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One-step phase transferring method on preparing CuInS2/ZnS QDs dispersion via ultrasonic treatment for bioimaging

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ABSTRACT

Sonochemistry has many applications in biomedical engineering owing to its ability to break chemical bonds. It can also be used to facilitate the preparation of aqueous quantum dots (QDs) dispersions during microemulsion formati on. Cavitation, bubble growth, and collapse during sonication facilitate the formation of microemulsions between a solvent and water. Sonication was employed in this study to prepare aqueous copper indium sulfide colloidal zinc sulfide (CuInS2/ZnS) QD dispersions using different solvent systems. The resultant QDs were characterized by UV-vis absorption, photoluminescence, and dynamic light scattering. Hexane was determined to be the best solvent for the preparation of QD dispersions with the resultant QDs (30 nm in diameter) retaining their chemical integrity and >30% of their quantum yield. CuInS2/ZnS QD dispersions in water can be directly prepared without any non-polar solvent and it has shown high quantum yield. Further, it was also shown that less-toxic, which is efficient in labeling tumor cells derived from human liver cancer (HepG2). It's evident that sonication was found to be an efficient alternative approach for preparing aqueous QD dispersions without the need for surface modification, or the use of non-polar solvents during microemulsion formation.

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1. INTRODUCTION

Quantum dots (QDs) have distinctive photophysical properties that make them suitable candidates for use in imaging probes, nanodiagnostics, photodynamic therapy, and targeted drug delivery [1]–[5]. Synthesis of QDs generally employs hydrophobic ligands to maintain their shape and to get good monodispersity. However, this process will render the QDs non-dispersible in water, thus limiting their use in environmental and biological applications [6]. Currently, several methods have been proposed for modifying the surface of QDs to facilitate their use in biological applications, such as i) ligand exchange, ii) silica coating, and iii) polymer surface coating [1], [7]. Even can successfully transfer the QDs in the water phase, most of the methods still have some problems relating to the complicated process and the difficulty of performing good dispersity of the resulting QDs. Therefore, improvement in phase transfer techniques has been deliberated to solve the above problems.

Sonochemistry has many applications in bio-medically related fields, especially in the phase transferring process. This phenomenon is based on the ability of ultrasonic waves to generate acoustic cavitation, which gives a chance for insertion of other phase materials and further exists on the new phase

after molecular modification. The usefulness of ultrasonic waves on chemical synthesis increases due to ultrasound energy (from 20 kHz) can also break chemical bonds [8] and induce radical formation [9]–[11]. A number of published "basic" theories explain these effects [12]. The bubbles formatted from ultrasonication, finally collapse and generate shock waves that are propagated by liquid with a higher velocity than the speed of sound, thereby imparting significant velocities to the suspended particles. Sometimes, such extreme conditions are applied to impart unique properties to synthesized particles [13]. Recent publications suggest that ultrasound can be used to particle size reduction, alter size distributions, and modify particle aggregation [14]–[17]. Research by Madigan *et al.* [18] study of the effect metal particles observed that in aqueo us conditions, non-metal and ebonex undergo significant rattling within minutes of being sonicated at a frequency of 20 kHz. Vajihe *et al*. demonstrated the silica fume particle size dramatically decreased within the first 15 seconds of sonication, and the size reduction rate was controlled with continued sonication [19].

The microemulsion techniques were initially developed by Wood and Loomis [20], then widely used to produce liquid phases for the preparation of several nanoparticles, such as cadmium sulfide (CdS) [21], cadmium selenide (CdSe) [22], cadmium selenide zinc sulfide (CdSe/ZnS) QDs [23], barium sulfate ($BaSO_4$) [24], and cadmium sulfide titanium dioxide (CdS/TiO_2) [25], [26], carbon nanotubes [27] and magnetite nanoparticles [13] with desired morphologies and size distributions. In this study, we propose a method to design a phase transfer technique of oil-soluble $CuInS_2$/ZnS QDs which was confirmed as low toxic material in biological application [27]–[30]. A simple phase transfer procedure was highlighted and how to prepare stable water-soluble $CuInS_2$/ZnS QDs, without complicating surface modification. We first applied various solvents, like toluene, hexane, cyclohexane, and chloroform as non-polar solvents accompanying oil-soluble QDs in the process. Further, we develop the phase transfer technique by using directly QDs in the process.

2. RESEARCH METHOD

2.1. Materials

Copper acetate ($Cu(OAc)_2$, 99.995%), Indium acetate ($In(OAc)_3$, 99.98%), Zinc stearate (ZS, 90%), potassium ethylxanthate (90%) 1-octadecene (ODE, 90%), 1-dodecanethiol (DDT, 97%), were obtained from Alfa-Aesar (USA). 4,6-diamidino-2-phenylindole (DAPI, >98%) and 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT, 97.5%) were obtained from Sigma-Aldrich (Milwaukee). Zinc chloride (90%) and all solvents were obtained from EM-Sciences. Zinc ethylxanthate (ZE) was prepared according to Chang and Cheng [31]. In these experiments, all reagents were used as received without any purgation.

