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Fabrication of Zn/ZnO Core/Shell Nanoparticles by Laser Ablation in Liquid Technique

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ABSTRACT

In this research, Zn/ZnO Nanoparticles (NPs) were prepared via the Pulse Laser Ablation (PLA) method using three liquids (Ethanol, Acetone, and Distilled Water). Zn/ZnO NPs were synthesized via an Nd-YAG laser with a wavelength of 1064 nm, applied energy of 800 mJ, a frequency of 6 Hz, and 100 laser pulses at room temperature. The Zn metal plate was dipped in Ethanol, Acetone, and Distilled Water, respectively. The UV-Vis results shows sharp and single peaks at 320, 341, and 333 nm for Zn/ZnO NPs in Ethanol, Acetone, and Distilled Water respectively. FTIR testing shows peaks at about 500 cm^{-1} for Zn/ZnO NPs in Ethanol, Acetone, and Distilled Water, which indicates Zn-O stretching vibrations. XRD investigation shows low-angle peaks at 23.31°, 23.81°, and 19.20° for Zn/ZnO NPs in Ethanol, Acetone, and Distilled Water, respectively. In addition, a sharp peak of high intensity was observed at 13.54° for Zn/ZnO Core/Shell NPs in Acetone. These peaks indicate that the structure is stable and undistorted. These patterns emphasize compact pore arrangements. The lower intensity of the gradient peaks indicates that ZnO formed at a preferred site. Nor did high-angle XRD patterns appear, indicating that the formed ZnO NPs are so small to be distinct from background noise or undetectable by widish angle XRD. The broad XRD peak at 2θ angles from 20° to 30° can also confirm that ZnO is low-crystalline. The TEM images show the presence of Zn/ZnO NPs in Ethanol, Acetone, and Distilled Water with a size of less than 50 nm, and TEM analysis confirms that the primary structure of Zn/ZnO NPs is a Core/Shell.

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تحضير جسيمات الزنك/أوكسيد الزنك نَواة/قِشرة النانوية عن طريق تقنية الاستئصال بالليزر في السائل

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الـــخُــلاصـــة

الكلمات المفتاحية:

في هذه الدراسة ، تم تحضير جسيمات الزنك/أوكسيد الزنك (Zn/ZnO) نَواة/قِشرة النانوية بطريقة الاستئصال بالليزر النبضي في ثلاثة أنواع من السوائل (الإيثانول والأسيتون والماء المقطر). تم تصنيع جسيمات الـ Zn/ZnO نَواة/قِشرة النانوية عبر ليزر Nd-YAG بطول موجة ١٠٦٤ نانومتر وطاقة مركزة ٨٠٠ مللي جول وتردد ٦ هرتز وعدد نبضات ١٠٠ نبضة ليزر ، عند درجة حرارة الغرفة. تم غمس صفيحة الـ Zn المعدنية في الإيثانول والأسيتون والماء المقطر على التوالي.. تظهر نتائج الـ UV-Vis قممًا حادة ومنفردة عند ٣٢٠ و ٣٤١ و ٣٣٣ نانومتر لجسيمات الـ Zn/ZnO نَواة/قِشرة النانوية في الإيثانول والأسيتون والماء المقطر على التوالي ، تشير قمم الامتصاص هذه بأطوال موجية قصيرة إلى وجود جسيمات الـ Zn/ZnO نَواة/قِشرة النانوية بأحجام صغيرة جدًا. يُظهر الـ FTIR قممًا عند حوالي ٥٠٠ سم$^{-١}$ لجسيمات الـ Zn/ZnO نَواة/قِشرة النانوية في الإيثانول والأسيتون والماء المقطر وهذا ما يشير إلى اهتزازات تمدد Zn-O. يُظهر الـ XRD قممًا منخفضة الزاوية عند ٢٣.٣١ ° و ٢٣.٨١ ° و ١٩.٢٠ ° لجسيمات الـ Zn/ZnO نَواة/قِشرة النانوية في الإيثانول والأسيتون والماء المقطر ، على التوالي. بالإضافة إلى ذلك ، يُظهر ذروة حادة عالية الشدة عند ١٣.٥٤ ° لجسيمات الـ Zn/ZnO نَواة/قِشرة النانوية في الأسيتون. تشير هذه القمم إلى أن الهيكل مستقر وغير مشوه. تؤكد هذه الأنماط على ترتيبات المسام المدمجة. تشير الشدة المنخفضة لقمم التدرج إلى أن ZnO تشكل في موقع مفضل. كما لم تظهر أنماط الـ XRD عالية الزاوية ، مما يشير إلى أن جسيمات الـ Zn/ZnO نَواة/قِشرة النانوية المتكونة صغيرة جدًا بحيث لا يمكن تمييزها عن ضوضاء الخلفية أو لا يمكن اكتشافها بواسطة الـ XRD عالي الزاوية. أيضًا يمكن أن تؤكد ذروة XRD الواسعة عند زوايا الـ ٢Θ من ٢٠ ° إلى ٣٠ ° أن ZnO منخفض التبلور. تُظهر صور الـ TEM وجود جسيمات الـ Zn/ZnO نَواة/قِشرة النانوية في الإيثانول والأسيتون والماء المقطر بحجم أقل من ٥٠ نانومتر ، ويؤكد تحليل الـ TEM أن الهيكل الأساسي لجسيمات الـ Zn/ZnO النانوية هو نَواة/قِشرة.

