

Fabrication of water-soluble L-cysteine capped CdTe quantum dots in zeolite confinement

Erandi Munasinghe¹, Yohan Jayawardane¹, Anuradha Rajapakshe¹, Athula Bandara²,
Rohan Weerasooriya¹, Lakmal Jayarathna^{1*}

¹Environmental Science Research Program, National Institute of Fundamental Studies, Kandy, 20000, (SRI LANKA)

²Department of Chemistry, University of Peradeniya, Peradeniya, 20500, (SRI LANKA)

E-mail: lakmal.ja@nifs.ac.lk, lakmalipj@yahoo.co.uk

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ABSTRACT

Quantum dots (QDs) are nano crystals with tunable energy levels with respect to size, shape and charge potential. Presently, the channel structure of zeolites, traditionally used as an adsorbent, was used as the substrate for the fabrication of CdTe QDs under inert environments. The unique structure of zeolites is used as reaction chambers for the fabrication of uniform size QDs. We successfully fabricated L-cysteine capped, highly fluorescent CdTe QDs on zeolite substrate at Cd²⁺: Te²⁻: L-Cysteine molar ratio as 1: 1: 19. Newly fabricated CdTe QDs were characterized by FTIR, XRD and SEM. The newly fabricated CdTe QDs has a great potential in biomedical applications in transporting therapeutic and diagnostic agents.

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KEYWORDS

CdTe QD; Zeolite; L-Cysteine; Water soluble; Ambient air condition.

INTRODUCTION

Recently researchers have paid attention to construct distinct varieties of nanomaterials such as quantum dots, due to their extensive usage in numerous fields^[1,2]. Quantum dots (QDs) are semiconductor nanometer-sized crystals derived from semiconducting bulk materials. The optical properties of the QDs are largely dependent on the particle size^[3]. Among many QDs such as CdSe, ZnS, CdTe, CdS, InP and ZnSe, CdTe are extensively used in biomedical applications with various modifications even though Cd containing QDs are considered to be highly cytotoxic^[4].

Among several methods utilized to synthesis

quantum dots, hydrothermal synthesis and organometallic methods are widely used^[5,6]. The nano QDs fabrication requires inert environments. Because, synthesis, functionalization, storage and fabrication of good quality QDs are performed under very controlled inert atmosphere due to following three reasons. Firstly, many precursors for QD synthesis are highly susceptible towards degradation by moisture and oxygen. Secondly, presence of oxygen during high temperature synthesis lowers the yield of desired QDs with concomitant formation of metal oxides as one side product as well as produce low quality QDs with many surface trap states^[7]. Thirdly, as prepared QDs are susceptible towards surface oxidation in presence of moisture,

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oxygen and light with generation of surface trap states and gradual decay of their luminescence intensity^[8].

Materials with distinctly defined cavities are used to synthesize QDs^[9]. These well-defined zones can be regarded as nano-confinements as reaction chambers. In this context zeolites can be considered as ideal hosts for the generation of highly uniform discrete QDs with sizes smaller than its pore cavity size (20 nm). Under inert conditions, the reaction cavities of zeolite protect QDs against interactions with water, air and other compounds. Due to the unique geometry of zeolites the QDs can be fabricated with uniform morphologies. Presently we used zeolite reaction chambers to confine Cd²⁺ under inert atmosphere. To stabilize, the surface of QD were capped with thiol groups in cysteine^[10,11]. Surface modified QDs are used in many biomedical applications such as immunofluorescence assays, tissue engineering, DNA array technology, targeted drug delivery and other cell biology techniques where fluorescence measurements are occupied.

The tunable optical properties of QDs have gained a lot of interest. With these optical properties, QDs use in various applications, such as sensors, drug delivery and biomedical imaging. QDs discern themselves in offering many inherent photophysical properties that are enviable for the purposes imaging and targeted drug delivery^[12]. QDs are nanometer-sized radiant semiconductor crystals and have inimitable chemical and physical properties due to their size and highly squashed structure. This enable the synthesis of QDs for relevance in *in vivo* imaging including live-cell and whole-animal imaging, blood cancer assay, and cancer detection and treatment. QDs constitute the part of technological future having intriguing and useful properties^[13]. They have ability to emit light when any source of energy excites their electrons^[13,14].