2.2. Synthesis of copper indium sulfide colloidal zinc sulfide quantum dots

Copper indium sulfide colloidal zinc sulfide ($CuInS_2$/ZnS) QDs were synthesized in accordance with the literature [7]. Briefly, 0.17517 g $In(OAc)_3$, 0.0245 g $Cu(OAc)_2$, and 5 mL ODE were stirred with 2.5 mL DDT then N2 gas was purged. After maintaining at 40 °C for 1 h, the reaction mixture was mildly warmed at 240 °C, which gave the reddish orange color solution. The other mixture was prepared by 0.1 mL of DMF, 0.031 g of ZE in 1 mL toluene, and 0.504 g of ZS in 3 mL ODE, which was promptly instilled into the boiling solution. The reaction mixture was cooled to 30 °C and centrifuged for 20 min at 6000 rpm. The resulting supernatant washed with a mixture of methanol/ acetone (1:1) and $CuInS_2$/Zns QDs was precipitated by centrifugation at 6000 rpm for 10 min.

2.3. Solvent-assisted preparation of aqueous dispersed $CulnS_2$/ZnS QDs

$CuInS_2$/ZnS QDs were prepared in different non-polar solvents (toluene, hexane, cyclohexane, and chloroform), by adding polar solvent (10 ml water, acetone, or DMF) and shaken for 0.5 min. The solutions were mixed for 10 min by means of 20 kHz with VCX 130 PB power using an ultrasonic processor (Sonics and Materials Inc, Newton, CT) and then centrifuged (for 30 min at 6000 rpm) to increase the rate of solid QD/aqueous phase separation. After centrifugation, the solution was warmed to 100 °C for 10 min. Finally, accumulated QDs were removed by a 0.2 μm nylon filter passing the $CuInS_2$/ZnS QDs in the dispersant.

2.4. Solvent-free preparation of water-dispersed $CulnS_2$/ZnS QDs

$CuInS_2$/ZnS QDs (100 mg) in water (10 ml) were sonicated for 25 minutes with a sonication amplitude of around 100 Hz. The solution was centrifuged for 30 min at 6000 rpm and warmed up to 100 °C for 10 min. The resulting $CuInS_2$/ZnS QDs were passed via a 0.2 μm nylon filter to give water-dispersed $CuInS_2$/ZnS QDs.

2.5. Characterization

Copper grids (thin Formvar-carbon film coating) were also coated with a dilute solution of QDs for transmission electron microscopy (TEM). Further solvent evaporation at room temperature of the above

coating gives a clear source for TEM imaging by Tecnai G2 F20 transmission electron microscope (Philps, Holland) furnished with an EDX detector (acceleration at 200 kv). Dynamic light scattering (DLS) analysis was done with Malvern instruments Zetasizer Nano (Malvern instruments) 3,000 HS with a He/Ne laser and a 90° scattering angle. Nanocrystals were deposited on a Si(100) wafer for X-Ray diffraction (XRD) measurements by Rigaku X-ray diffractometer (18 kW) with the Cu K a1 line (l=1.54 Å). UV and PL spectra were determined by a JASCO V-630 spectrometer, and a JASCO FP-6500 spectrofluorometer furnished with a 150 W xenon lamp respectively.

2.6. Preparation of MTT

The study cytotoxicity of $CuInS_2$/ZnS QDs dispersed in water, was done with an MTT assay in HepG2 cells (performed in triplicate) [2]. Briefly, HepG2 cells were cultivated in a 12-well plate at 5×10^4 cells per well for one day. Then, cells were cleaned with phosphate-buffered saline (PBS) and incubated for one day with 0, 15, 50, 100, 150, and 300 μg mL^{-1} $CuInS_2$/ZnS QDs which were dispersed in water. 1 ml of MTT reagent (500 μg mL^{-1}) was supplied to all wells after washing wells twice with PBS. The source was carefully aspirated after it was re-incubated for 4 h in 5% CO_2 at 37 °C. Next, 200 μL of dimethyl sulfoxide was added to dissolve the dark blue formazan crystals. The quantity of formazan crystals with a dark blue color that is formed by living cells is directly correlated with the number of living cells. It was fixed by calculating the absorbance at 570 nm with a Biotech power wave XS plate reader.