الاستئصال بالليزر النبضي
الزنك/أوكسيد الزنك
نَواة/قِشرة جسيمات نانوية

1. INTRODUCTION

Nanomaterial are globally and for a long time become the subject of research and development activities. Nanomaterials have many advantages due to their optical properties, structural properties, and else from properties, because these properties, they have the ability to make significant impacts in the field of electronics, medicine, space exploration, and others [1]. Nanomaterials feature a range of crystalline and amorphous materials from natural and inorganic materials with sizes ranging from 1 to 100 nm. They are categorized into nanoscale materials, nanophase materials, and nanostructured materials [2]. The Nanomaterials are the construction materials for the modern era and their basic construction blocks. The most important pillars of technologies are nanotechnology, biotechnology, information and communication technology, which is one of the criteria for the progress and civilization of nations and an indicator of their rise. Nanomaterials differ according to their source, such as whether they are organic or inorganic, natural or synthetic. Nanotechnology brings together all kinds of scientific possibilities, it is a metric unit known as a nanometer, which refers to one billionth of a meter. The nanostructure size is approximately 80,000 times less than the diameter of a hair. The unexpected results and goals of nanotechnology in the manufacture of materials made it used in all scientific fields, whether in physics, chemistry, biology, and others [3]. The industrial revolution of nanotechnology has made unfamiliar ideas a reality. It provided scientists with many of the important information in all fields. Examples of this are in medicine, such as treating cancer, renewable energy, computers, and others. Therefore, it has become possible to obtain more efficient devices in smaller sizes. They will change life on the planet [4]. Nanotechnology is the manufacture, engineering, and investment of nanomaterials, mainly understanding the links between physical properties and dimensions of materials [5]. Nanoparticles have a great scientific advantage because, in fact, they represent an embankment between bulk materials and atomic structures. A bulk material ought to have fixed physical properties regardless respecting its size, but this is not true for nanoscale materials most of the time. Size-following properties like quantum confinement in particles of semiconductor and surface plasmon resonance in some particles of metals have been observed [6]. One of the most significant methods is the fabrication of nanoparticles via Pulsed Laser Ablation in Liquid, they are used to produce nanoparticles from top to bottom. It is a plain and inexpensive method, that demands “a liquid system, a target metal, and a Laser system.”The mechanism of nanoparticle figuration is complicated and is as yet not completely comprehended.

