Characterization and photocatalytic activity of CdZnS nanoparticles incorporated with medicative leaf excerpt

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The characterizations of synthesized CdZnS nanoparticles with Clitoria ternatea (Asian pigeon wings) leaf extract were done by the chemical precipitation method. The formation of CdZnS nanoparticles with the extract was confirmed by making use of XRD, SEM analysis and EDAX. XRD disclosed the structure and also the particle size. SEM investigation of CdZnS NPs confirmed shape and size. The optical studies were executed for the prepared sample. From the obtained UV-visible spectrum, band gap energy was determined using the Tauc plot. The photocatalytic activity of the processed sample was also analysed.

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1. Introduction

A semiconductor can be treated as a material having a conductivity ranging between that of an insulator and a metal. A vital property of semiconductors is the band gap; a range of forbidden energies within the electronic structure of the material. Semiconductors typically have band gaps ranging between 1 and 4 eV, whilst insulators have larger band gaps, often greater than 5 eV [1].

The thermal energy available at room temperature is more or less 25 meV and is therefore significantly smaller than the energy needed to push an electron across the band gap. This implies that there are a few carriers present at room temperature, due to the high energy tail of the Boltzmann-like thermal energy distribution. It is the capability to regulate the number of charge carriers that produce semiconductors of great technological importance.

Group II-VI semiconductor compounds are compounds composed of a metal from either group 2 or 12 of the periodic table and a nonmetal from group VI. The wide band gap II-VI semiconductor compounds are expected to be very good candidates for high performance applications, such as light emitting diodes and laser diodes for blue and ultraviolet applications. Ternary compounds are one preference to vary the band gap of semiconductors around regularly over a vast energy range. This procedure is highly dependent on the materials as well as the growth techniques.

We have a number of group 2-6 semiconductors such as ZnS, CdTe, CdS, ZnTe etc. The present study concentrates on II-VI ternary alloy semiconductors like Cadmium Zinc Sulphide (CdZnS) nanoparticles. Nanoparticles synthesized by chemical route gives the chance to control their size, distribution and the most important is to improve the crystallinity by altering the concentration of the reagents and their mixing rate at differenttemperature [11]. These small-size nanostructures have an oversized surface to volume ratio, which plays a dominant role in optical properties of the nanostructures. For the good quality nanomaterials, various kinds of capping agents and inorganic shell are used to remove the displeasing sites, which results in the improvement of luminescence intensity. [1]. In the present study CdZnS nanoparticles are

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prepared by using triethanolamine acting as capping agent and surfactant to control the Cd^{2+} and Zn^{2+} ion concentration.

Clitoria ternatea, commonly known as Asian pigeonwings, blue pea or butterfly pea, is a plant species belonging to the legume family. In India, it is respected as a holy flower, used in daily puja rituals. The species name is thought to derive from the city of Ternate in the Indonesian island, from where Linnaeus's specimens originated. In traditional ayurvedic medicine, it is ascribed with various qualities including memory enhancing, nootropic, antistress, anxiolytic, antidepressant, anticonvulsant, tranquilizing, and sedative properties. In traditional Using its extract has also shown its ability to reduce intensity of behavior caused by serotonin and acetylcholine. Its extracts possess a wide range of pharmacological activities including antimicrobial, antipyretic, anti-inflammatory, analgesic, diuretic, local anesthetic, antidiabetic, insecticidal and use as a vascular smooth muscle relaxing properties. This plant includes a long use in ancient Ayurvedic medication for many diseases and the scientific studies have reconfirmed those with modern relevance. The flower can be used to dye natural fibers and is employed by traditional societies in Asia to do so.

2. Experimental details

2.1. Synthesis

CdZnS nanoparticles mixed with Clitoria ternatea were synthesized by the chemical precipitation method. Following chemicals were used for the synthesis. Cadmium acetate ($Cd(CH_3COO)_2.H_2O$) , Zinc acetate ($Zn(CH_3COO)_2.H_2O$), thiourea ($(NH_2)_2.CN$), ammonia (NH_3OH), triethanolamine, TEA ($N(CH_2CH_2OH_3)$). A specific amount of zinc acetate and cadmium acetate was added to water and mixed for 10 minutes using a magnetic stirrer. After stirring some triethanolamine was added to the solution and stirred for 10 minutes. Then ammonia was added to the solution and stirred well for 20 minutes, thiourea was added to the solution and it was colourless. The desired amount of Clitoria ternatea extract was added and stirred well. The solution was then placed in a constant temperature bath of 80°C for 1 hour to avoid any temperature gradient. And obtain a greenish-yellow coloured precipitated solution. The precipitate obtained is CdZnS nanoparticles mixed with Clitoria ternatea extract. The obtained precipitated solution was then centrifuged and washed with deionised water and dried in hot air at 70°C for 1.5 hours, a greenish-yellow powder was obtained. This powder was finely powdered with the help of Agate mortar for ½ an hour.