2.7. Cell culture and intracellular localization of QDs in human hepatocellular carcinoma cells

The human hepatocellular carcinoma (HepG2) cells were cultured in 1% L-glutamine, 1% antibiotic antimycotic formulation, and 10% fetal bovine serum supplemented Eagle's Medium which consists also 1.5 g L^{-1} sodium bicarbonate. The cells were cultured in the presence of CO_2 (5%, v/v) at 37 °C for cell expansion and senescence induction. Slide (6-well) (Nalge Nunc international, IL) was used to seed the HepG2 cells which were contained well at a density of $1x10^5$ cells per well in 500 mL of entire medium (RPMI 1640), and incubated for 24 h at 37 °C. After incubation 50μg mL^{-1} of PEGMA-coated $CuInS_2$ /ZnS QDs were supplied to the cells for five millimeters. The cells were cleaned with PBS after one hour. Then cells were stained with DAPI (1 mg/mL 21 in PBS) after fixing with 4% paraformaldehyde. The fluorescence images were obtained by confocal laser scanning microscope (CLSM) (LSM 510 META, Zeiss, Germany). Cell imaging was carried out on a Leica TCS SP2 microscope furnished with a 63×1.32 NA oil immersion objective (Leica Microsystems). Images were procured by illuminating the samples with in-line Ar (488 nm) and He–Ne (543, 633 nm) microscope lasers and with a 405 nm Violet laser.

3. RESULTS AND DISCUSSION

The initial oil-soluble $CuInS_2$/ZnS QDs were synthesized by literature [7]. The $CuInS_2$ QDs were prepared using DDT as a hydrophobic and ODE solvent which is cheap, less hazard, higher boiling point, and is also air-durable. The monomers were accumulated in ODE solution during heat treatment to the reaction mixture. After the accumulation nucleation bursting generated seeds above the critical temperature. To enhance the luminescence properties of $CuInS_2$ QDs, ZnS passivation was done as an inorganic shell on its surface. ZnS semiconductor is used since it has a direct wide band gap (3.91 eV).

Low-resolution TEM analysis of $CuInS_2$/ZnS QDs with a diameter of 5 nm shows (Figure 1) good crystallinity and is very similar to our reported one. Figure 2 shows the X-ray analysis of $CuInS_2$/ZnS. Energy dispersive X-Ray (EDX) Analysis shows QDs containing Cu, In, S, and Zn elements (Figure 2(a)). XRD patterns of CuInS2 QDs (Figure 2(b)) show 3 main peaks at 28.2°, 46.9°, and 55.2°, corresponding to the (1,1,2), (0,2,4), and (1,3,2) indices for reflections for chalcopyrite $CuInS_2$ and ZnS phases. The higher 2θ values of major peaks indicate that Zn dispersal modifies CuInS2 QDs' crystal structure during ZnS passivation which causes the lattice constant decrease. This alteration is slightly different from standard chalcopyrite $CuInS_2$ (JCPDS card no. 47−1372). This relatively broad peak indicates the produced CuInS2/ZnS QDs contain tiny crystalline particles.

Initially, we experimented with a polar-non-polar solvent combination to disperse $CuInS_2$/ZnS QDs. First, a non-polar solvent (hexane) as the oil phase was used to dissolve $CuInS_2$/ZnS QDs. $CuInS_2$/ZnS QDs soluble in non-polar solvents but insoluble in polar solvents. The process of solubilization of $CuInS_2$/ZnS QDs (solute) in non-polar solvent is similar to other solid material solubilization. The solute's agglomeration and chemical bonds are broken by the solvent, and the solute is then given space by the solvent molecules separating. Subsequently, interactions occur between the solute molecule or ion and the solvent. In this case, the solvent becomes non-participant to dissolve the solute that followed the "like dissolves like" rule.

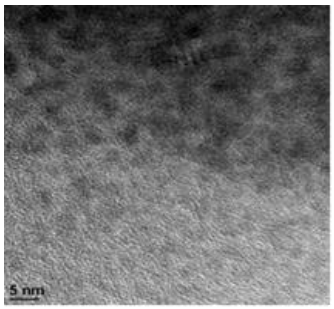
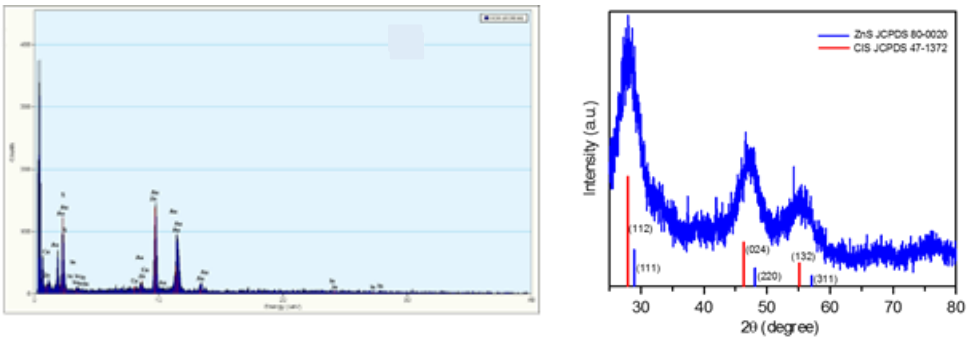


