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## Fast and easy synthesis of core–shell nanocrystal (CdS/TiO<sub>2</sub>) at low temperature by micro-emulsion under ultrasound

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### ABSTRACT

CdS nanoparticles were easily combined with TiO<sub>2</sub> through a reaction in micro-emulsion by means of ultrasonic irradiation. The formation of a uniform layer of TiO<sub>2</sub> on the CdS led to an increase of the size of nanoparticles. This is due to the appearance of a core–shell structure between the two combined semiconductors with a strong interface between them. TiO<sub>2</sub> shell depths were in the range of 1.4–2.3 nm. Nano-scale depths of TiO<sub>2</sub> layers on the CdS can be easily controlled by adjusting the concentration of TTIP (titanium tetra-isopropoxide). Important variables such as the preparation method, molar ratio of the reactants, and time of sonication were investigated. Ultrasonic irradiation can control the hydrolysis and condensation of TTIP and the formation of a gradient TiO<sub>2</sub> shell around the CdS core. The nanoparticles were characterized by X-ray diffraction (XRD), UV–visible spectroscopy, energy dispersed analysis of X-ray (EDAX), HRTEM, SEM, and surface area measurements (BET).

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### 1. Introduction

In recent years, semiconductor nanocrystals have attracted a great deal of attention due to their unique size-dependent optical properties. These materials have been investigated for their potential applications in photovoltaic cell, optical sensor device and photocatalysts [1–8]. Among them, the composites made of two or more semiconductor components have been recognized as attractive materials for using in solar cells, water splitting, organic decomposition, and photovoltaic devices [5,9–13]. This kind of composites can develop a high efficiency photocatalyst activated by visible light. They can also compensate the disadvantages of the individual components, and induce a synergistic effect such as an efficient charge separation and improvement of photostability [10,11].

One of the most serious problems of these materials is the tendency to form defects and surface-trap state under the growth conditions. This behavior leads to a low luminescence efficiency and photostability, especially when the sizes of quantum dots are less than 2 nm [14]. Many efforts have been made to overcome the problems, including the passivating with heterogeneous organic or inorganic shells to optimize their photostability [15–17]. It has recently shown that [7,15,16,18,19] the tunable optical proper-

ties can be achieved by modulating their compositions and internal structures in multi-component nanocrystals. For the synthesis of various core–shell nanocrystals, a lattice matching requires between shells and core materials to achieve a better passivation and minimize the structure defects [18–21]. In addition, the shells should have larger electronic band gap than the core to obtain higher quantum yields. Blocking the trap states by coating a thin shell of a wide band gap semiconductor can lead to a drastic enhancement of the photostability [15,16,22] with respect to the single phase nanoparticles and organic dyes.

CdS is a fascinating material with ideal band gap energy (2.4 eV). It is very unstable against photocorrosion in aqueous solutions. To overcome this problem, CdS has been combined with a wide band gap semiconductor such as ZnO and TiO<sub>2</sub> [9,11,23]. These materials improve the charge separation of photogenerated electrons and holes. In addition to the flat band potential of the components, the photocatalytic performance of the coupled semiconductors is also related to the geometry, the crystallinity, the size, and the surface contact of the particles [11,24,25]. These parameters strongly depend on the manner that the couples are prepared. Hence, various coupling nanocrystals are extensively studied through different methods like precipitation [13], solvothermal and sol–gel [9], chemical bath deposition [16], precipitation and sol–gel [26], micro-emulsion [27,28] and ultrasound [29,30].

In conventional synthesis of the coupled semiconductors like micro-emulsion, long time (at least 20–24 h of aging) and high

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temperatures (200–400 °C) requires for improving the contact of the two components and their crystallinity [27,28,31,32]. But, the preparation of uniform nanoparticles with ultrasound is easy and more effective under mild conditions [29,33,34]. This is due to high temperatures produced during the cavitation which can facilitate the crystallization of the semiconductors [35,36]. Our recent works confirmed that the synthesis of nanocrystal is easier with ultrasound than other methods [37,38]. Additionally, acoustic cavitation produced by ultrasonic waves can strongly increase the surface area and the mass transfer between the two phases [39,40]. It seems that the combination of ultrasound and micro-emulsion is a suitable method for the synthesis of coupled semiconductors. This combination could be useful for the control of crystal phase, morphology, and size of the nanoparticles. It has recently reported that ultrasonic treatment enhances the uniformity of nanoparticles obtained and improves the coating and formation of core-shell nanomaterial [1,30,41–45] in comparable with those reported already [46–48].