Photocatalytic activity of CdZnS and CdZnS with Clitoria ternatea at different concentrations was tested by decolourization of MB dye in aqueous solution. The experiments were performed under UV-Visible irradiation without any catalyst, with catalyst and in the presence of NPs. The reaction was set up by adding a pinch of nanoparticles into 50 ml of MB solution in a glass beaker. To obtain equilibrium before irradiating the light, the suspension in the beaker was stirred in dark for few minutes.

During the reaction, the solution of the nanoparticles was kept in room temperature. Different concentrations of MB after each 10 minutes were evaluated to check the reduction of known absorption peak. The relation given below is utilized for calculating percentage of degradation of methylene blue dye.

$$\text{\% of Degradation of MB dye} = \frac{A_0 - A_t}{A_0}$$

where A_0 is the initial absorbance of dye, A_t is absorbance of dye at time t.

2.2. Preparation of extract

Clitoria ternatea extract was prepared as follows, Clitoria ternatea leaves were collected, washed thoroughly with water and then with deionised water. The water content was dried and then crushed using a mortar. The crushed leaves were then squeezed to get the extract.

2.3. Characterisation

The prepared sample was subjected to XRD characterization using a Bruker d_2Phaser X-ray diffractometer. The data were recorded over a range (2□) □from 0° to 80° with a step size of 0.02° and of wavelength 1.50460 Å. The surface morphology of the nanoparticles was determined using Carel Zeiss, EV018 scanning electron microscope. Optical absorption spectra of the synthesized nanoparticles were recorded on the Perkin Elmer UV-visible spectrometer, model-Lambda35 in the wavelength range 190nm to 1100nm. The optical analysis of photocatalytic activity was done using Systronicsdouble beam UV-VIS Spectrophotometer: 2202.

3. Results and discussion

3.1. X-ray diffraction analysis

Figure 1 shows the X- ray diffraction analysis of CdZnS and CdZnS added with Clitoria ternatea extract at two different concentrations 10 ml and 20 ml. It is clearly seen that all the diffraction peaks of the prepared nanoparticles are well indexed as the Zinc blende (cubic) structure. It is observed that the three diffraction peaks corresponds to the lattice planes of (111), (220) and (311), suggests that the contents of Clitoria ternatea have been incorporated into the CdZnS lattice. The average particle sizes of pure CdZnS nanoparticles and Clitoria ternatea (10, 20) added CdZnS NPs, were calculated using the Debye-Scherrer equation, $PS=0.9\lambda/(\beta\cos\theta)$; where $\lambda=0.15418$ nm, is the x-ray wavelength provided from a Cu (α) radiation, β is the FWHM in radians and θ is the Bragg's angle, are 1.38, 1.48 and 1.47 respectively.

