Photoacoustic Effect of CdS Quantum Dot on TiO₂

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Abstract

The photoacoustic (PA) effect of cadmium sulfide (CdS) quantum dots on titanium dioxide (TiO₂) prepared by successive ionic layer adsorption and reaction (SILAR) method was investigated. The CdS quantum dots were deposited over TiO₂ nanoparticles and CdS: TiO₂ films with different SILAR cycles (0, 2, 4, 6, 8 cycles). The results of maximum acoustic signals were 179.8, 196.8, 221.5, 235.4, and 253.9 μ V, respectively. In addition, the corresponding energy band gap values were 3.34, 2.82, 2.55, 2.5, and 2.35 eV, respectively. The results of the PA measurement showed that the increased number of SILAR cycles improved the visible absorption, and the greatest absorbance at a wavelength of 490 nm is affected by the CdS bandgap energy. The lower the energy band gap, the more absorbance wavelength deviates towards a longer wavelength.

Keywords: Photoacoustic, Cadmium sulfide, Quantum dots, Successive ionic layer adsorption and reaction

1. Introduction

Quantum dot solar cells (QDSCs) are a new development in solar cell research that uses quantum dots as photovoltaic materials. Compared to most well-known materials such as silicon, it is intended for tuning in a wide range of energy levels by varying the size of the quantum dot. Quantum dot solar cells are currently gaining great attention for their high light absorption coefficients and tunable bandgap [1] and have a lower cost than silicon solar cells [2], [3]. For this reason, quantum dot structures (QDs) such as CdS [4], [5], PbS [6], [7], and CdSe [8], [9] have been studied due to their excellent electrical properties. Most of the advantages of QDs regarding energy band gap adjustment depend on the QD's size, which aids in charge separation within the solar cell [10], [11]. CdS is interesting because it absorbs light in the visible range [11] and has an energy bandgap of 2.4 eV [12], [13]. Titanium dioxide (TiO_2) can effectively absorb ultraviolet (UV) radiation and has an energy band gap of 3.0 eV for rutile and 3.2 eV for anatase [14]. Therefore, CdS films grown onto TiO_2 by successive ionic layer absorption and reaction (SILAR) is the process for depositing ions on film. A solution comprising positive and negative ions was used to submerge the film. As a result, the ions can bind to the film and produce new material or quantum dot compound of that type of substrate [14] in order to widen the solar absorption range and modify the energy bandgap according to the number of SILAR cycles [15].

The problem in measuring absorbance in nanoparticles is scattering, preventing accurate absorbance measurements. The scattering problem can be solved using the thermal radiation technique because this technique reduces light scattering problems. The heat radiation emitted by the sample only comes from the light absorbed by the sample [16]. Photoacoustic spectroscopy can measure light absorption and absorbance coefficient [17]. The use of ultraviolet-visible spectroscopy [18] in absorbance measurements still does not solve the problem of scattered light. However, photoacoustic spectroscopy solves the scattering

problem because only the light absorbed by the material is converted to heat energy, causing the air pressure inside the cell to fluctuate and produce a sound signal [17]. Moreover, there are limitations in measuring the absorbance of the materials. Photoacoustic spectroscopy is suitable for measuring samples of opaque materials.

In this work, photoacoustic spectroscopy was applied to measure the absorbance of QD on TiO_2 nanoparticles. The absorption values obtained from photoacoustic are more accurate than other techniques due to direct absorption measurement without scattering effect leading to a more accurate estimate of the energy band gap.

2. Experimental

2.1 CdS QDs film preparation

Titanium dioxide (TiO₂, Degussa P25) reagent grade was bought from Sigma-Aldrich and doctor blade coated onto a glass slide ($0.5 \times 0.5 \text{ cm}$). Doctor blade coating is a technique used to form films with well-defined thickness. This technique uses the stick to spread the film parallel to the glass slide. TiO₂ is placed in front of the film spreading rod and will pass along the same direction as the glass, resulting in a thin film of equal thickness. The TiO₂ was dried at room temperature for 30 minutes and annealed for 1 hour at 500°C.

CdS QDs were synthesized using the SILAR method. The TiO_2 film on glass was immersed in 0.1 M of cadmium nitrate tetrahydrate (Cd(NO₃)₂.4H₂O, 99%) for 30 s and dried in air. The film was then dipped in 0.1 M of sodium sulfide nonahydrate (Na₂S.9H₂O, 98%) for 30 s and dried in air. This process was repeated 2, 4, 6, and 8 times.