Figure 1. TEM image of $CuInS_2/ZnS$



(a) (b)

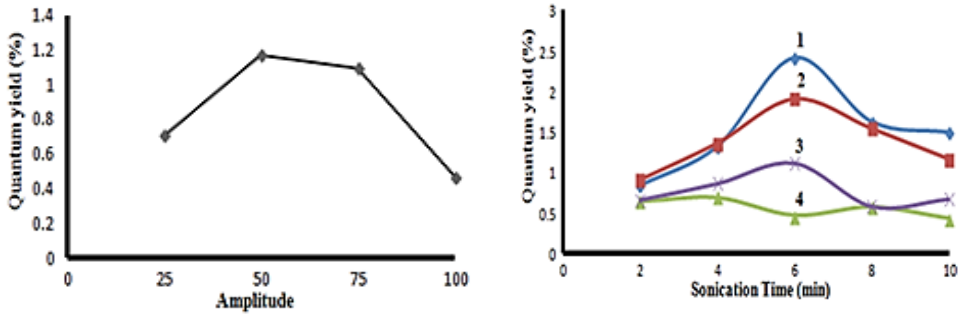
Figure 2. X-ray analysis of $CuInS_2/ZnS$ (a) EDX spectrum of $CuInS_2/ZnS$ and (b) XRD of $CuInS_2/ZnS$

Second, afterward, $CuInS_2/ZnS$ QDs in the oil phase were added to a polar solvent (water) as the water phase. The oil phase floats on the top of the water and doesn't penetrate the water phase. They are not wetted. Magnetic stirring was employed with varying speeds (500 and 1000 rpm) and times (5, 30, and 60 min). With these different times and stirring speeds $CuInS_2/ZnS$ QDs in the oil phase failed to disperse in the water phase. However, prolonged stirring in the water phase (for several hours) was found to lead to non-homogeneous QD dispersions [32].

Sonication was employed to break up particle aggregations; the application of sonic energy resulted in a rapid temperature rise and an increase in evaporation, resulting in the loss of the non-polar solvent. This can be explained as sonication producing erosion/cavitation [33], [34]. Meanwhile, Zeiger and Suslick found direct particle-shock wave interaction as a major cause of molecular crystal breakage under high-intensity sonication than the others possibility [17]. We performed TEM for QDs after dispersed in water, there is no change with oil soluble QDs image [33].

Dispersion of QDs was achieved at a sonication amplitude of 25% for 10 min (Figure 3), or at an amplitude of 50 for 2 min. These results suggested that an amplitude increase significantly reduced the time needed to disperse the $CuInS_2/ZnS$ QDs. Various sonication amplitudes were employed to disperse the QDs, i.e., 25, 50, 75, and 100. The results showed that the highest quantum yield was obtained at amplitude 50 in Figure 3(a). The quantum yield at amplitude 25 was low owing to low-pressure sonication that resulted in poorly dispersed QDs. When the amplitude was increased to 50, 75, or 100, the higher pressures dispersed the QDs more rapidly; unfortunately, this was accompanied by QD discoloration. Figure 3(b) shows that the QDs were dispersed by the ultrasonic process at amplitude 50 for 2 min. The longer the ultrasonication period, the higher the quantum yield, reaching a maximum at 6 min and decreasing thereafter. After sonication, the quantum yield decreased for 21 days with no precipitation.

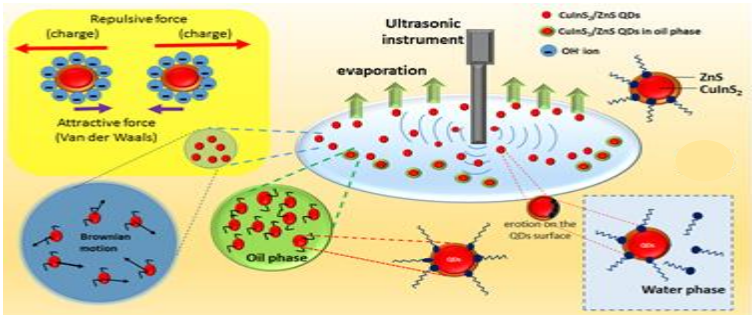
Water-dispersed $CuInS_2/ZnS$ QDs stability was influenced by sonication. The particles were prevented from coming close to one another because of stearic stabilization created by ultrasonic cavitation waves. After 21 days, precipitation was observed in the samples prepared at ultrasonication times of 2, 4, and 6 min. This finding suggested that prolonging the ultrasonication period reduced the precipitation rate of QDs. The nanoparticles approach close enough to cross the potential barrier after 21 days, re-agglomeration happens (precipitation), and the Van Der Waals force as an attractive force exceeds repulsive forces between particles. The dispersant or surfactant coating of the particle surface can be added to avoid re-agglomeration.



