

Luma H. Abed
Sahib N. Abdulwahid

Department of Physics,
College of Education for Girls,
University of Kufa,
AL-Najaf, IRAQ



Characterization of CdS@Cu Core-Shell Nanostructures Synthesized by Laser Ablation Method

Core-shell nanoparticles, known for their structural, optical, and electrical properties, being investigated for optoelectronic and medicinal applications. CdS and Cu nanoparticles are synthesized via laser ablation in a liquid media, concentrating on the core-shell technique's effect on laser ablation and CdS@Cu nanoparticle characteristics. Nd:YAG laser pulses at 1064 nm and 480 mJ ablate CdS and Cu nanoparticles in water, with CdS being the core and Cu the shell. Ablation improves crystallinity and CdS production, according to structural studies. The core or shell morphology reduces particle aggregation. UV-VIS spectroscopy, XRD, FESEM, and AFM verify unique features. The CdS@Cu phase is cubic according to XRD. FE-SEM shows 34.2-90.7 nm spherical particle clusters, and AFM confirms synthesis.

Keyword: Cadmium sulfide; Laser ablation; Core/shell; Nd:YAG laser

Received: 30 October; **Revised:** 27 November; **Accepted:** 04 December 2023

1. Introduction

Recently, core-shell nanoparticles made by laser ablation have got a lot of attention for the special things they can do and how they are made. Under this method, a laser is used to vaporize a target material in a liquid. This makes core and shell forms with different properties [1].

The main focus of this study is on making Cu@CdS nanoparticles using a core-shell method and pulse laser ablation (PLA) Fig. (1). Along with judging the nanomaterials' ability to kill germs, the basic ideas and methods used for result analysis will also be talked about.

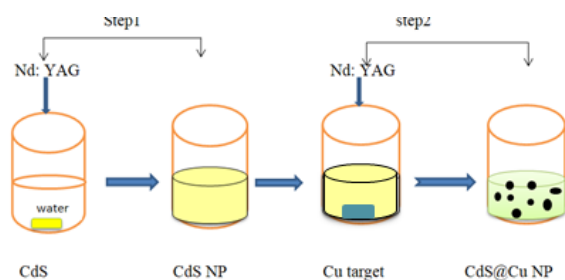


Fig. (1) The preparation process of CdS@Cu nanoparticles

Metal nanomaterials have become popular because they have interesting qualities. Notably, cadmium sulfide (CdS) and copper (Cu) have unique properties at the nanoscale level, which makes them useful in many different ways. There are different ways to make nanomaterials [2,3].

In this work, we use "top-down approaches", which involve using physical [4] or chemical [5] methods to break down large materials into nanoscale ones. Because of its unique electrical and optical qualities, CdS is an important semiconductor that is used in optoelectronics and nanotechnology. Copper

is a well-known metal that has unique physical, chemical, electrical, and heat properties that make it essential in many fields.

PLA can make core-shell nanoparticles that could be useful in health, electronics, and catalysis [6,7]. A high-power pulsed laser is used in this method to cut through a target material, creating nanoparticles with clear core and shell shapes. A high-power pulsed laser, a target material (core), and a liquid around it that has the shell predecessor are the main parts of the setup. When the laser hits the target material, it heats it up and creates a plasma plume that turns the material into smoke and small pieces.

The material that was ablated cools down and condenses in the liquid, making core nanoparticles. The qualities of the core depend on the target material that is used. During this process, a shell material builds up on top of the core nanoparticles. The shell can be made of a different metal, metal oxide, or a polymeric material, based on the properties and uses that the core-shell nanoparticles are meant to have.

This research aims to produce nanomaterials with unique optical, compositional, and structural attributes using the core-shell method via laser ablation. These nanomaterials exhibit superior characteristics compared to those produced using other methods and have shown promise in Applications, which has been validated through research findings.

