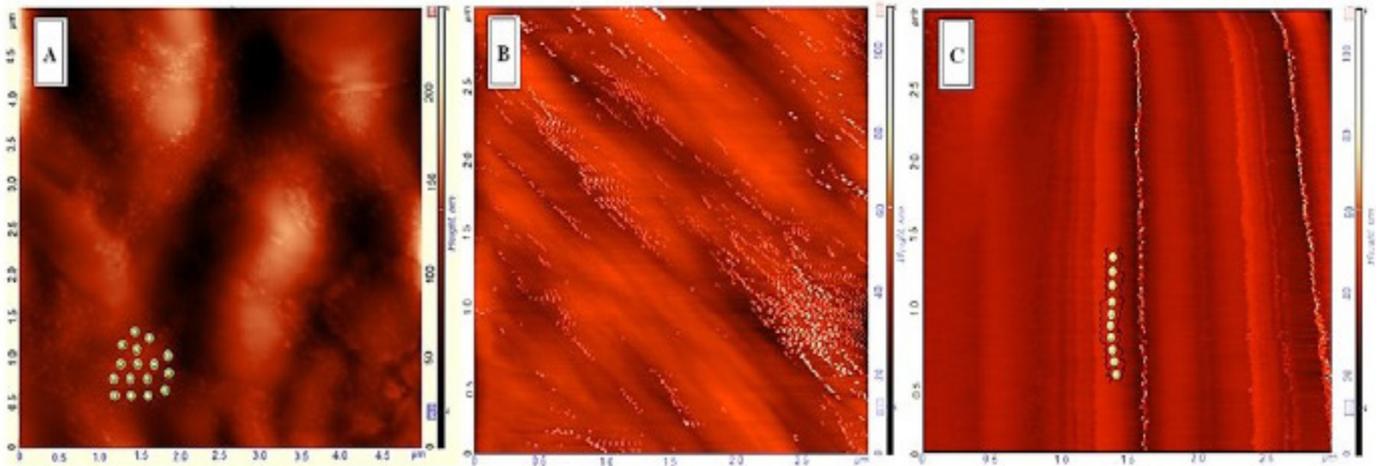


Fig.4. A) AFM micrograph of the TGA-CdTe, B) TGA-CdTe-wdp QDs, C) Self assembling of TGA-CdTe-wdp QDs.