To the best of our knowledge, there is no report on the preparation of CdS/TiO<sub>2</sub> nanocomposite based on micro-emulsion under ultrasound. In this study, CdS nanoparticles were combined with TiO<sub>2</sub> and leading to a core/shell type nanocrystals, through a simple sonochemical reaction in micro-emulsion medium. We have used this method to reach a highest uniformity of core-shell nanoparticles under mild conditions. Without any post-thermal treatment, the nanocomposite crystals prepared with a better control of the deposition of TiO<sub>2</sub> on CdS in a short time.

## 2. Experimental

### 2.1. Materials

Ethylenediamine, sulfur, p-xylene, titanium tetra-isopropoxide (TTIP), CTAB and 1-butanol from Merck and CdCl<sub>2</sub>·2H<sub>2</sub>O from Fluka have been used without further purification. De-ionized water was used for the sample preparation.

### 2.2. Synthesis of nanoparticles

First, 1000 mg of sulfur was dissolved in 50 mL of p-xylene at about 313 K. Then, a quaternary oil-in-water micro-emulsion formed by CTAB/1-butanol/p-xylene/water with a proper ratio and used as a reaction medium for CdS nanoparticles preparation. The composite of micro-emulsion was set with weight ratio between oil and CTAB, water and oil, co-surfactant and surfactant at 0.6, 44, and 2 respectively. The micro-emulsion was prepared in two separate parts (A = 80% and B = 20% w/w). The part of A contained sulfur (37.8 mg) in oil phase and the part of B contained cadmium chloride (0.025 M) and ethylenediamine (0.41 M) in aqueous phase of micro-emulsion. The clear micro-emulsion of B was added slowly into clear micro-emulsion of A. The mixed micro-emulsion was irradiated with ultrasound (20 kHz Sonifier W-450, output acoustic power 45.5 W (amplitude%75), horn with 1.9 cm diameter) for 10 min. During sonication, the temperature was increased from 30 °C to 60 °C by stopping the circulating bath. Nucleation processes were began in initial times and after 5 min a large amount of nuclei was formed. Then 0.25 mL and 1.0 mL titanium isopropoxide were added in separate experiments drop by drop (the mole ratio of TiO<sub>2</sub> to CdS was 2.5 and 6.0).

The precipitate was separated by centrifugation, washed with distilled water and then 2–3 times with absolute ethanol for removing the excess surfactant, and then dried in a dessicator at room temperature. Another sample was prepared by stirring method under the same conditions of sonication method.

### 2.3. Characterization of nanoparticles

The structure and morphology of the final products has been studied by transmission electron microscopy (HRTEM, Hi-TEM is Hitachi 300 kV H-9500 TEM with accelerate voltage 300–100 kV and resolution 0.1 nm for crystal lattice and 0.18 nm for point to point), X-ray diffraction (XRD) patterns were recorded in a wide angle range ( $2\theta = 10\text{--}70^\circ$ ) by Bruker-axs, D8 Advance in scanning step of  $0.02^\circ/\text{s}$ , with monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The optical properties of the nanoparticles were studied by UV-Vis spectroscopy (Unico 2800). The energy dispersed analysis of X-ray (EDAX) was carried out using a Philips, XL30 model, and the surface area measurement (BET) was done by MONOSORB and the out-gassing of the samples were carried out at 85 °C for 3 h. The SEM analysis was carried out by LEO1450VP made in Germany.