2. Experimental Part

A quantity of 5 g of CdS powder was subjected to compression using a 5-ton press. Following the necessary preparations, a laser with a wavelength of 1064 nm, specifically an Nd:YAG laser, was employed. The laser beam was directed towards a sample of CdS [8], which was submerged in a liquid medium. To achieve this, a lens with a focal length of

10 cm was utilized to concentrate the laser beam. The distance between the laser and the CdS sample was maintained at 12 cm.

When the target is irradiated, the liquid undergoes a color shift, as depicted in Fig. (2). This color change corresponds to a pulse count of 300.

The core-shell approach, as depicted in Fig. (1), involved the initial placement of CdS in water to obtain the nanoparticle through laser-induced synthesis as the core.

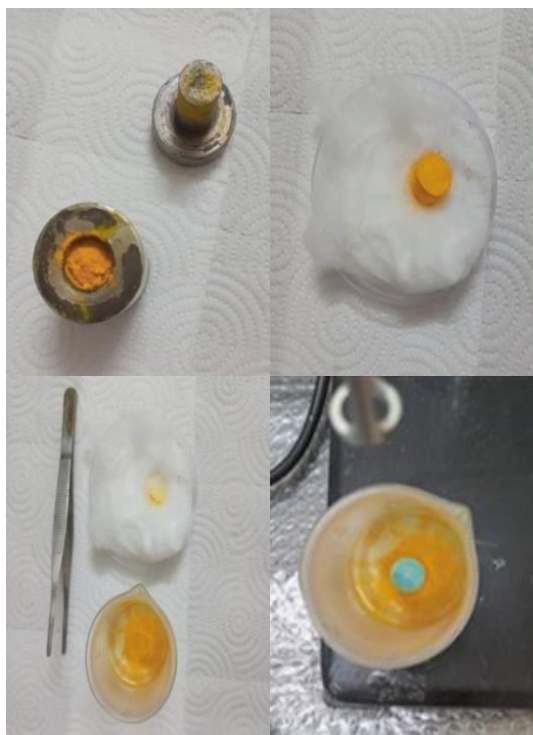


Fig. (2) Steps of synthesis of CdS NPs

Next, a copper (Cu) specimen was subjected to 500 pulses from Nd:YAG laser. The method is meticulously regulated to guarantee consistent covering of CdS particles with the copper layer [9].

The term "plasmon" is derived from the phenomenon of laser-nanostructure interaction, wherein the laser induces a high-energy interaction on the surface. The generation of plasmon's electromagnetic oscillation of electron density occurs as a result of the contact between a laser and a metal surface.

Plasmonic oscillation serves to augment chemical reactions and expedite the diffusion of Cu atoms onto the surface of CdS, as depicted in Fig. (3).

3. Results and Discussion

X-ray diffraction is a significant methodology employed for elucidating the structural characteristics of crystals. It serves as a means to ascertain the atomic configuration, lattice parameters, strain, crystalline size, phase arrangement, and crystalline phases. Figure (4) illustrates the crystalline phase of CdS@Cu nanoparticles that were manufactured using

the process of laser ablation of CdS and Cu pellets (targets) in water, utilizing a laser with a wavelength of 1064 nm. The crystalline phase was then verified through analysis of the XRD pattern. The crystal structure and content were determined by utilizing Cu Ka radiation (1.540\AA) to get an XRD pattern spanning the 2θ range of 10° to 80° . The diffraction patterns generated by CdS@Cu core-shell nanoparticles are illustrated in Fig. (4). The presence of three prominent intensity peaks at specific angles (27.74° , 31.81° , 45.47° , and 53.85°) in the diffraction pattern of CdS@Cu confirms the face-centered cubic (FCC) crystal structure. These peaks correspond to the (111), (200), (004), and (311) diffraction planes, respectively, as indicated by the JCPDS card no. 75-0581 for CdS and JCPDS card no. 00-0333-0492 for Cu. The presence of Cu (JCPDS card no. 04-0836) in the diffraction pattern suggests that the copper atoms have undergone protection and transformation into core-shell nanoparticles of CdS@Cu [10,11]. The Cu atoms exhibit a kinematic diffraction condition, wherein only the metallic peaks of the shell are identifiable. The preference for core-shell structures over alloys and blends arises from the disparity in lattice constants between the two metals, which measures 2.2 nm. The XRD pattern depicted in Fig. (4) provides evidence that the synthesized nanoparticles possess a core-shell nanostructure. The enhancement of crystallinity is facilitated by the creation of a core-shell structure.