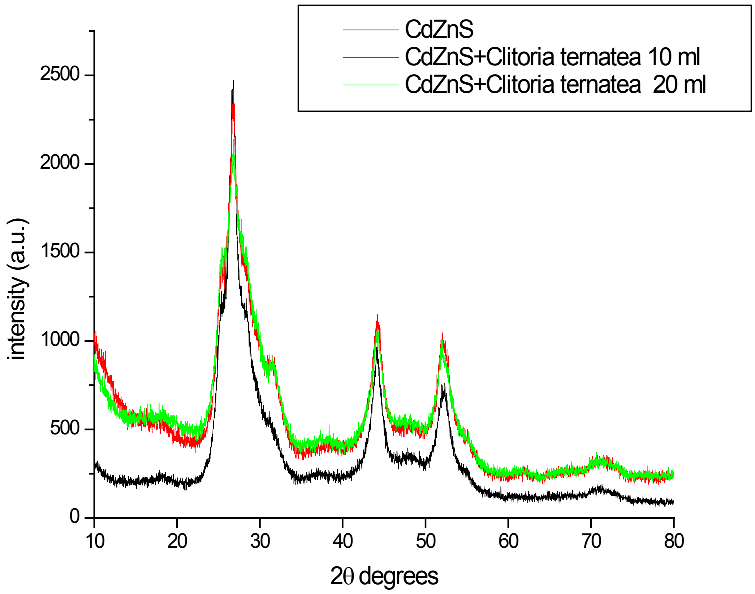

Fig. 1. X-Ray diffraction patterns of CdZnS and Clitoria ternatea (10 ml, 20 ml) added CdZnS nanoparticles.

3.2. Morphological and elemental analysis

3.2.1. Scanning Electron Microscope

The Scanning Electron Micrograph of CdZnS, Clitoria ternatea added CdZnS nanoparticles are shown in figure 2 (a-c). From the image obtained, it is found that the prepared nanoparticles have tightly packed surface morphology. The particle size of the prepared nanoparticles was also confirmed using IMAGE J software

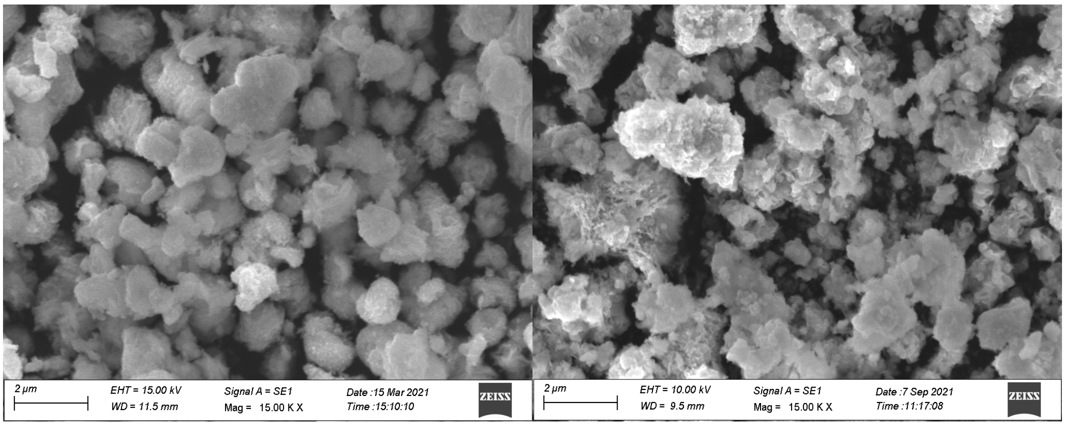

Fig. 2 a, b SEM images for CdZnS, Clitoria ternatea (10 ml) with CdZnS nanoparticles.

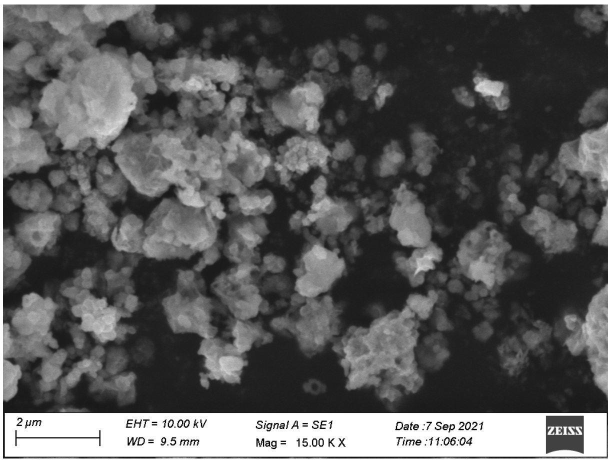

Fig. 2 c SEM image for CdZnS added with Clitoria ternatea 20 ml.

3.2.2. Energy Dispersive X-ray Analysis

The EDAX spectrum was used to confirm the elemental compositions of CdZnS and Clitoria ternatea added CdZnS nanoparticles. The peaks obtained from the spectrums for CdZnS and Clitoria ternatea (10 ml,20 ml) added CdZnS nanoparticles are shown in figure 3.a,b,c respectively, shows the presence of major elements Cadmium, Zinc and Sulphur in the figure and the presence of carbon, nitrogen and oxygen in figures confirms the presence of Clitoria ternatea with CdZnS nanoparticles. The elemental composition analysis for CdZnS and Clitoria ternatea 10ml, 20ml added to CdZnS nanoparticles are shown table 1 a, b, c respectively.