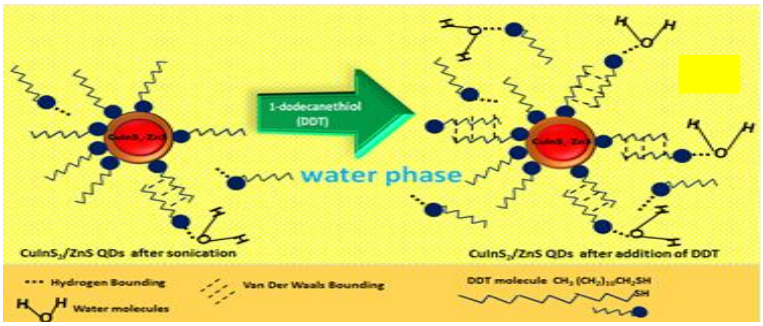
(a) (b)

Figure 3. The effect of sonication on $CuInS_2$/ZnS quantum yield (a) quantum yields at different amplitudes and (b) quantum yields at different sonication times

Processes occurring in $CuInS_2$/ZnS QDs during sonication are not well characterized. We proposed two schemes that occur in the sonication process as shown in Figure 4. First, ultrasonic waves produce microscopic bubbles (cavitation) which cause agglomerates of $CuInS_2$/ZnS QDs to be broken apart (Figure 4(a)). Then the broken agglomerates become smaller agglomerates and aggregates. This means there is a reduction in particle size. The particles of QDs were wetted in the form of small agglomerates and their solubility increased in the water. In this scheme, no chemical bonds are altered, there is only a physical process. Second, sonication also causes the release of DDT molecules which are then reversed. It is known that the pressure and temperature during sonication leads to the release of a part of the shell (ZnS), while collisions between particles impart to increase localized temperatures and give modification in the surface structure of QDs (Figure 4(b)). The QDs release some DDT molecules that become reversed. Thus, the SH (thiol) group faces and interacts with oxygen from water to form hydrogen bonds, while the carbon chains interact with the carbon chain of the DDT, which has the SH (thiol) group attached to the CuInS2/ZnS QDs, to form Van Der Walls bonding structures.



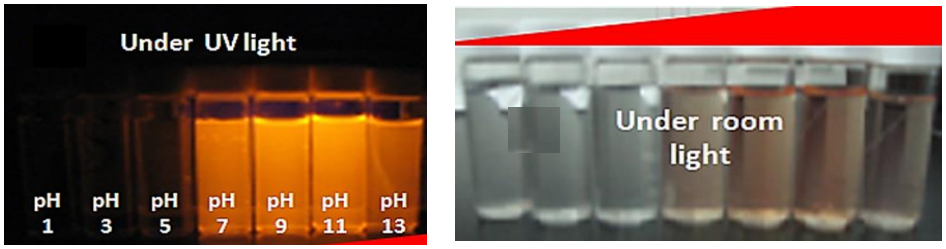
(a)



(b)

Figure 4. Two schemes occur in the sonication process (a) ultrasonic waves produce microscopic bubbles and (b) sonication also causes the release of DDT molecules

Because of Sonication, many particles of QDs interact with molecules of water making the solubility of QDs in water increase. $CuInS_2$/ZnS QDs may be dispersed in water due to the presence of hydrogen bonding. This is confirmed by the addition of DDT to $CuInS_2$/ZnS QDs preventing QD aggregation. We found that the addition of 60-70 µL DDT increases the QY from a primary value of 0.2 to 0.6%. This increase can be attributed to DDT supplying thiol groups which bind with the thiol chain of CuInS2/ZnS QDs. We confirmed that the addition of DDT (30-90 µL) to $CuInS_2$/ZnS increases its aqueous solubility, resulting in better-dispersed QDs with reduced diameters (Figure 5). Figure 5(a) shows $CuInS_2$/ZnS QDs dispersed in water at pH values of 1, 3, 5, 7, 9, 11, and 13 under UV light. After the addition of HCl (pH 1 in the final solution), direct aggregation became apparent; moreover, aggregation also occurred at pH 3 and 5 after 1 day. At $pH > 5$ (i.e., in the precipitation-free region), this method can be used for staining cells with no precipitation. The value of pH influences the dispersion stability of the system (colloids). While at physiological pH, the zeta potential of particles is not high enough to stabilize the dispersion. Therefore, steric stabilization such as sonication or dispersant is used for nanoparticle dispersion stabilization in physiological solutions. Figure 5(b) shows a photograph of CuInS2/ZnS QDs in water with different pH values, viewed under room light.



(a) (b)

Figure 5. Photographs of $CuInS_2$/ZnS QDs in water with different pH values, viewed under (a) UV light and (b) room light

The cytotoxicity of water-dispersed $CuInS_2$/ZnS QDs toward HepG2 cells in a standard MTT assay (Figure 6) was done briefly before the optical imaging. We found that more than 90% of cell survival after 24 h of incubation, even at higher QDs concentrations (300 µg ml^{-1}), implying that water-dispersed $CuInS_2$/ZnS QDs are less toxic to living cells. Toxicity of $CuInS_2$/ZnS QDs can come from QDs stability such as surface oxidation of core material and environmental conditions. Several groups have confirmed the effectiveness of the ZnS shell in reducing cytotoxicity, but not eliminating cytotoxicity Oxidation due to air exposure before solubilization was nearly eliminated when QDs contained a ZnS Shell.