2.2 Characterization of materials and QD

The optical properties of CdS QDs were analyzed using photoacoustic spectroscopy (MTEC Photoacoustic Model 300) and UV-visible spectroscopy (UV 2200). Photoacoustic spectroscopy uses a chopper frequency cycle of 80 Hz to obtain CdS QD absorbance data. A wavelength of 400-700 nm is used to measure the absorbance because of well-absorbed wavelength range of CdS. X-ray diffraction (XRD) was used to search for the crystal structure of the samples.

3. Results and discussion

Photoacoustic signals of CdS QDs on TiO₂ prepared by the SILAR method were 0, 2, 4, 6, and 8 cycles were measured. The normalized photoacoustics signal was obtained from the sample signal compared with the carbon black signal, as shown in Fig. 2 b). Fig. 2 a) shows an increase in signal values as the number of SILAR cycles increases.



Fig. 1. The structure of the absorbance layer of CdS QDs film



Fig. 2. a) Photoacoustics signal for CdS QD on TiO_2 prepared with different SILAR cycles and b) Normalized photoacoustics signals

The energy bandgap of CdS QD on TiO₂ at the SILAR 0, 2, 4, 6, and 8 cycles can be obtained from normalized photoacoustics signals, as shown in Fig. 3. The energy bandgap values of CdS QDs on TiO₂ are 3.34 (0 cycle), 2.82 (2 cycle), 2.55 (4 cycle), 2.5 (6 cycle), and 2.35 eV (8 cycle), respectively.

The UV-VIS absorption spectra of CdS QDs on TiO_2 are shown in Fig. 4. As the number of cycles increased, the absorbance increased. The increasing absorbance indicates that the amount of CdS QD on TiO_2 increases, as indicated in Fig. 4 a). The optimal absorbance range is between 400 and 500 nm.



Fig. 3. The bandgap of CdS QD on TiO_2 at the SILAR a) 0, b) 2, c) 4, d) 6, and e) 8 cycles, respectively

The energy band gap can be calculated using the equation.

$$\alpha h \nu = A(h \nu - E_g) n \tag{1}$$

The direct band gap for various immersion cycles is determined by extrapolating the straightline portion to the energy axis. α is the absorption coefficient, A is constant, hv is the photon energy, E_g is the energy bandgap, and n = 0.5 for direct bandgap transition. Tauc's plots of $(\alpha hv)^2$ and photon energy are depicted. Fig. 4 b) shows the energy band gap of CdS QD on TiO₂ wherein the energy band gap of the samples with 2 and 4 SILAR cycles cannot be determined due to low light absorption or high light transmittance of these samples. The energy gap values were 2.15 eV and 2.23 eV for the samples prepared at 6 and 8 SILAR cycles, respectively.



Fig. 4. a) UV-VIS absorption spectra of CdS QDs on TiO₂ at the SILAR 0, 2, 4, 6, and 8 cycles and b) corresponding Tauc plot showing bandgap of CdS QDs on TiO₂



Fig. 5. X-ray diffraction patterns of CdS quantum dots on TiO2 at different SILAR cycles

Fig. 5. shows the X-ray diffraction (XRD) patterns for CdS QD on TiO_2 for undoped CdS and CdS with 2, 4, 6, and 8 SILAR cycles. The diffraction peaks are (101), (004), and (200) of CdS. The Debye-Scherrer formula was applied to find the average crystallite size of CdS QDs.

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

Where *D* is the crystallite size, λ is the X-ray wavelength (0.1541 nm), β is the full width at half maximum of the peak in radians, and θ (theta) is the glancing angle. The average crystallite size of the CdS QDs particles synthesized samples was 4.1 nm.

4. Conclusion

Different SILAR cycles change the energy bandgap to be close to the energy bandgap of CdS and affect TiO₂ films absorbance capability, leading to the absorbance diverging towards visible light, with maximum absorbance at 490 nm. The maximum absorbance obtained is in the CdS absorption wavelength. The increased number of cycles causes a change in the energy band gap, resulting in TiO₂ thin films having a greater absorbance amplitude and improving the visible absorption range. Moreover, increasing the SILAR cycle increases the amplitude of the absorbed wavelengths.

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