METHODOLOGY

Materials and methodology

CdTe quantum dots were synthesized according to the procedure published by Kim *et al* (2015)^[15] with modifications using zeolite in the medium. Briefly, under ultra-sonication, L-Cysteine and Zeolite was added in to deionized (DI) water containing CdCl₂. The mixture was sonicated for 50 minutes at 40 °C. The pH was

adjusting until pH reaches 8. The temperature of the solution was brought up to 100 °C. At the meantime, Te and of NaBH₄ was added in to a sealed vial bottle containing 600 µL of DI water and heated at 50 °C for 30 minutes. The molar ratio of Cd²⁺: Te²⁻: L-Cysteine was maintained as 1: 1: 19. When the temperature reached to 100 °C, Te²⁻ precursor solution was injected suddenly, using a syringe. Samples were collected at different reaction time intervals (0.5, 2 min, 5 min, 10 min, 30 min and 50 min).

Characterization

X-ray diffraction (XRD) spectroscopy patterns of powdered specimens were obtained using Rigaku Ultima IV automated diffraction system. The infrared spectra were collected by Nicolet iS-50 Fourier transform infrared spectrophotometer (FTIR), scanning electronic microscope (SEM) and energy dispersive x-ray spectroscopy (EDS) analysis by FEI Quanta 400FEG=EDAX Genesis X4M high resolution scanning electronic microscope and absorption spectra by UV-2100 UV-vis spectrometer.

RESULTS AND DISCUSSION

The zeolite A structure consists of sodalite (or β) cages and large α -cages with 11.7 Å diameter, which are bounded by eight sodalite cages^[16]. The effective diameter of the 8-ring windows depends strongly on the identity of these ions. The 8-ring diameter in this case is 4.4 Å. The diameters of Cd²⁺, Te⁰, and Te²⁻ are 1.6, 4.2, and 4.4 Å, respectively. Comparing these ionic and atomic sizes to the size of the 8-ring, it is apparent that the diffusion of Te⁰ and Te²⁻ will be much slower than Cd²⁺ in these α -cages^[16]. Aqueous Cd²⁺ ions were introduced to the zeolitic media which migrate through the pores and creating inert conditions. These phenomena will prevent to interaction of Cd²⁺ with atmospheric O₂ or CO₂.

Characterization of L-cysteine capped CdTe quantum dots

FTIR spectra of both L-cysteine and L-cysteine capped CdTe QDs are shown in Figure 1. L-cysteine has potentially three binding sites i.e., -thiol, amino and carboxylate groups. peaks are assigned in TABLE 1^[17]. In the FTIR spectra of CdTe capped by L-cysteine

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these bands for $-SH$ are absent. This arises because of the cleavage of the $S-H$ bond and the formation of new $Cd-S$ bond. This observation provides a clear evidence of surface bonding of L-cysteine with the $CdTe$ QDs. The sharp peaks in the region of $1040-1580\text{ cm}^{-1}$ in the case of L-cysteine became weaker and get merged at three broad peaks in the case of L-cysteine capped

$CdTe$, which is probably due to the change in pH and change in the dipole moment when L-cysteine binds with the metal surface with high electron density. It can also be seen that the characteristic frequency at 1400 cm^{-1} and 1580 cm^{-1} , which corresponds to COO^- symmetric stretch and NH_2 asymmetric bending mode, respectively are present in both the spectra^[18].