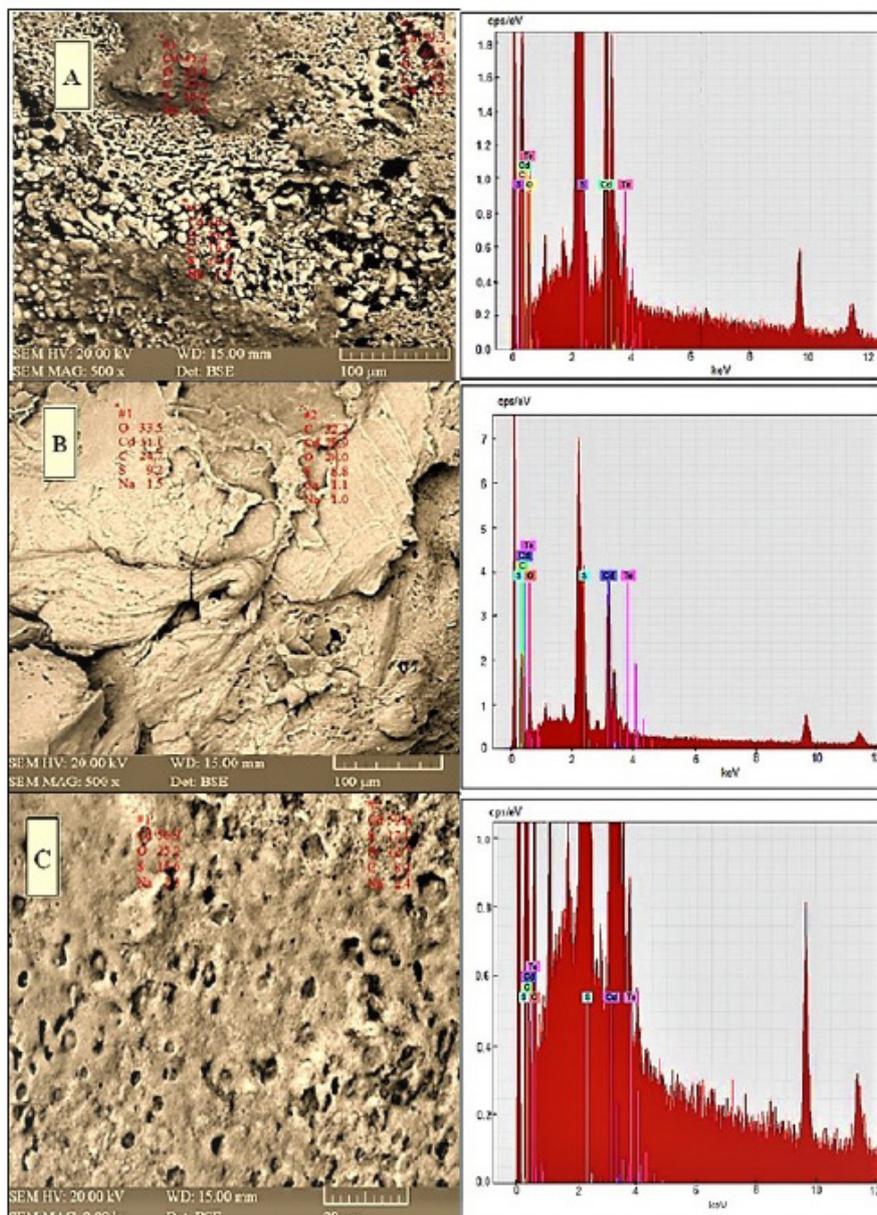


Fig. 5. SEM with the localized elemental analysis (inset) and EDS spectra of TGA-CdTe-wdp QDs containing 3.03 nm (A), 2.32nm (B) and 1.98 nm size QDs (C).

3.4.3. Fluorescence image by BAB image analysis system spectroscopy

To definitively confirm the CdTe QDs inside CdTe-wdp matrix, fluorescence microscopy was employed and demonstrated very well-defined, punctuate fluorescence .

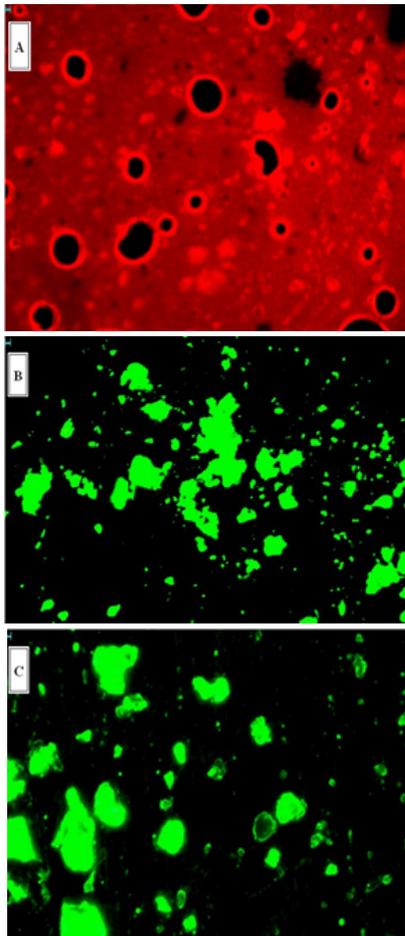


Fig. 6. Fluorescence images of TGA-CdTe-wdp QDs. All images were taken using red (A) and blue (B, C) fluoresce in filter at 400 \times .

3.4.4. Transmission electron microscopy (TEM)

TEM micrographs of the synthesized TGA-CdTe-wdp composites are shown in Figure 7. The TEM micrographs suggest mono disperse nature of TGA-CdTe-wdp composites. The CdTe QDs are uniformly dispersed in wdp matrix which is good agreement with fluorescence spectra and AFM micrographs. We have found each aggregated TGA-CdTe-wdp composites particle size is about 3-4 nm with spherical shapes which were arrowed in the Figure (see Figure 7).

3.4.5. X-ray diffraction (XRD)

The X-ray diffraction (XRD) was used to characterize the crystal structure of the as prepared CdTe QDs, and the XRD patterns are illustrated in Figure 8. The three diffraction peaks of CdTe QDs at 23.4, 42.7, and 50.6, can be indexed to the crystal planes (1 1 1), (2 2 0) and (3 1 1) of zinc blende structure and is consisted with the cubic CdTe lattice (JCPDS Card: 01-075-2086).

4. Conclusions

In summary, we have demonstrated that water dispersible polymer (wdp), RM-DMP which is anchored on the surface of the TGA modified CdTe QDs are easily synthesized, robust, safe and self-assembled. The prepared QDs-wdp nano composite material is no longer water soluble with its unique nature.

