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The Optical Limiting of Prepared Palladium Nanoparticles

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Abstract: Palladium nanoparticles are produced by Polyol method. The characterization of the Pd nanoparticle has been conducted by various techniques such as SEM and AFM. The results of Pd powder showed that the particle size is directly proportional to the temperature and the reaction time. The optimum conditions for obtaining minimum nanoparticles size are 45 ^{o}C reaction temperature and 60 min reaction time and the smaller particle size achieved is equal to 25 nm. The optical limiting of smaller size nanoparticles has been studied. The palladium nanoparticles appear to be attractive candidates for optical limiting applications.

Introduction

Following the invention of the laser, it was recognized that intense laser beams can easily damage delicate optical instruments, especially the human eye. Nowadays, lasers have become common in daily life and they are even being incorporated into toys. Many scientists have sought the so-called optical limiting materials that exhibit ‘nonlinear extinction’, in which it can strongly attenuate intense, potentially dangerous laser beams, while readily transmitting low-intensity ambient light [1].

Optical limiting is a field of growing interest owing to its application for the protection of eyes and sensors from intense laser pulses. Candidates for optical limiting materials should have low transmittance for strong incident light, and instantaneous response over a broad spectral range. An optical limiter function is to keep the power, irradiance, energy, and fluence transmitted by an optical system below some specified value, regardless of the magnitude of the input. It must achieve this while maintaining high transmittance at low input powers.

Noble metal nanoparticles play an important role in different fields of science due to the physical and chemical extraordinary properties. Palladium has attracted great attention as a popular material for catalysis, pollutant degradation, as well as hydrogen sensor/storage [3, 4].

The most efficient chemical method for nanoparticles fabrication is the Polyol method. It is a typical example of down-top approach in fabrication of nanoparticles by reduction the metal salt in the presence of ethylene glycol and Poly Vinyl Pyridine [5].

The present work aims to test the optical limiting of prepared Pd nanoparticles.

Materials and **Methods**

Palladium nanoparticles (Pd NPs) are prepared by adding 500 mg $Pd(NO_3)_2.2H_2O$ (>98%, Fluka) in 5 ml of ethylene glycol (E. G). Also 100 mg PVP as a stabilizing agent dissolved in 25 ml of E.G. On the other hand 45 ml of E.G was heated by magnetic stirrer at (45, 65,100) ± 2°C for different reaction times of (20, 40, 60, 80,100) min. The two solutions in the heated ethylene glycol were injected with a burette and mechanical syringe pump and fed to reaction mixture for 13 minute after dosing the precursor/stabilizing agent solution. A light of brown coloration was observed indicating the formation of Pd nanoparticles. After completing the process, the resulting mixture was heated at the same temperature of the E.G for reaction time of 20, 40, 60, 80 and 100 min at each temperature value. Finally the solution was cooled at room temperature.

The excess quantity of PVP was removed by repeating suspension for (2-3) times of the particles in ethanol and acetone at 6000 rpm for 3 minutes each time by centrifuge (EBA 20-Germany). The final product was then dispersed in ethanol.

Results and Discussion:

The morphology of Pd NP was checked by (SEM). Figure (1) shows the SEM images of Pd NPs at room temperature (25 °C) .