## 3. Results and discussion

### 3.1. Mole ratio of TiO<sub>2</sub>/CdS

Fig. 1 shows the XRD patterns of TiO<sub>2</sub>/CdS nanoparticles at two different mole ratios. The most intense peaks at angles ( $2\theta$ ) 25.1°, 48.1°, 62.5° correspond to (1 0 1), (2 0 0), (2 0 4) planes of the anatase phase of TiO<sub>2</sub>. Meanwhile, additional prominent peaks at angles ( $2\theta$ ) 24.7°, 26.5°, 28.3°, 43.8°, 48.1° and 51.8° could be indexed to the reflection from (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 0 3) and (1 1 2) planes of hexagonal structure of CdS. The relatively low intensities and broadness of X-ray diffraction peaks are assumed to arise from

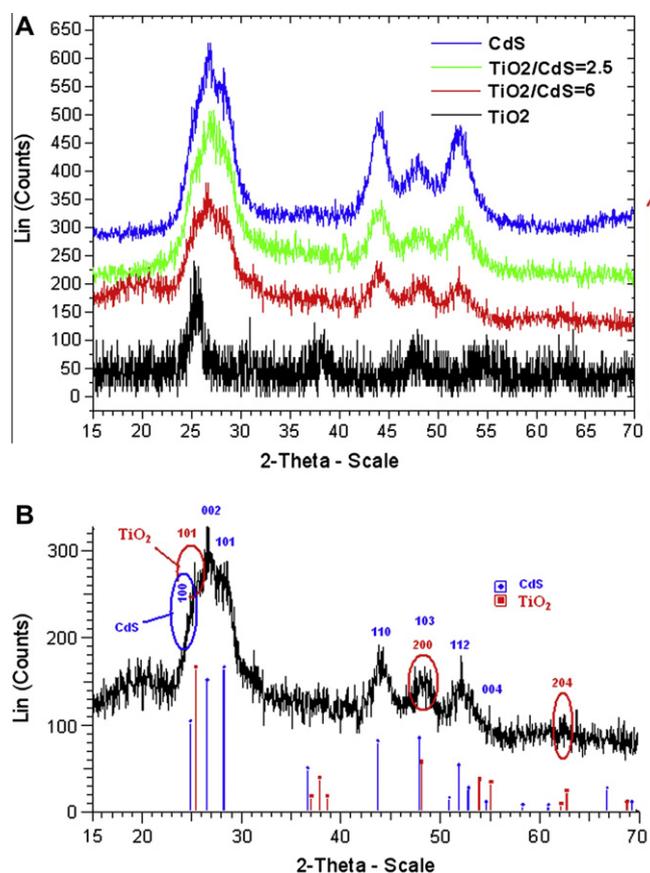


Fig. 1. (A) X-ray diffraction patterns of the samples with different molar ratios and (B) X-ray diffraction pattern of the sample with molar ratio of 6.0 (irradiation time 1.5 h).

the fact that the particles are nano-sized and the TiO<sub>2</sub> is thinly coated on the CdS [43]. The sample prepared at lower ratio (2.5) did not show the main peak of the anatase phase of TiO<sub>2</sub>. This is indicating a low thickness of TiO<sub>2</sub> shell or a high dispersion of TiO<sub>2</sub> with the less crystallinity on the CdS [49]. The presence of low amount of TiO<sub>2</sub> on the CdS can reduce the intensity of the peaks related to the CdS. At higher ratio (6.0), the intensity of the peaks of CdS is more reduced with respect to the lower ratio. In addition, Fig. 1B shows the diffraction peaks of the anatase TiO<sub>2</sub> phase which is due to the thicker thickness of the shell. It indicates that TiO<sub>2</sub> nanoparticles at higher ratio had a better crystallinity.

The nanocrystal morphology and the growth of the shell are further characterized by the high resolution-transmission electron microscopy (HRTEM). Fig. 2 shows the images of the TiO<sub>2</sub>-coated nanoparticles with core-shell structure. These images show that TiO<sub>2</sub> is uniformly coated on the surface of CdS and lead to an enlargement of the nanoparticle size. The average size of the bare CdS nanoparticles was about 2–3 nm in diameter and in case of core-shell structure, the size was found to be about 9.0 nm for mole ratio 2.5 and about 15.6 nm for mole ratio 6.0. The particle size can be easily controlled by controlling the amount of reactants (Table 1). At higher concentration of TTIP, the TiO<sub>2</sub>-coating depths are about 1.4–2.3 nm. Thus, various CdS nanoparticles with different TiO<sub>2</sub>-coating depths can be formed in this system. Moreover, the core is directly used without any purification in this work. We expected the formation of alloyed cases without abrupt boundary between core and shell under such condition. But, we observed core-shell nanocrystals with the strong interface between core and shell in contrast to the case of CdTe/CdS [21].