2. EXPERIMENT SETUP

Zn/ZnO NPs were manufactured using Pulsed Laser Ablation in three types of liquids; Ethanol, Acetone, and Distilled Water. A piece of highly purified Zn was put at the bottom of a Pyrex container containing 2 ml of Ethanol, Acetone, and Distilled Water, respectively. The distance between the target and the laser source was 100 mm, the focused energy was 800 mJ, the frequency was 6 Hz, the wavelength was 1064 nm for the Nd-YAG laser, and the number of applied laser pulses was 100 pulses. The latter was done at room temperature. The experiments were conducted at the (Department of Physics, Faculty of Science, University of Kufa, IRAQ).

3. RESULTS AND DISCUSSION

3.1. Ultraviolet-Visible Spectrophotometer

Figures (1), (2), and (3) show the UV-Vis absorption spectra of Zn/ZnO NPs prepared in three types of liquids. The absorption peaks at 320, 341, and 333 nm were observed for Zn/ZnO NPs in Ethanol, Acetone, and Distilled Water, respectively. These absorption peaks at the short wavelength indicate the presence of Zn/ZnO NPs of a very small size. As it is well known, as the size of Zn/ZnO NPs lessen, the UV peak was inclined to go to the blue-wavelength zone which is well known by the “blue shift” as an outcome of the quantum size effect. This means that the size of the Zn/ZnO NPs is very small. These outcomes match primarily in agreement with the literature [7,8,9,10].

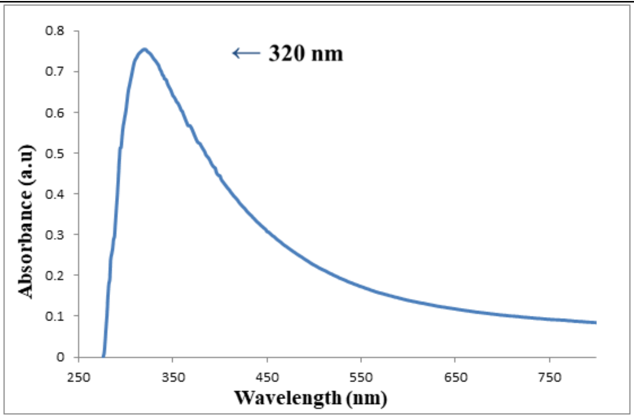

Figure 1: UV-Vis Spectrophotometer of Zn/ZnO NPs Prepared via PLA in Ethanol.

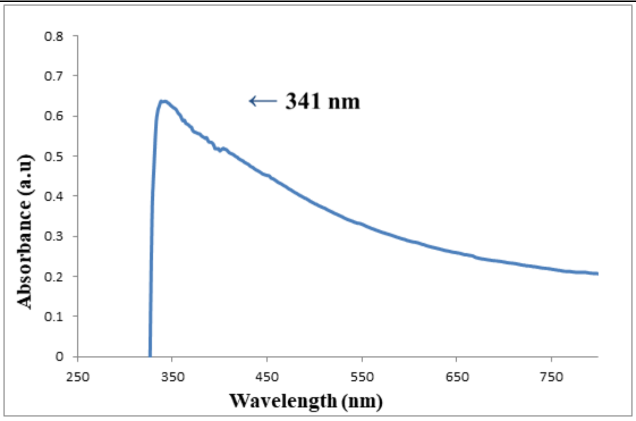

Figure 2: UV-Vis Spectrophotometer of Zn/ZnO NPs Prepared via PLA in Acetone.