Table 1.a EDAX elemental analysis of CdZnS nanoparticle.

Element	Weight% of CdZnS	Atomic %
Cd	70.60	46.12
Zn	11.53	12.95
S	17.88	40.94

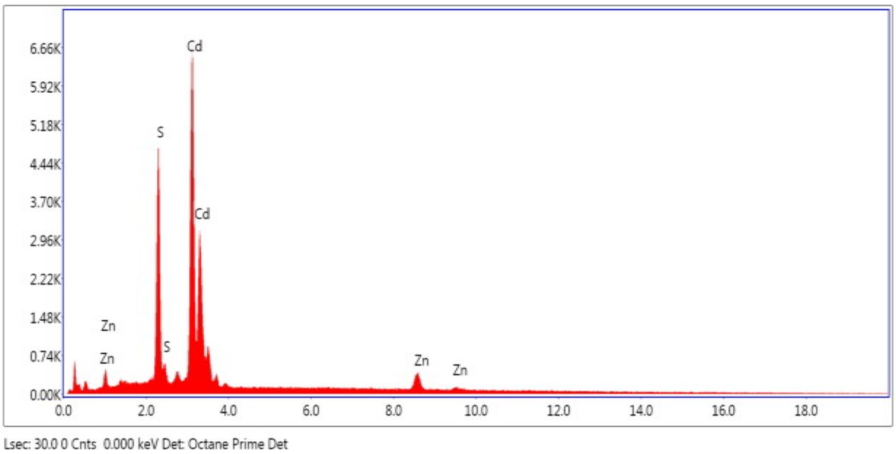

Fig. 3.a EDAX spectrum of CdZnS nanoparticles.

Table 1.b EDAX elemental analysis for CdZnS: Clitoria ternatea 10 ml.

Elements	Weight% of CdZnS: Clitoria ternatea 10 ml	Atomic %
Cd	51.62	16.01
Zn	11.30	6.03
S	13.10	14.24
C	15.83	45.96
O	8.13	17.72
N	0.02	0.04

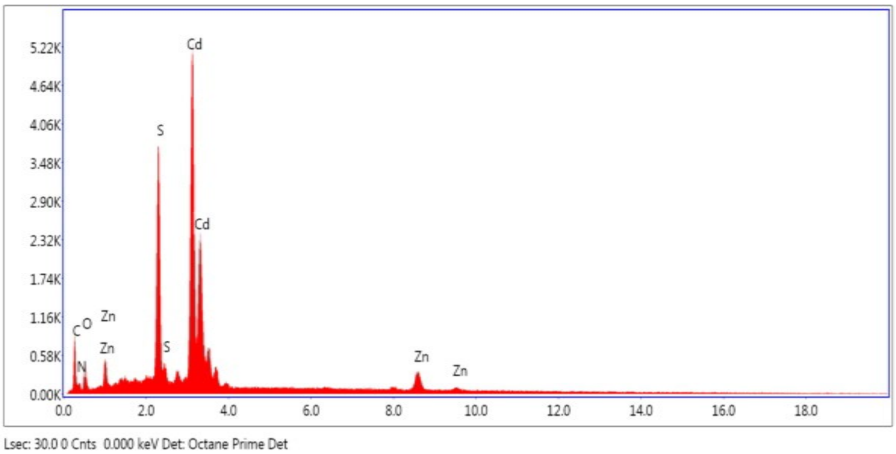

Fig. 3.b EDAX spectrum Clitoria ternatea (10 ml) added CdZnS nanoparticles.

Table 1.b EDAX elemental analysis for CdZnS: Clitoria ternatea 20 ml.