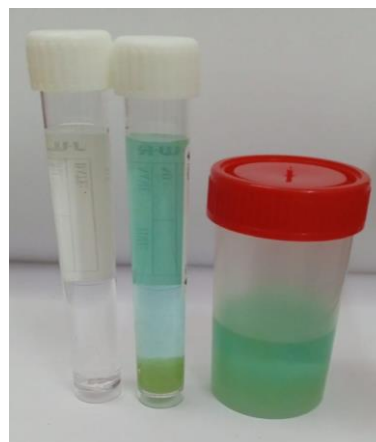


Fig. (3) The CdS@Cu core-shell nanoparticles

Figure (5) presents a 3D AFM image of CdS@Cu nanoparticles, which were synthesized using the core-shell approach using PLA. The substrate exhibits a comprehensive coverage of CdS@Cu nanoparticles, which are evenly dispersed across its surface. The figure clearly demonstrates that the nanoparticles synthesized with laser energy of 480 mJ, as shown in Fig. (5), have a uniform distribution of small, ordered particles. These particles possess a semispherical, tapering shape and are accompanied by the presence of a few monopod rods. The software-assisted estimation yielded an average particle size of around 14.16 nm. The measured particle size is greater than

the value obtained from XRD results. The reason for this distinction is that XRD relies on the measurement of the size-defect free volume, but AFM provides a direct visualization of the grain without considering the extent of crystal defects [8]. The process of particle aggregation is responsible for the production of bigger particles [12]. The surface roughness of CdS@Cu particles was measured using the root mean square method, yielding a value of 2.397 nm. This measurement was obtained using a laser energy of 480 mJ. Additionally, the roughness average was determined to be 1.936 nm, while the average diameter of the particles was found to be 14.29 nm, as indicated in table (1).

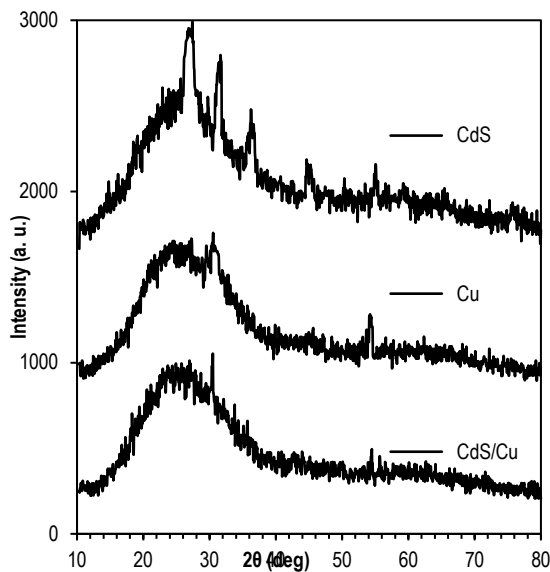


Fig. (4) XRD patterns of the prepared CdS@Cu core-shell nanoparticles synthesized by PLA method

Figure (6) displays the surface morphology of the generated samples, which was examined by the utilization of FE-SEM. The FE-SEM image and accompanying image information (7.01×7.83 inches (512×572); 8-bit, 286k) seen in Fig. (6) reveal that the samples with 4.8 mJ energy have a structural composition characterized by a distribution of spherical particles. The images depict funnel-shaped structures resembling a core-shell configuration. These structures exhibit various variations, including conical cylinders and other geometric shapes. They are characterized by an outer layer encompassing a core. These shapes are distributed across different regions and have an average diameter of 38.42 nm for the sample of CdS@Cu nanoparticles with energy of 480 mJ.

Upon closer examination of the FE-SEM image, it was observed that the samples (CdS@Cu) exhibited a rough surface and high pore size. This characteristic led to a significant increase in the specific surface areas of the samples. This observation is consistent with the findings obtained from AFM analysis. In general, it has been determined that there exists a

direct correlation between laser ablation using the core shell approach and particle size.