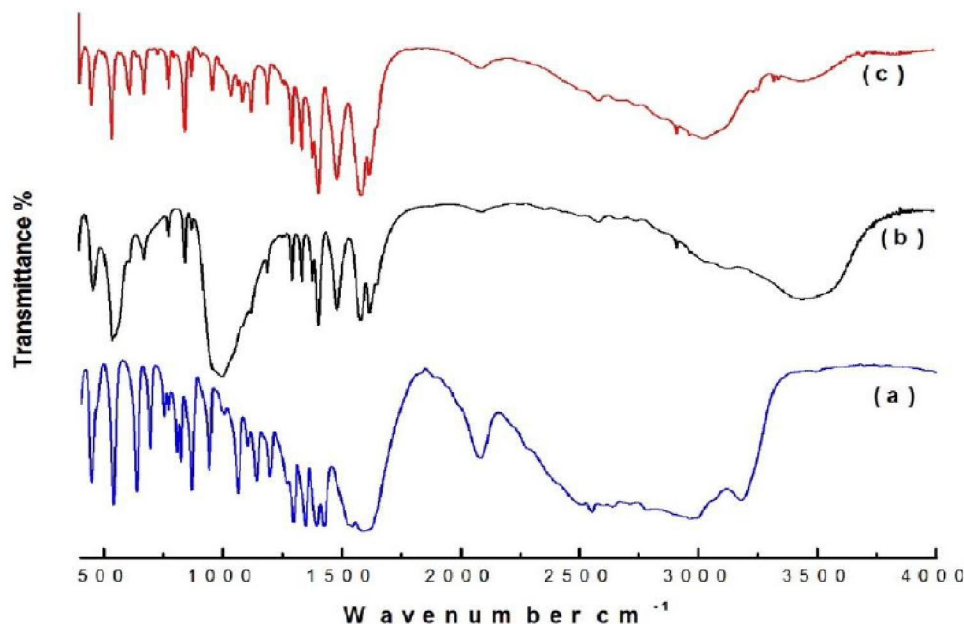


Figure 1: FTIR spectra of (a) L-cysteine, (b) L-cysteine capped $CdTe$ QDs in zeolitic media and (c) L-cysteine capped $CdTe$ QDs

TABLE 1: Peak assigning for L-cystine capped $CdTe$ QDs

Peak position/ cm^{-1}	Peak Assigning
1595	$-NH_2$ Asymmetric bending
1400	COO Symmetric stretching
3500-2700	$-OH$, $-NH$ Symmetric vibration
1130	$-NH_3^+$ Rocking
1480	$-COO-$ Asymmetric stretching
1380	$-COO-$ Symmetric stretching
1040	$-CN-$ Stretching
~ 2500	$-SH$ Stretching
960	$-SH$ Bending

XRD studies

XRD pattern gives information about crystalline structure, grain size, and strain. XRD studies were carried out for the powder samples and the typical diffractograms of L-Cysteine capped $CdTe$ QDs in zeolite media are shown in Figure 2. However, due to predominance of XRD pattern of zeolite, it difficult to distinguish the corresponding XRD patterns for $CdTe$ QDs. Therefore, corresponding peaks for $CdTe$ QDs

indicates in expanded images in Figure 2. The broad peaks confirm the nano-crystalline nature of the samples. The peaks were observed with the XRD pattern of zeolite^[19]. As shown in Figure 2, XRD peaks observed at the angles (2θ) of 26.3 , 43.5 and 51.5 corresponding to the reflections from $(1\ 1\ 1)$, $(2\ 2\ 0)$ and $(3\ 1\ 1)$ crystal planes respectively. The crystalline structure of L-cysteine capped $CdTe$ QDs was confirmed with a cubic zinc-blende structure. Further, minor peaks observed at 24.81 , 28.1 , 35.91 and 47.52 correspond to $(1\ 0\ 0)$, $(1\ 0\ 1)$, $(1\ 0\ 2)$ and $(1\ 0\ 3)$ planes, respectively^[20].

SEM studies

The morphological and surface behavior of L-Cysteine capped $CdTe$ QDs were investigated with scanning electron microscopy. It clearly indicates formation of rod type $CdTe$ QDs on the cubic structure of the zeolite surfaces. Rod type particles bunched together to form spherical structure of zeolite surface to minimize surface charges^[11,21].