It should be noted that the rapid synthesis of nanocomposite with a suitable homogeneity under the described sonochemical conditions might be attributed to the physical and chemical effects of cavitation. For example, the rate of hydrolysis of TTIP can be highly accelerated by several orders in the presence of ultrasound [43].

In the stirring method, the SEM and TEM images (Fig. 2c–e) indicate that TTIP hydrolysis in the presence of CdS nanoparticles led to the formation of large irregular aggregates. This aggregation with extremely heterogeneous distribution was achieved under the same conditions as sonication method. Hence, treatment of solutions with power ultrasound not only disperses solid particles

**Table 1**

Surface and size of different nano-particles (the size deduced from the full width at half maximum of the second sharp peak).

Sample	Size crystal (XRD) (nm)	Size (TEM) (nm)	Surface (m <sup>2</sup> /g)
CdS	2.19	<5	84.1 ± 0.3
TiO <sub>2</sub> /CdS = 2.5	5.16	9–10	133 ± 3
TiO <sub>2</sub> /CdS = 6	7.28	15–16	22.2 ± 4.3
TiO <sub>2</sub> (500 kHz) [38]	4.8–4.9	<8	317 ± 1
TiO <sub>2</sub> (20 kHz, method microemulsion)	7	–	225 ± 7

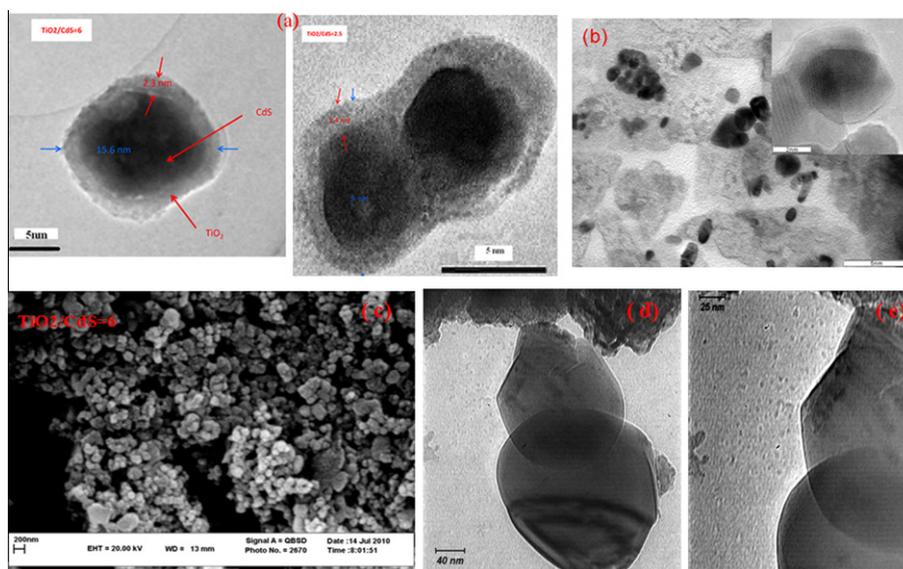
in the liquids but also provides a unique set of conditions to produce uniform coating. Furthermore, it should be mentioned that such a thin and homogeneous coating cannot be obtained through other methods such as the chemical bath deposition method or dip coating [46–48].

### 3.2. Effect of preparation method

The preparation method has an important role on the structure and properties of the composites. Two methods were applied for the synthesis. One method was explained in the experimental section (method a). In another method (b), the micro-emulsion was sonicated by 20 kHz apparatus for 10 min which led to a yellow precipitate (CdS). Then, the TiO<sub>2</sub> powder synthesized by 500 kHz in our laboratory [38] was dispersed in alcohol and added into the yellow mixture prepared by 20 kHz ultrasound. The procedure was followed by further sonication for 30 min. During the sonication, the temperature was about 60 °C. The crystalline phases of the products were determined by X-ray diffraction (Fig. 3). In method (b) the products were different than method (a) which led to a core-shell structure. In another words, a mixture of anatase (TiO<sub>2</sub>) and hexagonal (CdS) nanocrystals was appeared in method (b).