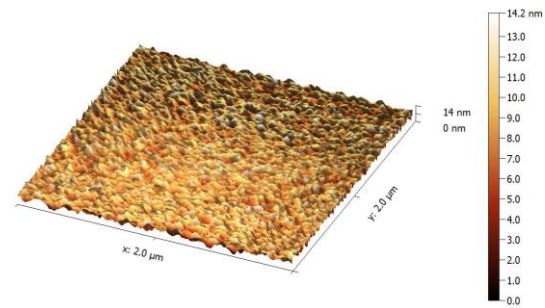


Fig. (5) 3D AFM of CdS@Cu nanoparticles prepared by PLA

Table (1) AFM parameters of CdS@Cu nanoparticles prepared by core-shell PLA

Sample	Root mean square S_q (nm)	Roughness average S_a (nm)	Average diameter (nm)
CdS@Cu	2.397	1.936	14.16

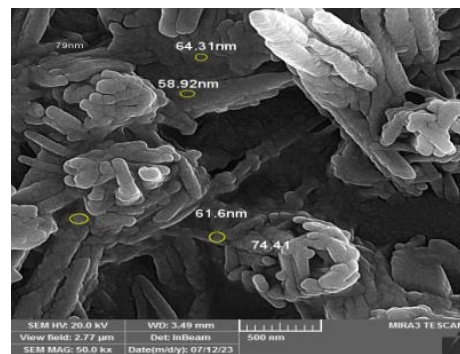


Fig. (6) FE-SEM image of CdS@Cu nanoparticles prepared by core-shell PLA method

The measurements were conducted on a set of 10 particles at the nanoscale level. The findings indicate that the mean diameter of these particles is 38 nm, with the smallest diameter recorded at 38 nm and the largest diameter observed at 73 nm. The standard deviation calculation was applied to analyze the given measurements, revealing an average standard deviation of 17.2. This finding provides confirmation that the particles in question are indeed nanoscale in nature.

Figure (7) depicts the absorption spectra of CdS@Cu nanoparticles that were synthesized using laser energy of 480 mJ. Furthermore, according to Fig. (7), it is anticipated that there will be an increase in absorption as the wavelength goes from 196 nm to 260 nm, with a prominent peak observed at a wavelength of 220 nm.

The transmittance of CdS@Cu nanoparticles synthesized using laser energy of 480 mJ exhibits its lowest value at a certain wavelength. Furthermore, the absorption behavior of these nanoparticles starts to decline beyond 220 nm, which is opposite to the behavior observed in transmittance. The appearance of these peaks can be ascribed to the quantum size

effect. The dependence of both laser energy and the number of laser pulses on the intensity and width of these plasmon peaks was observed. The observation of sedimentation of CdS@Cu following a period of ablation spanning many days aligns with the results documented by Anikin et al. [13,14].