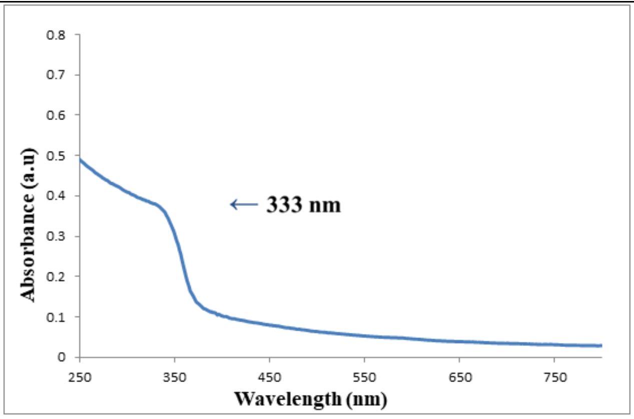

Figure 3: UV-Vis Spectrophotometer of Zn/ZnO NPs Prepared via PLA in Distilled Water.

Table 1: UV-Vis Spectrophotometer of Zn/ZnO NPs Produced by the PLAL Technique.

Material	Wavelength [nm]	Absorbance [a.u]
Zn/ZnO NPs in Ethanol	320	0.75
Zn/ZnO NPs in Acetone	341	0.63
Zn/ZnO NPs in Distilled Water	333	0.37

3.2. Fourier Transform Infrared Spectroscopy

FTIR studies of Zn/ZnO NPs in liquid is presented in Figures (4), (5), and (6). These studies were performed to demonstrate the purity and nature of Zn/ZnO NPs in the liquid. Liquid media such as alcohols, ketones, etc., can react with the Zn surface to help stabilize it. The broad peaks observed in the range of 3318, 3469, and 3255 cm^{-1} for Zn/ZnO NPs in Ethanol, Acetone, and Distilled Water, respectively, that indicate O-H expansion vibrations. The 2972 and 2885 cm^{-1} peaks of Zn/ZnO NPs in Ethanol indicate C-H stretching vibrations. Also, the 3002 cm^{-1} peak of Zn/ZnO NPs in Acetone indicates C-H stretching vibrations too. The peaks observed at 1655, 1708, and 1638 cm^{-1} correlate with C=O stretching vibrations of Zn/ZnO NPs in Ethanol, Acetone, and Distilled Water, respectively. Another peaks at around 500 cm^{-1} for Zn/ZnO NPs in Ethanol, Acetone, and Distilled Water were observed, which indicate Zn-O stretching vibrations. Metal oxides generally give absorption peaks. These outcomes match primarily in agreement with the literature [8,9]

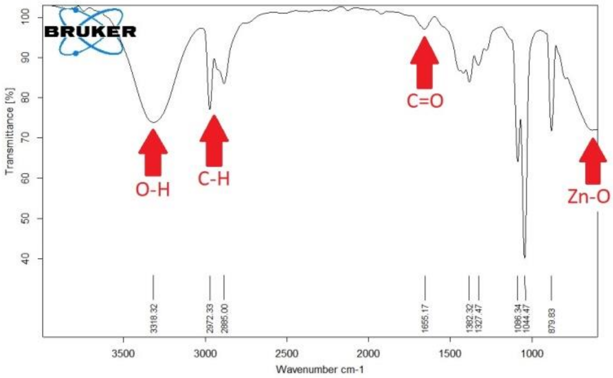

Figure 4: FTIR Spectrograph of Zn/ZnO NPs Prepared via PLA in Ethanol.

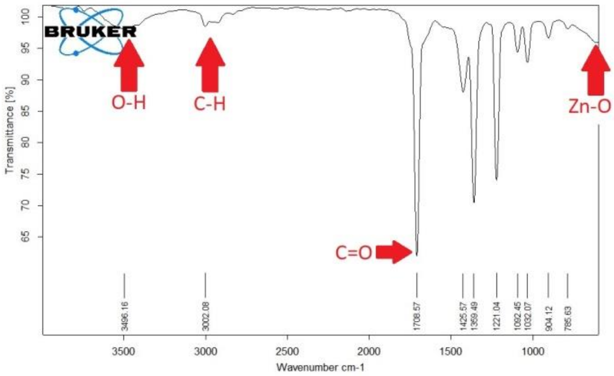

Figure 5: FTIR Spectrograph of Zn/ZnO NPs Prepared via PLA in Acetone.