Elements	Weight% of CdZnS: Clitoria ternatea 20 ml	Atomic %
Cd	59.82	20.60
Zn	6.92	4.10
S	13.56	16.36
C	13.16	42.41
O	4.43	10.71
N	2.11	5.82

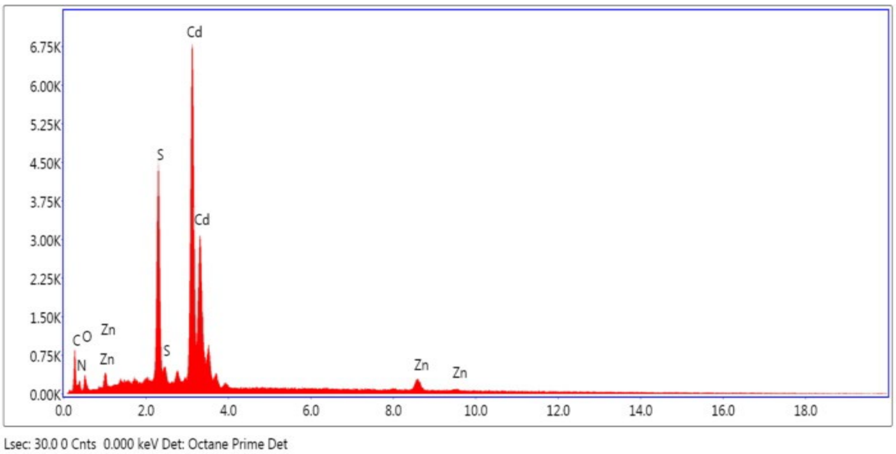

Fig. 3.c EDAX spectrum Clitoria ternatea (20 ml) added CdZnS nanoparticles.

3.2.3. Optical analysis

The optical properties of CdZnS nanoparticles and Clitoria ternatea added CdZnS nanoparticles were investigated. The bandgap energy of the prepared samples was also analysed using UV- visible absorption spectroscopy. Figure 4. reveals the absorption spectra of CdZnS and Clitoria ternatea added CdZnS in two different concentrations in the wavelength range 200-800 nm.

The particle size of the nanoparticles and defects in the structure are factors that can change the absorbance of the samples. The UV-visible absorption spectra show the cut-off absorption of Clitoria ternatea added CdZnS nanoparticles shifts to lower energy (higher wavelength) compared to CdZnS nanoparticles. The absorption edge is found to shift towards a higher wavelength (red shift) ie the bandgap decreases as the particle size increases.

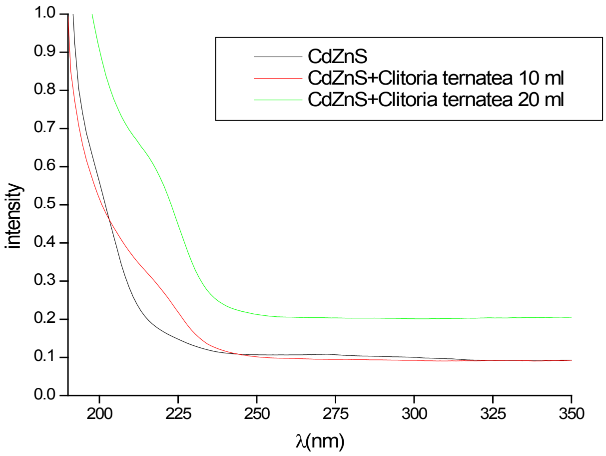

Fig. 4.The absorption spectra of CdZnS and Clitoria ternatea (10 ml and 20 ml) added CdZnS.

The bandgap energy of the synthesised samples was calculated using the Tauc relation

$$\alpha h\nu = C(h\nu - E_g)^n$$

where α is the absorption coefficient, n=1/2 or 2 direct or indirect allowed transition, C is the characteristic parameter for respective transitions, hν is the photon energy, and E_g is the bandgap energy. Plots for CdZnS and Clitoria ternateaadded CdZnS nanoparticle is shown in figure 5.
From the figure, the energy bandgap of Clitoria ternateaadded CdZnS nanoparticles are found to be decreased than the pure CdZnS nanoparticles.

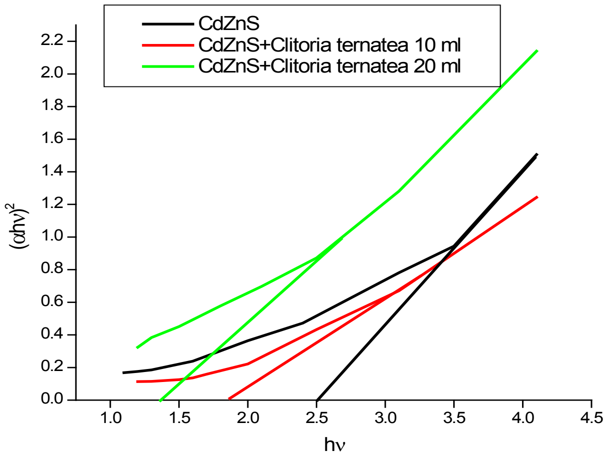

Fig. 5.Plot for bandgap energy of CdZnS nanoparticles and Clitoria ternatea (10 ml and 20 ml) added CdZnS.