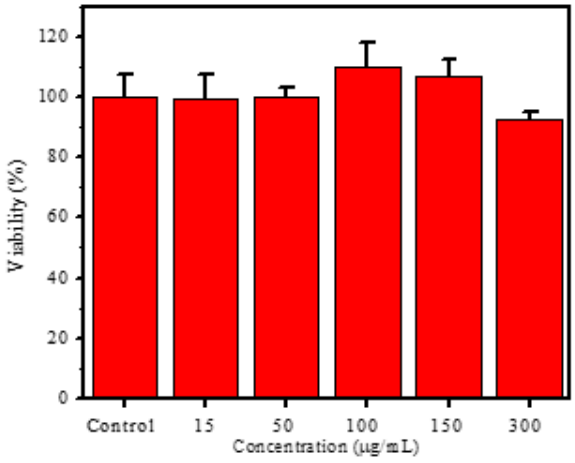


Figure 6. Cytotoxicity of HepG2 cells incubated at 37 °C for 24 h with $CuInS_2$/ZnS QDs dispersed in water at varying concentrations: 0 (control), 15, 50, 100, 150, and 300 µg mL^{-1}

To demonstrate the cellular fluorescence imaging potential of $CuInS_2$/ZnS QDs, it was incubated for 1 h with HepG2 cells, and cleaned the cells to expel non-internalized QDs. Then it was smeared with DAPI to envision the nuclei (Figure 7). The HepG2 cells' cellular boundaries are certainly shown in Figure 7(a) without fluorescence. The clearly blue fluorescence from DAPI in the area surrounding the cell nuclei is shown in Figure 7(b). The red fluorescence is also clear in Figure 7(c), which shows that the water-dispersed labeled $CuInS_2$/ZnS QDs were mainly localized on the membranes of the cell with punctuated QD staining completely in the cytoplasm. The combined image of Figures 7(a) to (c) is shown in Figure 7(d).

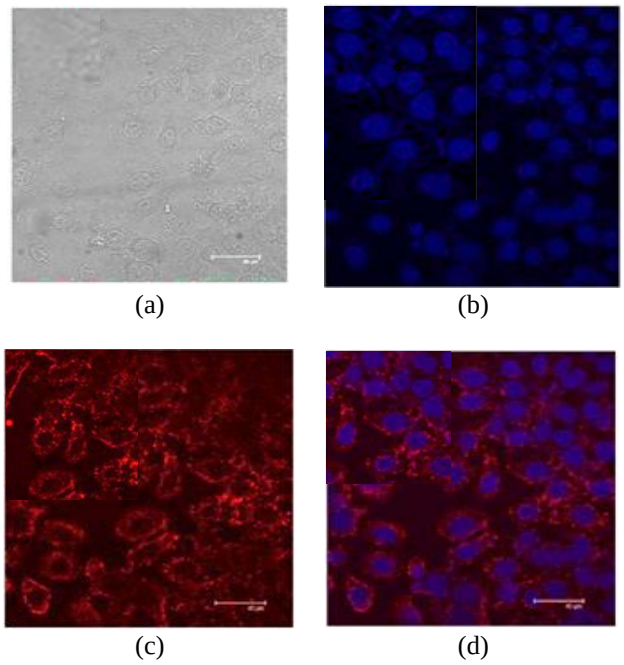


Figure 7. HepG2 cells confocal images stained with water-dispersed $CuInS_2$/ZnS QDs (a) image under visible light; (b) localization of DAPI in HepG2 cell nuclei at 460 nm emission; (c) red fluorescence arising from water-dispersed $CuInS_2$/ZnS QDs; and (d) combined image of Figures. The scale bar represents 20 μm

Figure 8 shows the testing of cyclohexane, toluene, and chloroform as potential solvents. As in the case of hexane, $CuInS_2$/ZnS can be dispersed in water assisted by cyclohexane, toluene, and chloroform under room light (Figure 8(a)) and UV light (Figure 8(b)). Then, Figure 8(c) shows a comparison of the quantum yields with water-dispersed $CuInS_2$/ZnS QDs in non-polar solvents. Interestingly, the results show that hexane has the highest quantum yield, followed by cyclohexane, toluene, and chloroform. The luminescence quantum yields were 5.74, 4.55, 3.95, and 2.52% for hexane, cyclohexane, toluene, and chloroform, respectively; thus, hexane appears to be the best solvent for the transfer phase owing to its high quantum yield. The quantum yield was calculated by using Rhodamine 6G perchlorate as a standard (QY=95%). The original PL quantum yield of $CuInS_2$/ZnS QDs was 16.71%.