Applying surface modification by wdp also affords the excellent stability of QDs and maintained the efficient fluorescence,

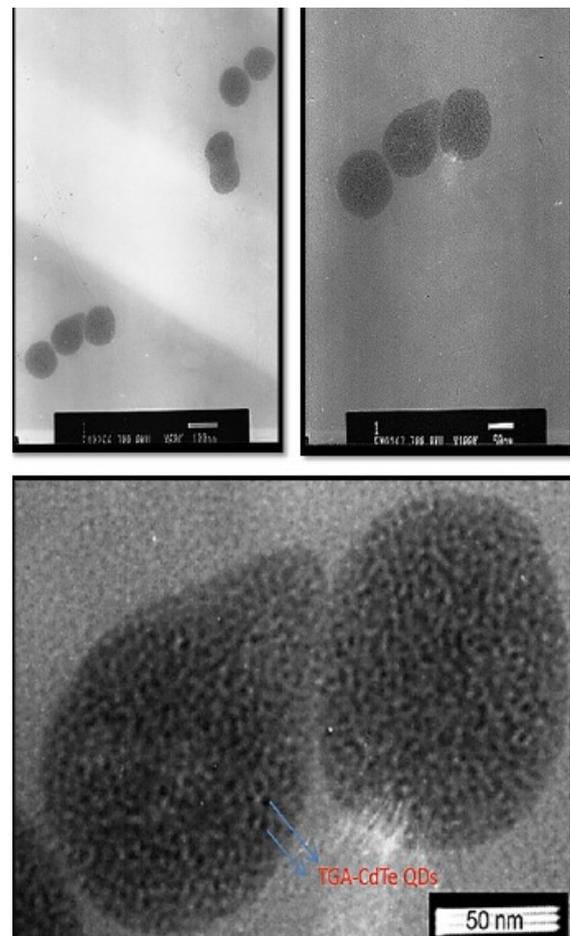


Fig. 7. TEM images of TGA-CdTe-wdp composite nanoparticles.

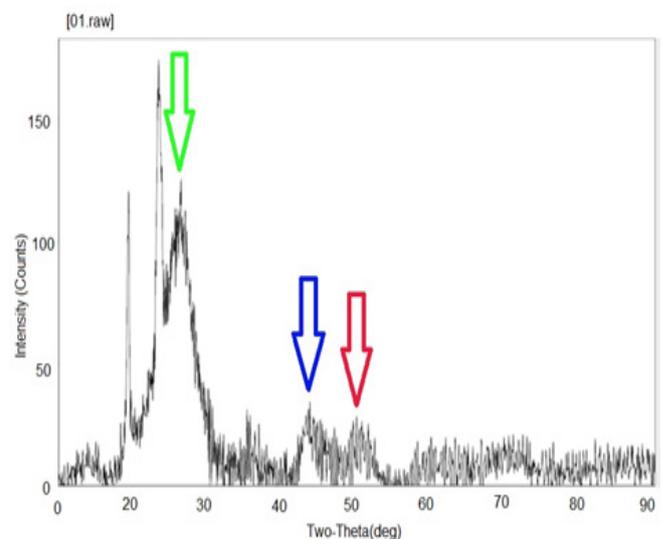


Fig. 8. Typical XRD patterns of the prepared TGA-CdTe-wdp composite nanoparticles.

and it may protect from toxicity. According to our results wdp stabilizes the thioglycolic acid-capped CdTe nano crystals giving a new type of material which might be considered one of the potential candidates for biomedical/analytical applications.