3.2.4. Photocatalytic degradation analysis

In the presence of air, the irradiated semiconductor nanoparticles are capable of destroying many organic contaminants. The activation of CdZnS by light produces electron-hole pairs which are powerful reducing and oxidizing agents. To get the response of photocatalytic activities of CdZnS and Clitoria ternatea added CdZnS the absorption spectra of exposed samples at various time intervals were recorded and the rate of decolorization was observed in terms of change in intensity at 665 nm of the dye. MB was used as a test contaminant since it has been extensively used as an indicator for photocatalytic activities due to its absorption peaks in the visible range. Methylene blue shows the most intense absorption peak at 665 nm.

Figure 6 (a) shows the absorption spectrum of CdZnS nanoparticles, the complete degradation of methylene blue takes place within 80 minutes. Figure 6 (b) shows the photocatalytic degradation of Clitoria ternatea added CdZnS nanoparticles. From the plot it is clear that by adding Clitoria ternatea the nanoparticle act the photocatalytic activity of the nanoparticles increased.

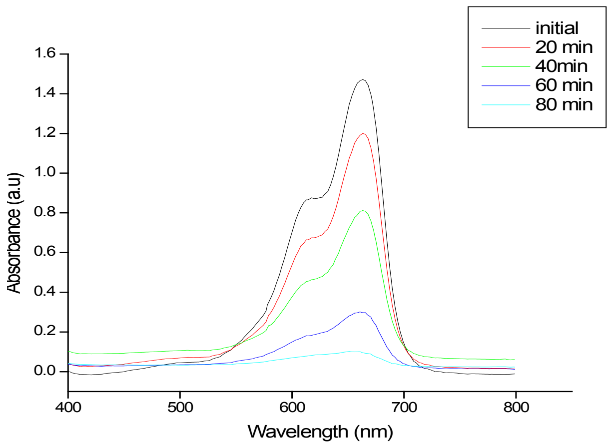

Fig. 6. (a) photocatalytic degradation of CdZnS nanoparticles.

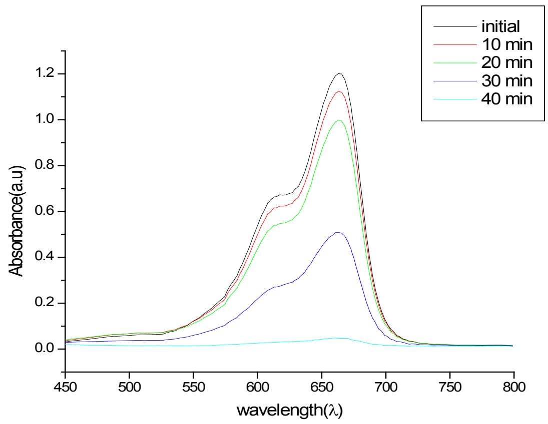

Fig. 6 (b) Photocatalytic degradationof CdZnS added with Clitoria ternatea 10 ml.

4. Conclusion

In the present study, group II-VI ternary semiconductor nanoparticle CdZnS and Clitoria ternatea extract added to the nanoparticles were prepared using chemical precipitation method. Structural, optical, morphological, elemental studies and photocatalytic activities were done. Structural studies were employed using XRD confirms the structure and particle size. The particle size of the ternary semiconductor nanoparticle was increased by adding the plant extract. SEM images give the morphology of prepared nanoparticles. Elemental analysis was done to identify the elements present in the prepared samples. Optical studies were done using UV-Visible spectroscopy; absorbance shows that the cut-off absorption of Clitoria ternatea added CdZnS nanoparticles shifts to lower energy (higher wavelength) compared to CdZnS nanoparticles. The band gap energy was calculated and found to be decreased when Clitoria ternatea added to CdZnS. The photocatalytic activities were also studied, which gives the information that the photocatalytic activity increased by adding the plant extract.

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