### 3.3. Time of sonication

Fig. 4 shows the XRD of the nanocomposites at three different times of sonication. After 30 min of sonication, one small peak



**Fig. 2.** HRTEM images of the samples under ultrasound: (a) two different molar ratios and (b) pure CdS synthesized by ultrasound in 45 min. Stirring method under the same conditions as ultrasound: (c) SEM, (d) TEM, and (e) Zoomed TEM.

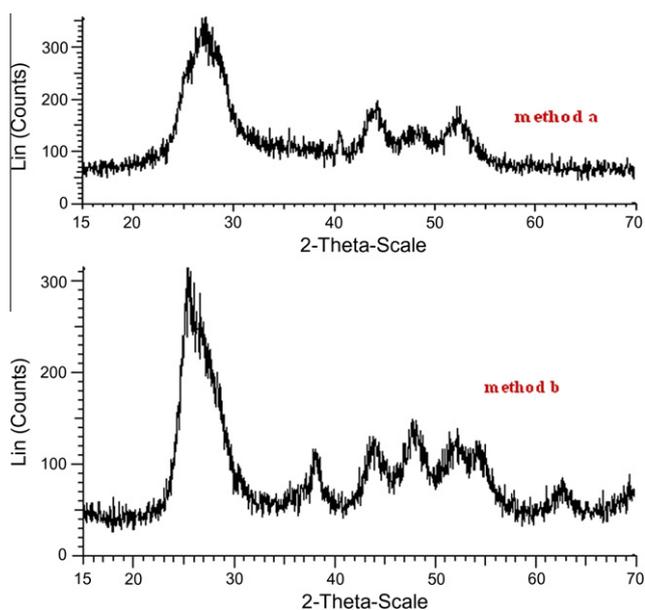


Fig. 3. Effect of two different preparation methods on the structure of nanocomposite.

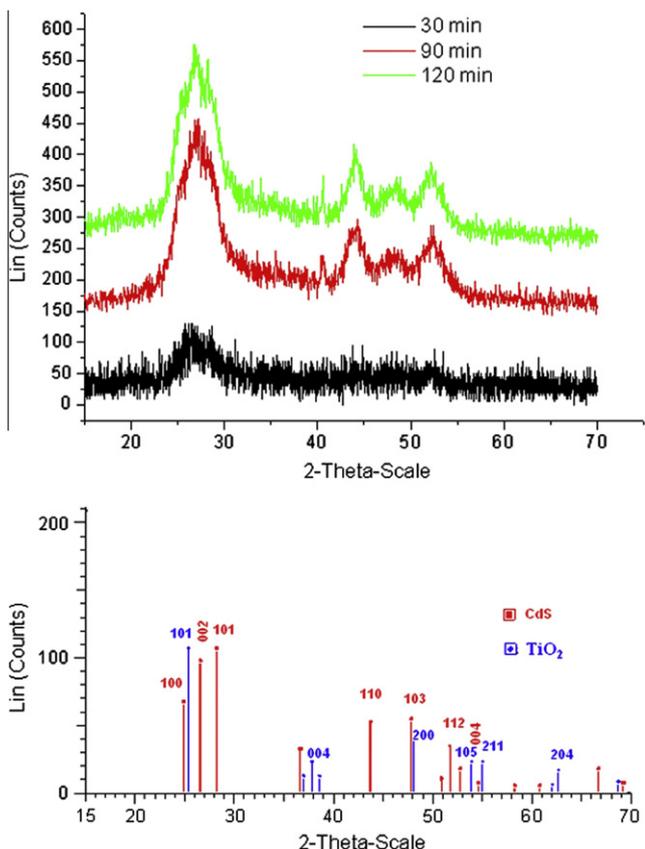


Fig. 4. X-ray diffraction patterns of the prepared composite at different sonication times (mole ratio = 2.5).