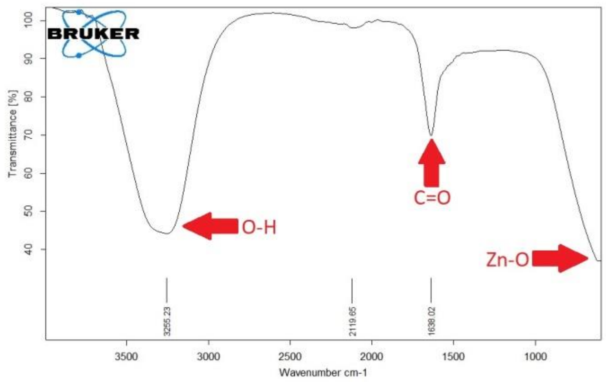

Figure 6: FTIR Spectrograph of Zn/ZnO NPs Prepared via PLA in Distilled Water.

Table 2: FTIR Spectroscopy of Zn/ZnO NPs Produced by the PLAL Technique.

Material	Wavenumber [cm^{-1}]	Stretching Vibrations	Transmittance [%]
Zn/ZnO NPs in Ethanol	٣٣١٨ ٢٩٧٢ـ٢٨٨٥ 1655 ~ 500	O-H C-H C=O Zn-O	٧٣ ٧٨ـ٨٤ 98 72
Zn/ZnO NPs in Acetone	٣٤٩٦ ٣٠٠٢ 1708 ~ 500	O-H C-H C=O Zn-O	٩٧ ٩٨ 61 95
Zn/ZnO NPs in Distilled Water	٣٢٥٥ 1638 ~ 500	O-H C=O Zn-O	44 70 35

3.3. X-Ray Diffraction

Figures (7), (8), and (9) of Zn/ZnO NPs in liquid show low-angle XRD patterns. These patterns can confirm that all three samples are compact porous arrangements with the manifestation of the major peaks 23.31˚, 23.81˚, and 19.20˚ for Zn/ZnO NPs in Ethanol, Acetone, and Distilled Water, respectively. In addition, shows a sharp peak of high intensity at 13.54˚ for Zn/ZnO Core/Shell NPs in Acetone. These peaks indicate that the structure is stabilized and not deformed. The intensity of the gradient peaks decreased, signalizing that the ZnO NPs were created at a preferred site. No high-angle XRD patterns appeared, signalizing that the formed ZnO NPs are very small to be featured from background noise or undetectable by high-angle XRD. Using Scherrer equation, the average size of Zn/ZnO Core/Shell NPs is 53 nm. Also, the broad XRD peak at the 2θ angles from 20˚ to 30˚ establishes that ZnO NPs are low-crystalline. These outcomes match primarily in agreement with the literature [11,12].

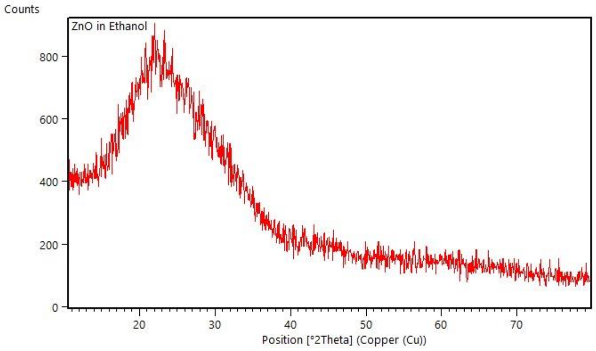

Figure 7: XRD Pattern of Zn/ZnO NPs Prepared via PLA in Ethanol.