It can be explained that different solvents as media for dispersion influence the photoluminescence and absorption spectra of colloidal $CuInS_2$/ZnS QDs. The different values of quantum yield arise from the various solvents for dispersion. The quantity of surface-adsorbed molecules available for surface passivation and the elimination of surface ligands are influenced by solvent-dependent equilibriums. A comparison between the PL emission and absorption spectra of the $CuInS_2$/ZnS QDs in hexane- and water-dispersed $CuInS_2$/ZnS QDs is shown in Figure 9. The highest emission peak for $CuInS_2$/ZnS QDs in hexane (560 nm) was moved to a higher wavelength (575 nm), because of the energy transfer associated with fluorescence resonance that arises from the overlap of absorption spectra. These observations are consistent with those reported previously [19]–[22]. Figure 9(a) shows the absorption and emission spectrum curves of CuInS2/ZnS QDs and Figure 9(b) shows the fluorescence emission spectrum curves of CuInS2/ZnS QDs.

We successfully prepared water-phase dispersions of the $CuInS_2$/ZnS QDs in the absence of non-polar solvents. PL emission spectra and absorption spectra of the $CuInS_2$/ZnS QDs prepared in the absence of any non-polar solvent are shown in Figure 9. The effect of the absence of a solvent can be compensated for by an increase in the sonication amplitude intensity (×1.6), sonication time (×2.5), and quantity of

$CuInS_2$/ZnS QDs (×5). Strong inter-particle collisions lead to the direct dispersion of $CuInS_2$/ZnS QDs in water. We also conducted experiments with other polar and non-polar solvent combinations, the results are presented in Table 1. It can be observed that $CuInS_2$/ZnS QDs can be dispersed in water, acetone, and DMF with toluene, hexane, cyclohexane, and chloroform. However, owing to toxicity considerations, we recommend water as the polar solvent of choice for staining cells. In spite of that, we also approve of the solubility behavior of water molecules inside solvent effect in QDs surfaces. The phrase "like dissolves like" refers to the phenomenon of solubility, which frequently arises when the interactions between the solute and the solvent are similar to one another. For this reason, nonpolar solutes dissolve in nonpolar solvents while polar solutes dissolve in polar solvents only. Since solvent polarity cannot be precisely measured, experimental scales can be used to classify solvents according to their polarity.

DLS was used to compare the size distribution between $CuInS_2$/ZnS QDs, prepared with and without the assistance of non-polar solvents (Figure 10). The resulting diameters of both QDs were ~32–33 nm (Figures 10(a) and (b)). CuInS2/ZnS QDs had a luminescence quantum yield of 2.95% without the use of a solvent (Figure 10(c)). We believe that QDs disperse in water both in the existence and absence of a non-polar solvent because of DDT breaking away from $CuInS_2$/ZnS QDs.

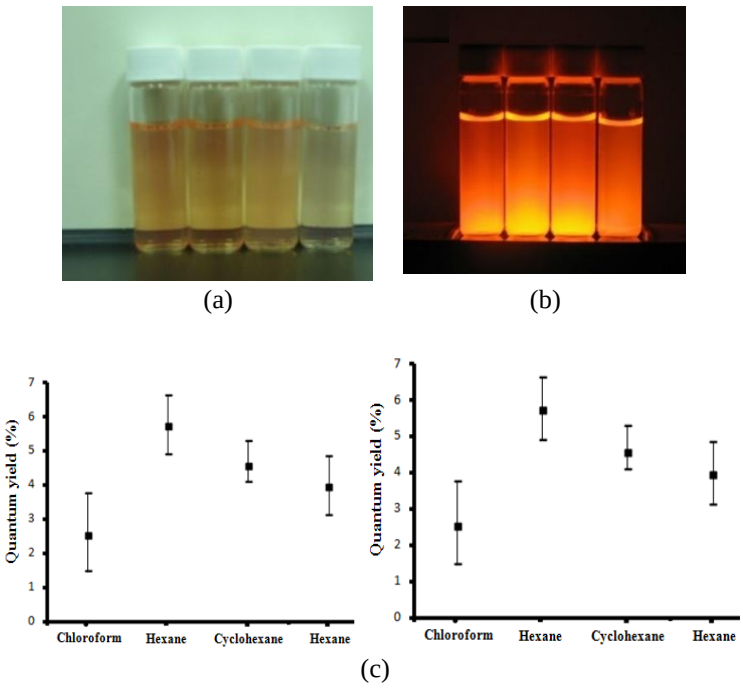


Figure 8. Water-assisted dispersal of $CuInS_2$/ZnS QDs in non-polar solvents (toluene, hexane, cyclohexane, and chloroform) under (a) room light, (b) UV light, and (c) shows the quantum yield