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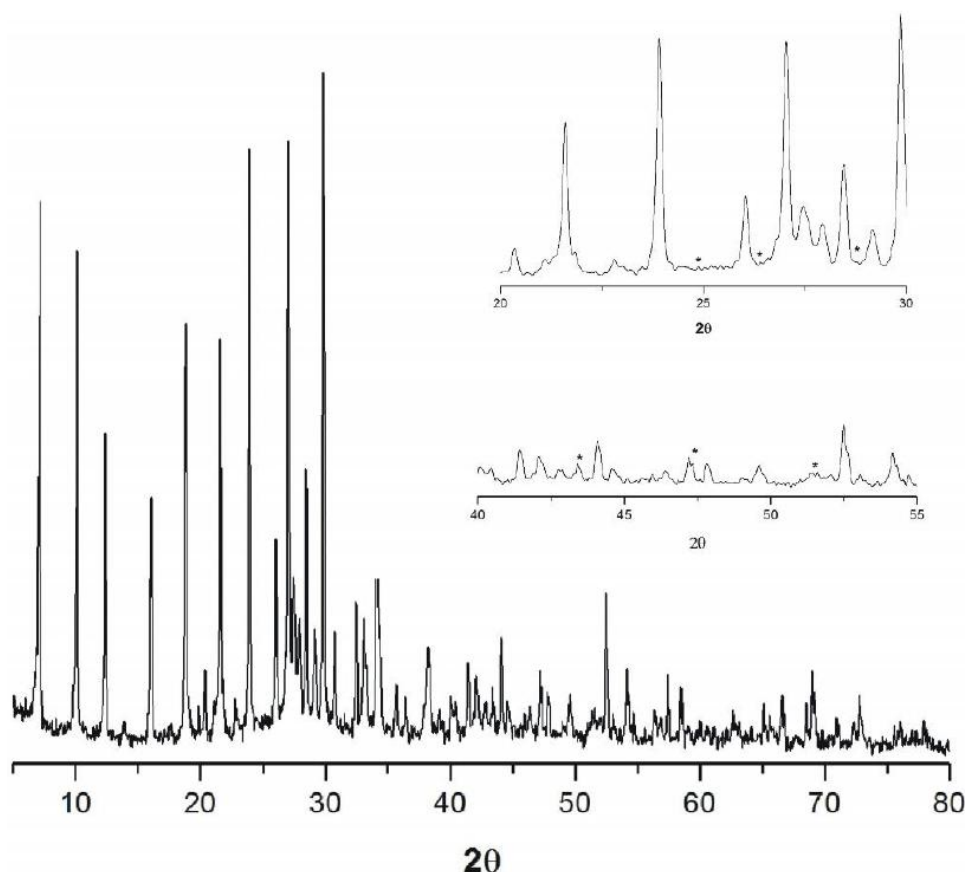


Figure 2: XRD pattern of CdTe QDs in zeolite media. Corresponding XRD peaks for CdTe QDs indicates with “*” in expanded images.

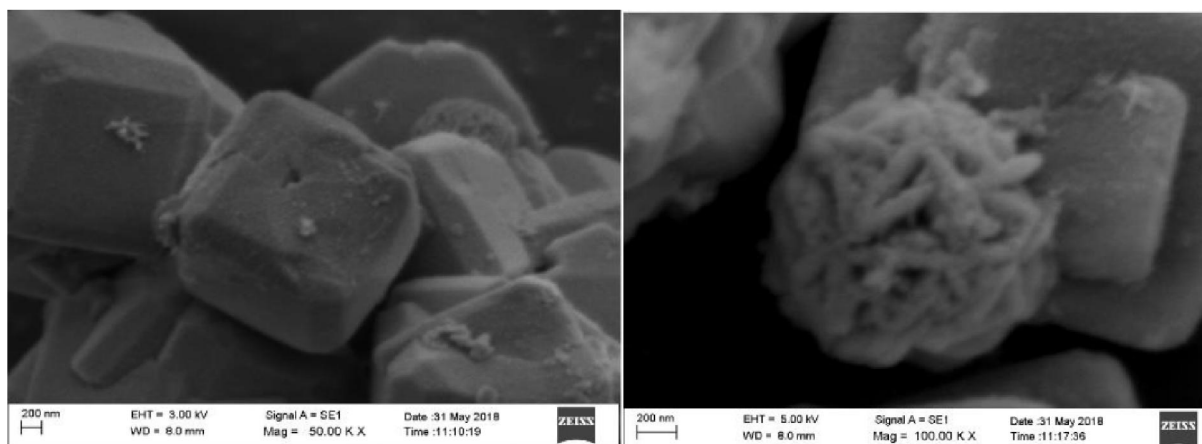


Figure 3: SEM images of synthesis CdTe QDs in zeolatic media.

UV and fluoresce spectroscopy

Figure 4 shows the UV absorption and emission spectra of CdTe QDs synthesized with L-cysteine as a capping agent for different synthesizing time durations. All samples exhibited the well-resolved absorption maxima of the first electronic transition. Due to the quantum confinement effect, a red shift of the absorption

edge could be observed with the increment of synthesizing time, indicating the growth of CdTe QDs^[20].