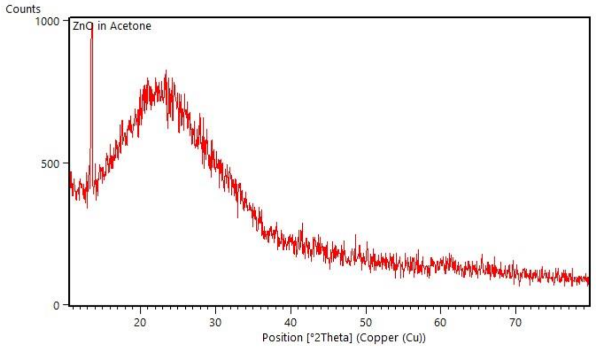

Figure 8 XRD Pattern of Zn/ZnO NPs Prepared via PLA in Acetone.

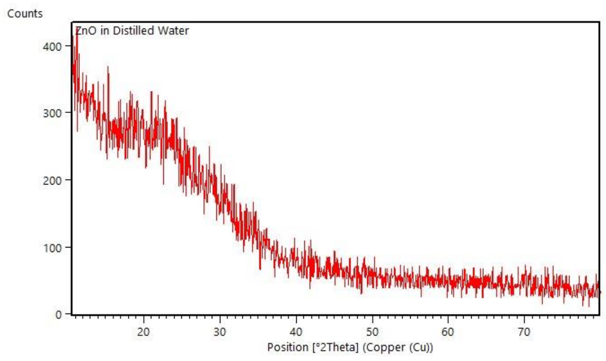

Figure 9: XRD Pattern of Zn/ZnO NPs Prepared via PLA in Distilled Water.

Table 3: XRD Pattern of Zn/ZnO NPs Produced by the PLAL Technique

Material	**Pos. [°2Th.]**	**Height [cts]**	**FWHM [°2Th.]**	**d-spa. [Å]**	**Cry. Size [nm]**
Zn/ZnO NPs in Ethanol	٢٣.٣	٤٩٣.٣	٠.٢٩	٣.٨١	٢٨
Zn/ZnO NPs in Acetone	١٣.٥ ٢٣.٨	٩٢٦.٤ ٧٣٢.٩	٠.١٩ ٠.٠٩	٦.٥٣ ٣.٧٣	٤٢ ٨٦
Zn/ZnO NPs in Distilled Water	١٩.٢	٢٨٨.٢	٠.١٤	٤.٦٢	٥٧
Average Crystallite Size = 53.5 nm					

3.4. Transmission Electron Microscope

The TEM images in Figures (10), (11), and (12) show the presence of Zn/ZnO NPs in Ethanol, Acetone, and Distilled Water, with a size of lower than 50 nm, that is, the Zn/ZnO NPs are very small. The TEM images in Figures (13), (14), and (15) clearly show Zn/ZnO NPs in Ethanol, Acetone, and Distilled Water, as a Core/Shell model with a structure-forming of Zn as the Core and ZnO as the Shell. Zn NPs were painted with a ZnO coating. TEM analysis confirms that the primary structure of the Zn/ZnO NPs is the Core/Shell. These outcomes match primarily in agreement with the literature [7,9,11,13,14].

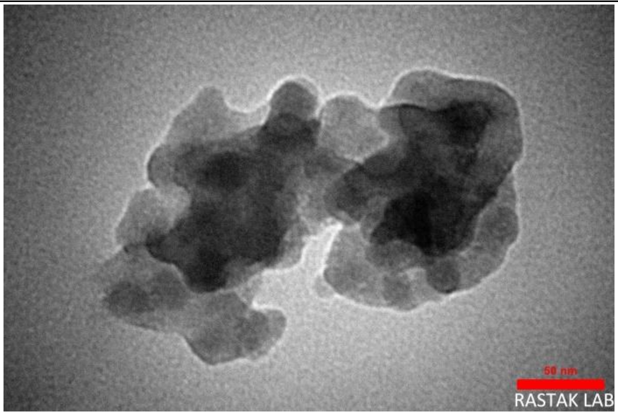

Figure 10: TEM Images of Zn/ZnO NPs Prepared via PLA Ethanol.