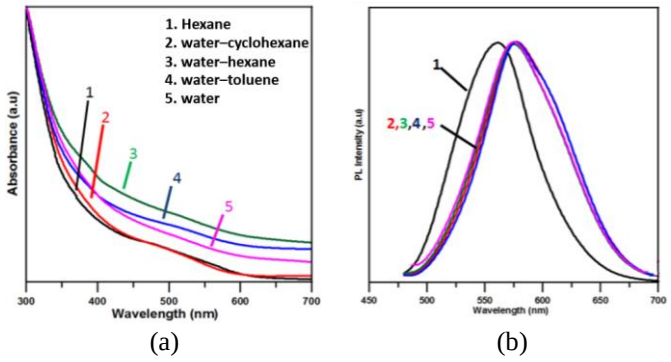
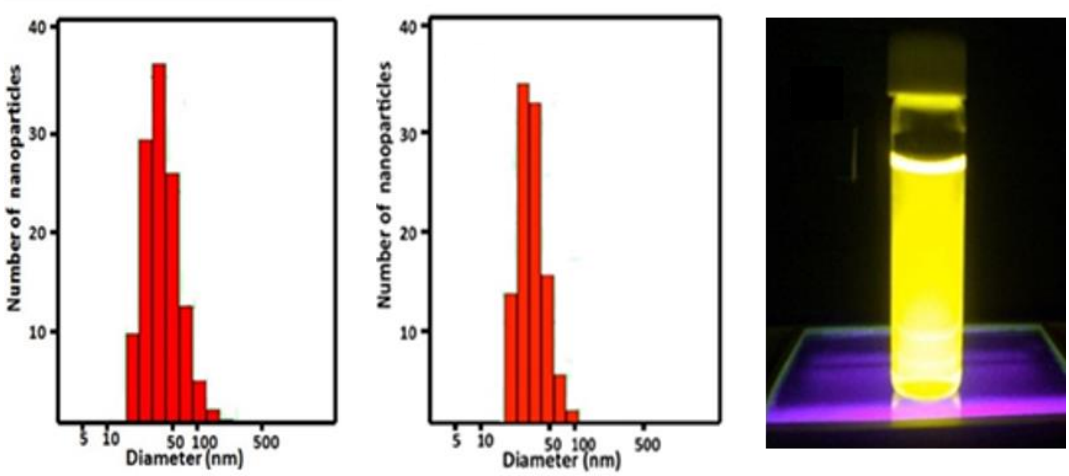


Figure 9. Emission spectra curve of $CuInS_2$/ZnS QDs (a) absorption and emission spectra of $CuInS_2$/ZnS QDs and (b) fluorescence emission spectra of $CuInS_2$/ZnS QDs

Table 1. The dispersion of $CuInS_2$/ZnS QDs with non-polar solvents (toluene, hexane, cyclohexane, and chloroform) in polar solvents (water, acetone, and DMF)

Polar solvent	$CuInS_2$/ZnS QDs in non-polar solvent			
	Toluene (C_6H5CH_3)	Hexane (C_6H_{14})	Cyclohexane (C_6H_{12})	Chloroform ($CHCl_3$)
Water (H_2O)	Dispersed	Dispersed	Dispersed	Dispersed
Acetone (C_3H_6O)	Dispersed	Dispersed	Dispersed	Dispersed
DMF (C_3H_7NO)	Dispersed	Dispersed	Dispersed	Dispersed



(a) (b) (c)

Figure 10. Particle diameter distribution of $CuInS_2$/ZnS QDs (a) assisted by a non-polar solvent at a sonication amplitude of 50, (b) assisted by water at a sonication amplitude of 80, and (c) photographs of water-dispersed $CuInS_2$/ZnS QDs prepared without solvent assistance

4. CONCLUSION

In summary, a fast and facile method for preparing water-dispersed $CuInS_2$/ZnS QDs by an ultrasonic process has been developed. Ultrasonic waves can be used to decrease the operation time and avoid precipitation in the transferring process of QDs. The presence of hydrogen bonding between hydrogen and sulfur, and in aqueous solutions (between water, acetone, and DMF) causes $CuInS_2$/ZnS QDs to be soluble in aqueous solutions. Hexane, as a non-polar solvent that gave the highest quantum yield on water-soluble QDs, was used successfully as a HepG2 cellular fluorescence marker. Thus, the biocompatible $CuInS_2$/ZnS QDs are exceptionally auspicious material for cancer bio-imaging and other medical applications. Further, the dispersion of $CuInS_2$/ZnS QDs in water, without the assistance of a non-polar solvent, was demonstrated and still capable of transferring QDs. Higher amplitudes and longer operation times can be employed as alternatives to non-polar solvents like toluene, cyclohexane, hexane, and chloroform for dispersing $CuInS_2$/ZnS QDs in aqueous solutions. We believe that the method presented in this paper can be readily extended to other QDs.

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