appears which shows that the particles are mostly amorphous for this time of sonication. By increasing the time of sonication to 90 min and 120 min, the XRD peaks became sharpness in longer sonication times. Compared to the conventional synthesis which requires thermal treatment at 673–723 K to induce and improve

the crystallinity of the chemically deposited layer [9,26–28,50], sonochemical preparation is more effective as it takes advantage of the ultrasonic power for the crystallization of TiO<sub>2</sub> and CdS [37,38]. The crystalline TiO<sub>2</sub> can be formed in the dispersion and inherently bound on CdS particles without any post-thermal treatment. Based on the Debye–Scherrer equation, the average particle size is estimated to be about 8 nm from the half-width of the XRD peak of the 1 0 1 plane. The enhancement of the crystal phase of the composite in the presence of ultrasound should be explained according to the cavitation process. The chemical and physical effects of ultrasound arise from acoustic cavitation. When a bubble is formed in the micro-emulsion system, there is a possibility for small droplets of oil to accumulate at the interface of the bubble produced by ultrasound (model in our earlier work [37]). This behavior arises from the higher tendency of the oil droplets for the bubble interface than water phase. The implosion of bubble generates many local hot spots in the solution and promotes the reactions. The formation, growth and crystallization of composite nuclei are accelerated under these conditions. A high temperature produced during the cavitation can facilitate the crystallization of the product. It means that the hot spots produced during sonication play a role the same as calcination process.

### 3.4. Mode of sonication

Sonochemical reactions are also sensitive to the mode of sonication (i.e. continuous or pulse). The nanocomposites were prepared by 20 kHz ultrasound with continuous and pulse modes. The time-scale for the pulse mode was selected at 30 s on and 30 s off, and the total time was 180 min (the pure sonication time was 90 min). During the sonication, the temperature was about 60 °C. Fig. 5 shows that the sharpness of the XRD peaks is almost similar for both methods.

In some cases, ultrasound irradiation in an “on-off” mode may be more effective than the continuous one. This is due to more utilizing of hydroxyl radicals and a better temperature control for this kind of processes [51].

The measurement of the surface area confirms that particles formed in continuous mode were smaller than the particle formed under pulse mode (Table 2).

### 3.5. UV-visible absorption

The UV-visible absorbance spectra of the pure and composite semiconductors are shown in Fig. 6. The absorption band of CdS

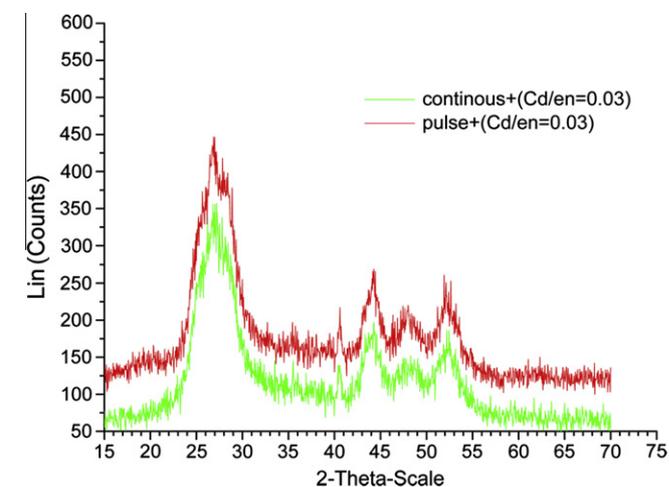
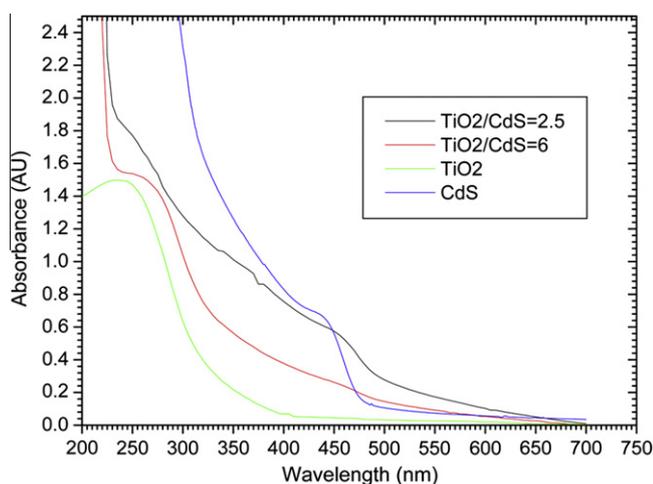


Fig. 5. X-ray diffraction patterns of the prepared composites by applying two different modes of sonication (mole ratio = 2.5, sonication time: 90 min).