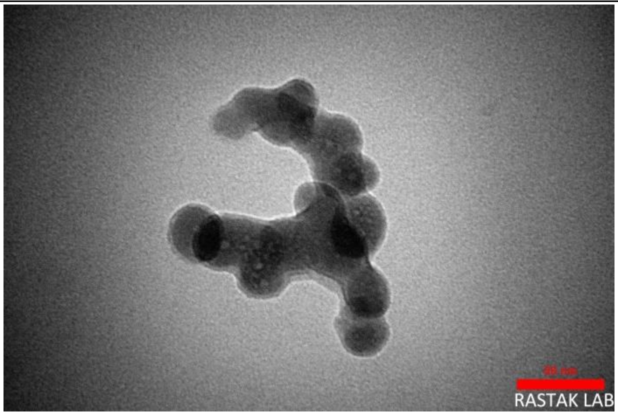

Figure 11: TEM Images of Zn/ZnO NPs Prepared via PLA in Acetone.

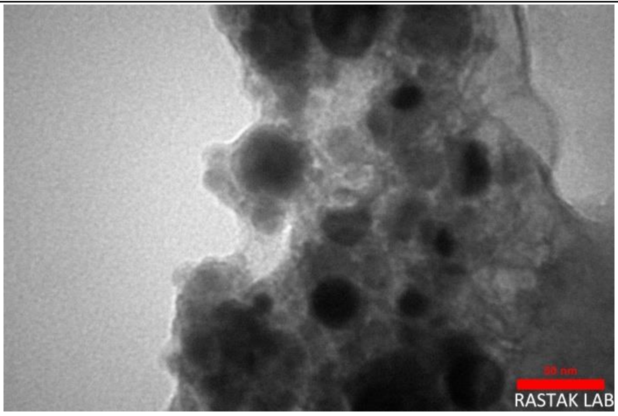

Figure 12: TEM Images of Zn/ZnO NPs Prepared via PLA in Distilled Water.

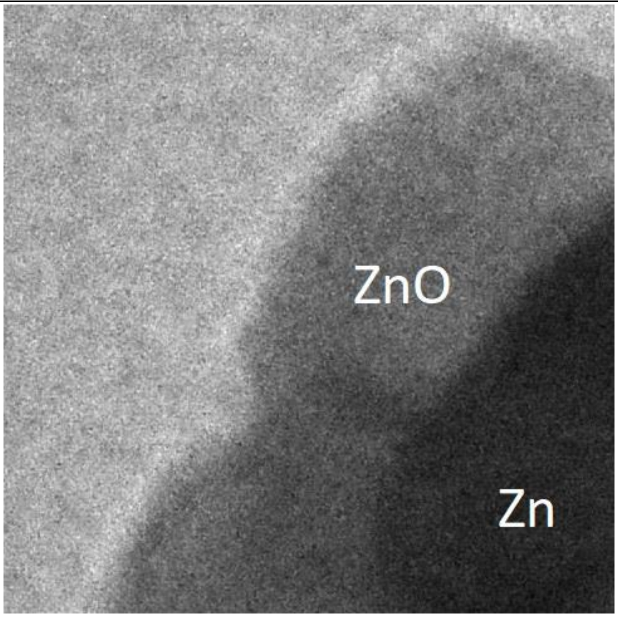

Figure 13: TEM Images of Zn/ZnO NPs as Core/Shell Model Prepared via PLA in Ethanol.