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References

1. Gan, T., Zhang, Y., Zhao, N., Xiao, X., Yin, G., Yu, S., Wang, H., Duan, J., Shi, C., Liu, W., *Spectrochim. Acta. A* 2012, 99, 62.
2. Ali, E. M., Zheng, Y., Yu, H. H., Ying, J. Y., *Anal. Chem.* 2007, 79, 9452.
3. Wang, H., Chen, Q., Tan, Z., Yin, X., Wang, L., *Electrochim. Acta.* 2012, 72, 28.
4. Guo, C., Wang, J., Cheng, J., Dai, Z., *Biosensors and Bioelectronics.* 2012, 36, 69.
5. Zhang, L., Shang, L., Dong, S., *Electrochem. Commun.* 2008, 10, 1452.
6. Xu H, Miao R, Fang Z, Zhong X 2011 *Analytica Chimica Acta.* 687 82.
7. Tao H, Liao X, Xu M, Li S, Zhong F, Yi Z 2014 *J. Lumin.* 146 376.
8. Wang X, Lv Y, Hou X 2011 *Talanta* 84 382.
9. Roushani M, Shamsipur M, Rajabi H R 2014 *J. Electroanal. Chem.* 712 19.
10. Wang Y, Zheng J, Zhang Z, Yuan C, Fu D 2009 *Colloids Surface A.* 342 102.
11. Wang J, Li Y, Zhang H, Wang H, Lin S, Chen J, Zhao Y, Luo Q 2010 *Colloids Surfaces A.* 364 82.
12. Zhang M, Wan F, Wang S, Ge S, Yan M., Yu J 2012 *J. Lumin.* 132 938.
13. Tang G, Du L, Su X 2013 *Food Chem.* 141 4060.
14. Zhan L, Zheng H, Long Y, Huang C, Hao J, Zhou D 2011 *Talanta* 83 1716.
15. Wang Y, Zang D, Ge S, Ge L, Yu J, Yan M 2013 *Electrochim. Acta.* 107 147.
16. Zhao D, Jimei Z, Quanxi D, Ning G, Schichao X, Bo S, Bu Y 2007 *Chinese J. Chem. Eng.* 15 791.
17. Sun J F , Ren C L, Liu L H 2008 *Chinese Chem. Lett.* 19 855.
18. Vaishnavi E, Renganathan R, 2013 *Spectrochim. Acta. A.* 115 603.
19. Sorouraddin M, Nabiyyi A, Gehraz S, Rashidi M 2014 *J. Lumin.* 145 253.
20. Ge S, Lu J, Ge L, Yan M, Yu J 2011 *Spectrochim. Acta A.* 79 1704.
21. Li J, Zou G, Hu X, Zhang X J 2009 *Electroanal. Chem.* 625 88.
22. Yu X, Liu J, Zuo S, Yu Y, Cai K, Yang R 2013 *Forensic. Sci. Int.* 231 125.
23. Badawi A, Al-Hosiny N, Abdullah S, Negm S and Talaat H 2013 *Sol. Energy.* 88 137.
24. Ruan J, Song H, Qian Q, Li C, Wang K, Bao C 2012 *Biomaterials* 33 7093.
25. Yu Y, Xu L, Chen J, Gao H, Wang S, Fang J, Xu S 2012 *Colloids Surfaces B* 95 247.
26. Chu M, Pan X, Zhang D, Wu Q, Peng J, Hai W 2012 *Biomaterials* 33 7071.
27. Dong W, Guo L, Wang M, Xu S 2009 *J. Lumin.* 129 926.
28. Ma Q, Lin Z, Yang N, Li Y, Su X 2014 *Acta Biomaterialia* 10 868.
29. Casals E, Gonzalez E, Puentes V F 2012 *J. Phys. D. Appl. Phys.* 45 443001.
30. Clapp A R, Mendintz I L, Mauro J M, Fisher B R, Bawendi M G, Mattoussi H 2004 *J. Am. Chem. Soc.* 126 301.
31. Yan M, Zhang Y, Xu K, Fu T, Qin H, Zheng X 2011 *Toxicology* 282 94.
32. Su Y, Hu M, Fan C, He Y, Li Q, Li W, Wang L, Shen P, Huang Q 2010 *Biomaterials* 314829.
33. Chen N, He Y, Su Y, Li X, Huang Q, Wang H, Zhang X, Tai R, Fan C 2012 *Biomaterials* 33 1238.
34. Li J, Zhang Y, Xiao Q, F Tian, Liu X., Li R., Zhao G, Jiang F, Liu Y 2011 *J. Hazard. Mater.* 194 440.
35. Zeng Y, Tang C, Tian G, Yi P, Huang H, Hu N, Li S, H Huang, Li C, Lin B, Yu X, Ling Y, Xia X 2010 *Chem. Eng. J.* 156 524.
36. Lai L, Lin C, Xu Z, Han X, Tian F, Mei P, Li D, Ge Y, Jiang F, Zhang Y, Liu Y 2012 *Spectrochim. Acta A.* 97 366.
37. Murcia M J, Minner D E, Mustata G, Ritchie K, Naumann C A 2008 *J. Am. Chem. Soc.* 130 15054.
38. Ma Q, Song T, Yuan P, Wang C, Su X 2008 *Colloids Surfaces B.* 64 248.
39. Liu J, Liang J, Han H, Sheng Z, 2009 *Materials Lett.* 63 2224.
40. Kumar H, Srivastava R, Dutta P K 2013 *Carbohydr. Polym.* 97 327.
41. Premkumara T, Geckeler K E 2012 *Prog. Polym. Sci.* 37 515.
42. Wang Y, Liu S, Yang K, Zhou L 2013 *Colloid. Polym. Sci.* 2911313.
43. Yu W W, Qu L, Guo W, Peng X 2003 *Chem. Mater.* 15 2854.
44. Peng J, Hu X 2011 *J. Lumin.* 131 952.
45. Dwarakanath S, Bruno J G, Shastry A, Phillips T, John A, Kumar A, Stephenson L D 2004 *Biochem. Biophys. Res. Co.* 325 739.
46. Gautier J L, Monras J P, Osorio-Roman I O, Vasquez C C, Bravo D, Herranz T, Marco J F, Perez-Donoso J M 2013 *Materials Chem. Phys.* 140 113.

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