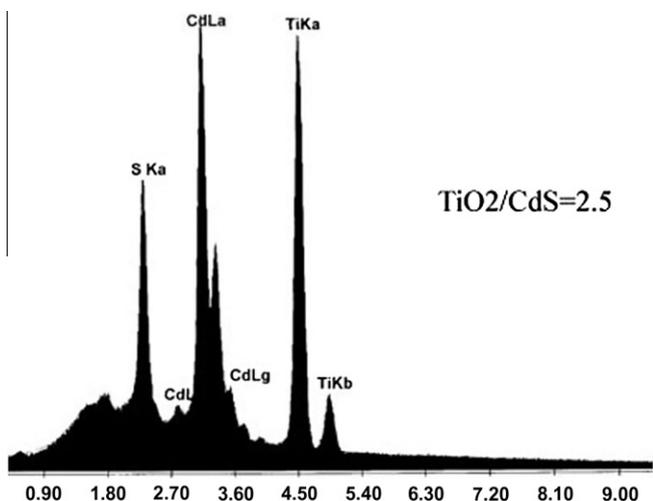
**Table 2**

Effect of sonication mode on the surface and size of nano-composite (the size deduced from the full width at half maximum of the second sharp peak).

Sample	Size crystal (XRD) (nm)	Size (TEM) (nm)	Surface (m <sup>2</sup> /g)
TiO <sub>2</sub> / CdS = 2.5			
Continuous	5.16	9–10	133 ± 3
Pulse	6.35	–	128 ± 3



**Fig. 6.** The UV-vis absorbance spectra of pure and composite semiconductors (sonication time: 90 min).



**Fig. 7.** The EDAX of the nanocomposite.

nanoparticles synthesized under ultrasound was found at around 450–470 nm in comparison with the bulk crystalline which appeared at about 515 nm ( $E_g = 2.4$  eV)[52]. In the case of TiO<sub>2</sub>, the onset absorption for nanoparticles prepared under ultrasound was about 360 nm, while for the bulk it is about 385 nm ( $E_g = 3.2$  eV) [53]. It is found that modification of TiO<sub>2</sub> with CdS particles extends the optical absorption spectrum into the visible region in comparison with that of pure TiO<sub>2</sub> and pure CdS. Increasing the amount of TiO<sub>2</sub> led to a red-shift of the absorption band in composite photocatalysts. The red-shift of spectra are typical characteristics of core-shell nanocrystals, originating from the efficiently diminishing of the surface defects of core nanocrystals

after capping core nanocrystals with higher band gap shells [21]. This is in agreement with the previous report by Kisch et al. that the band gap of CdS employed in composite photocatalysts is shifted by an electronic semiconductor-support interaction [54,55].

The results of EDAX measurement reveal that the core-shell nanocrystals have a high purity and the ratio of Cd/S is nearly 1:1, and that of TiO<sub>2</sub>/CdS is about 2.5:1 (Fig. 7).

#### 4. Conclusions

In the present work we have developed a new method for the synthesis of core-shell nanoparticles through the combination of ultrasonic waves and micro-emulsion (O/W). The composite with strong interface between core and shell was prepared at a relatively low temperature (60 °C) with a larger size than individual ones. The increase of particle size can be attributed to the formation of core-shell structure. The crystalline phases of TiO<sub>2</sub> and CdS in the resulting particles were anatase and hexagonal, respectively. The depth of coated TiO<sub>2</sub> onto CdS nanoparticles can be controlled by this method. The preparation method, molar ratio of the reactants, and time of sonication were important variables on the resulting products. In addition, the optical investigations revealed a red-shift in the absorption by increasing the amount of TiO<sub>2</sub> in the nanocomposite.

Easier workup, higher efficiency, shorter reaction time, better crystallinity, and higher control of coating for preparation of core-shell with uniform shape can be considered as advantageous of this study. This is due to the cavitation process which produces strong shock waves and intense local heating that results in an increase mass transfer and diffusion of species to each other and enhances the crystallinity of the nanoparticles.

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