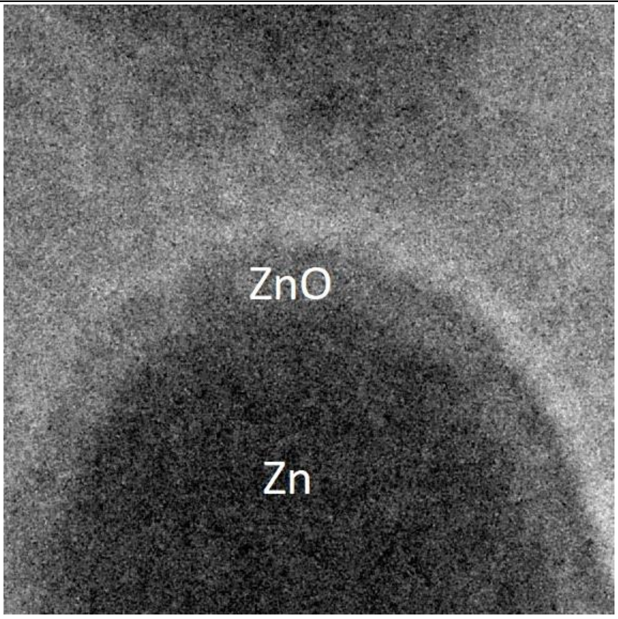

Figure 14: TEM Images of Zn/ZnO NPs as Core/Shell Model Prepared via PLA in Acetone.

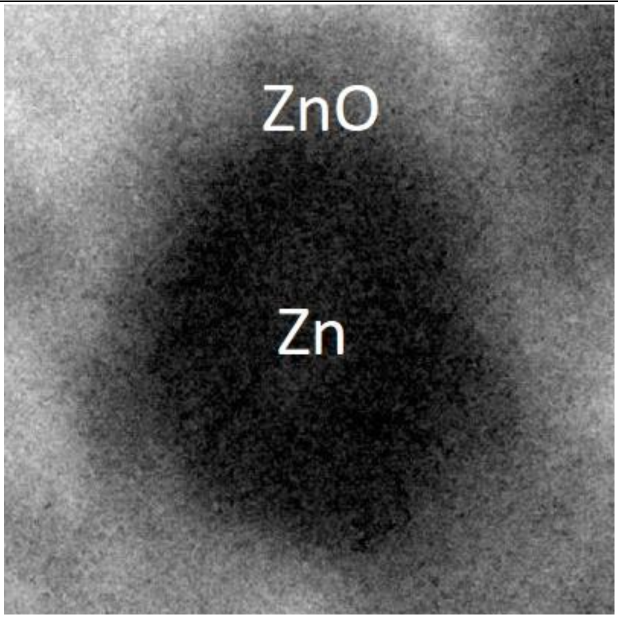

Figure 15: TEM Images of Zn/ZnO NPs as Core/Shell Model Prepared via PLA in Distilled Water.

4. Conclusions

The study confirmed the successful manufactured of Zn/ZnO nanoparticles by pulsed laser ablation in a liquid (Ethanol, Acetone, and Distilled Water). The findings showed that the manufactured Zn/ZnO nanoparticles possess a very small size and nanostructure in the shape of a Core/Shell model where Zn is the Core and ZnO is the Shell. The results showed that the liquid media (Ethanol, Acetone, and Distilled Water) in which Zn/ZnO nanoparticles were manufactured possess a great effect on them.

Acknowledgments

In my name, Mustafa Raad Taher Alfahham. Above all, praise be to Allah almighty. I would not have been able to write this research without the help and support of those around me. I want to express my heartfelt thanks and respect to my supervisor at the University, Dr. Abbas M. Ali Al-Kifaie, for his supporting me in writing this research. I want to express my sincere thanks and respect to my professor at the University, Dr. Adel H. Omran Alkhayatt, for supporting me in the practical part of this research. I would like to express my thanks and respect to all my professors in the Department of Physics, Faculty of Science, University of Kufa, who taught me throughout my studies, and to all the staff. My special thanks, appreciation, and sincere gratitude to my family for their patience and great efforts that made this research possible.

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