From the absorption spectra, the band gap for pure CdTe QDs was determined to be 1.7–2 eV, which is higher than the bulk CdTe ($E_g = 1.45$ eV) due to quantum confinement, i.e. the band gap value could be attributed to the small size of the QDs. At the same

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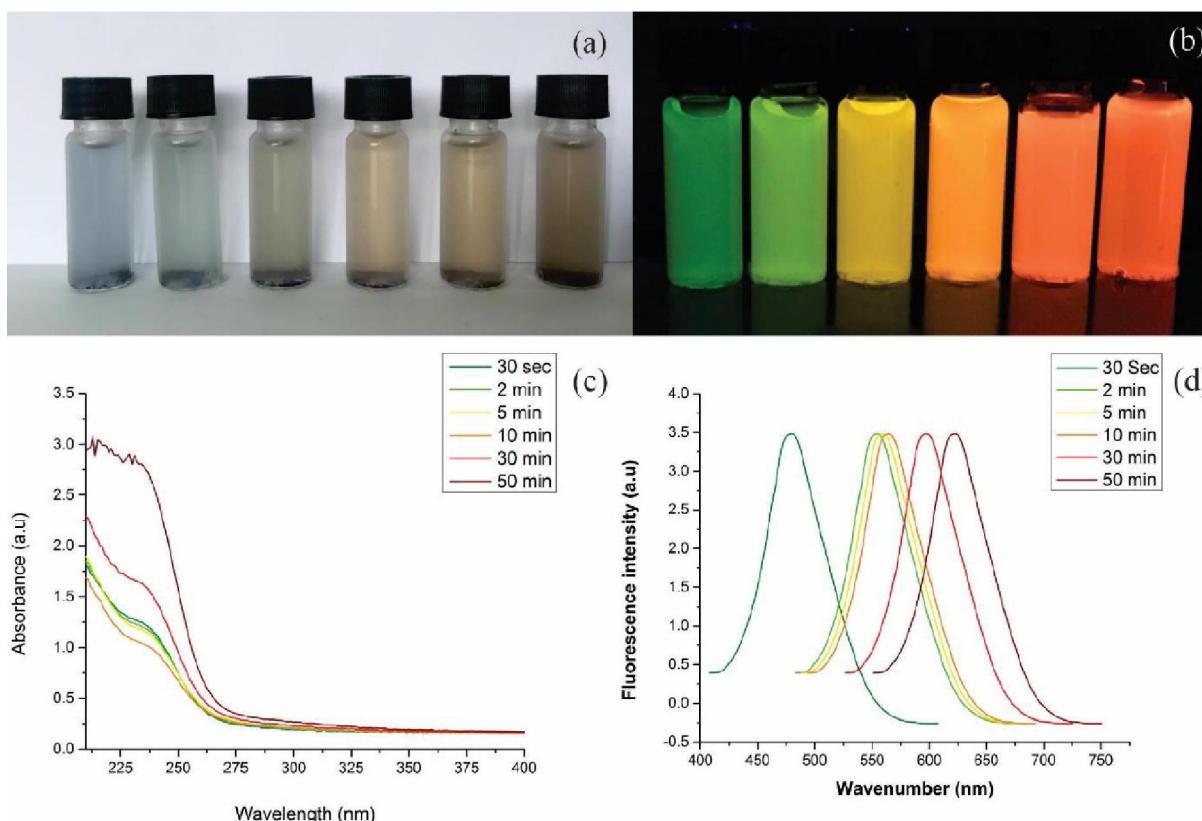


Figure 4: Image shows the synthesized CdTe QDs under (a) normal light and (b) UV light irradiation, (c) UV-Vis adsorption spectrum and (d) fluorescence spectrum

time the optical band gap of CdTe:CdS nano-composite phase was slightly increased over the pure CdTe QDs due to the lowering of absorption edge^[20].

CONCLUSIONS

We fabricated water-soluble L-cysteine capped CdTe QDs in zeolite media where zeolite is used as an agent to connote an inert environment without disrupting zeolite framework. The CdTe QDs are decorated on zeolite surface. Highly fluorescent CdTe QDs can be used as a drug carrier in biomedical applications.

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CONFLICTS OF INTEREST

All the authors declare that there are no potential

conflicts of interest in any financial or nonfinancial.

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