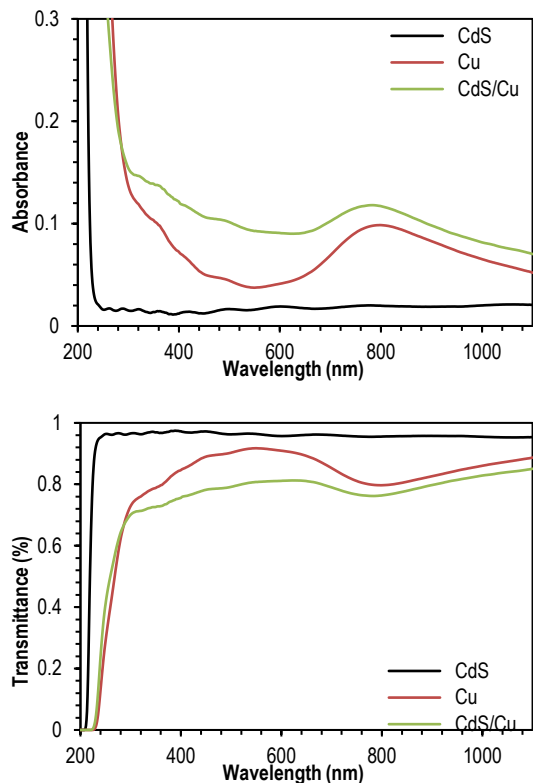


Fig. (7) UV-visible absorption and transmission spectra of CdS@Cu nanoparticles

4. Conclusion

One step synthesis of multi-pod rods and nanoparticles from CdS@Cu was demonstrated and analyzed by using 10ns duration laser ablation of CdS@Cu target in distilled water without using any surfactant. The synthesized nanoparticles are FCC and phase cubic structure of CdS@Cu with morphology and size are controlled by the laser energy. Multi-armed CdS@Cu structures with spherical particles were formed using laser energy of 480 mJ in a funnel-shaped. The existence of highly agglomerated 65nm CdS@Cu particles with nearly equal sizes was confirmed. These nanoparticles synthesized with core-shell method can be advantageously used in many physical applications.

References

- [1] P.V. Kazakevich et al., "Formation of core-shell nanoparticles by laser ablation of copper and brass in liquids", *Solid State Phenom.*, 1(6) (2005) 23-26.
- [2] J. Mohammad and H. Azamal, "**Nanomaterials for Agriculture and Forestry Applications**", in *Micro Nano Technol.*, Elsevier (2020), Ch. 6, pp. 135-166.
- [3] N.A. Singh, "Nanotechnology definitions, research, industry and property rights", *Nanosci. Food Agricul.*, 1 (2016) 43-64.
- [4] M.H. Haji Jumali et al., "Characterization of SnO₂ nanoparticles prepared by two different wet chemistry methods", *Adv. Mater. Res.*, 364(30) (2012) 322-326.
- [5] E. Wiberg, N. Wiberg and A.F. Holleman, "**Inorganic Chemistry**", Academic Press (2001).
- [6] R. Hultgren and P.D. Desai, "Selected Thermodynamic Values And Phase Diagrams For Copper Am) Some of Its Binary Alloys", Incra Monograph I, Int. Copper Res. Assoc., Inc. (NY, 1971).
- [7] P.D. Shankar et al., "A review on the biosynthesis of metallic nanoparticles (gold and silver) using bio-components of microalgae: Formation mechanism and applications", *Enzyme Microbial Technol.*, 95(1) (2016) 28-44.
- [8] N.A. Abd, N.F. Habubi and R.A. Ismail, "Preparation of colloidal cadmium selenide nanoparticles by pulsed laser ablation in methanol and toluene", *J. Mater. Sci.: Mater. in Electron.*, 25 (2014) 3190-3194.
- [9] A. Qona'ah et al., "Synthesis of Colloidal Copper (Cu) Nanoparticles by Pulse Laser Ablation Method (Nd:YAG 1064 nm) in Deionized Water", *Int. J. Sci. Res. Sci. Technol.*, (2022) 147-150.
- [10] C.H. Tsai et al., "Thermal stability of Cu@Ag core-shell nanoparticles", *Corr. Sci.*, 74(1) (2013) 123-129.
- [11] W. Zhang et al., "Designed self-assembled hybrid Au@CdS core-shell nanoparticles with negative charge and their application as highly selective biosensors", *J. Mater. Chem. B*, 3(2) (2015) 217-224.
- [12] A. Pyatenko et al., "Mechanism of pulse laser interaction with colloidal nanoparticles. Laser & Photonics Reviews. (2013) Jul;7(4):596-604.
- [13] A.C. Kuriakose et al., "Modulation of nonlinear optical properties in CdS based core shell nanocolloids fostered by metal nanoparticles", *Opt. Laser Technol.*, 134 (2021) 106626.
- [14] M.H. Rashid et al., "Optical dynamics of copper-doped cadmium sulfide (CdS) and zinc sulfide (ZnS) quantum-dots core/shell nanocrystals", *Nanomater.*, 12(13) (2022) 2277.