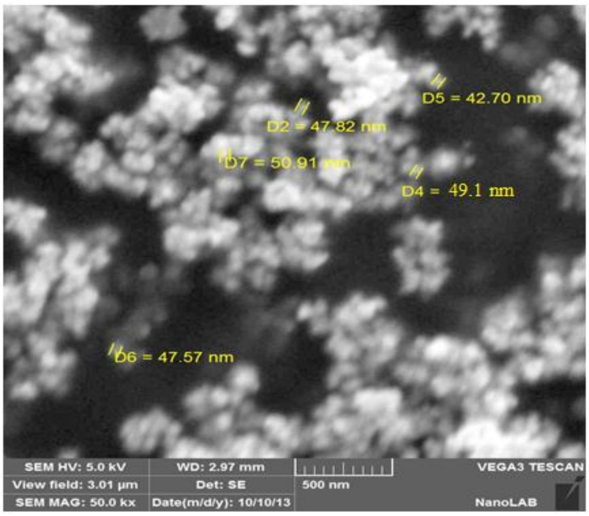
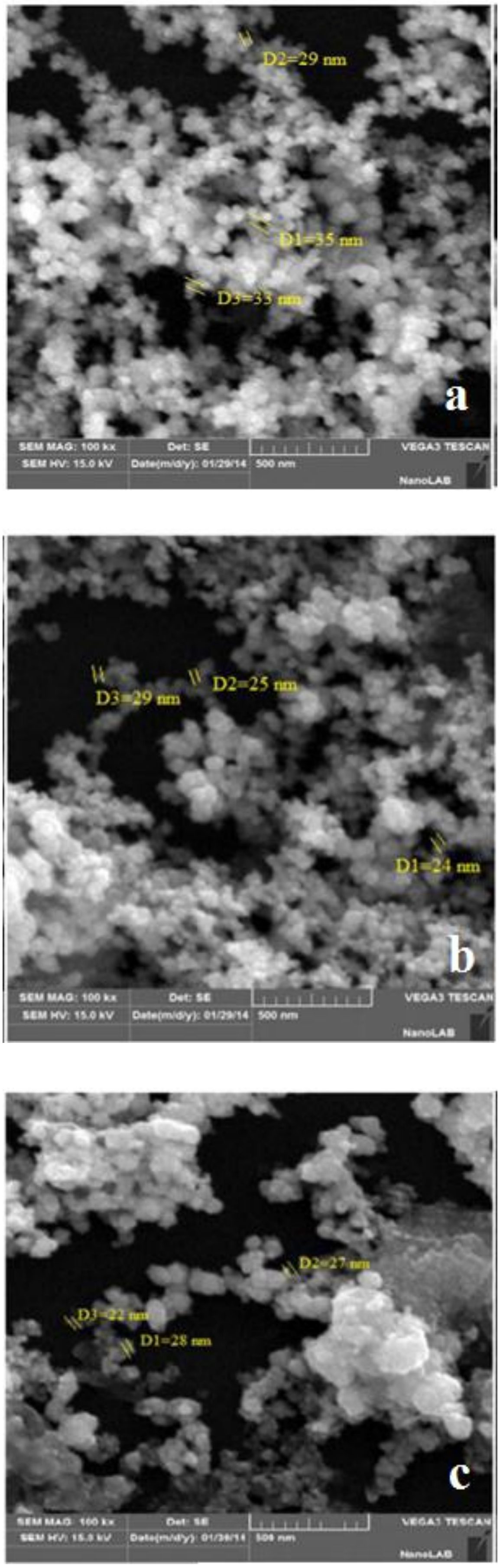


Fig. (1): Scanning electron microscopy image for Pd NPs at room temperature (25°C).

Figure 2 (a, b, c, d and e) show the SEM images of Pd NPs at 45 ℃ for (20, 40, 60, 80, 100) min.



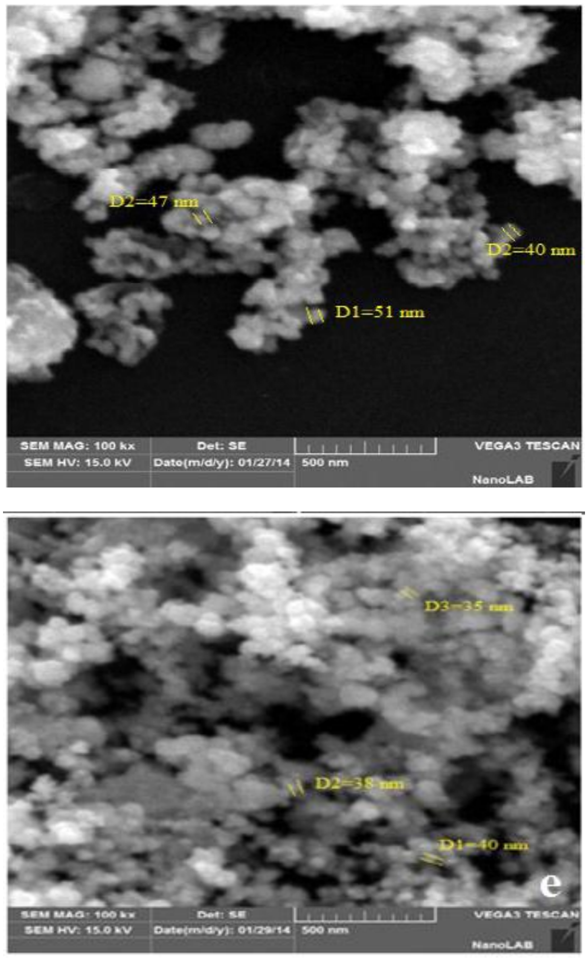


Fig. (2): SEM image of Pd NPs at 45 ^{o}C: (a) 20 min, (b) 40 min, (c) 60 min, (d) 80 min, and (e) 100 min.

By increasing the temperature to 45 ^{o}C for reaction time of (20, 40, 60, 80, 100) min, the corresponding average particle size achieved are (32, 26, 25, 37, and 38) nm respectively.

Figure (3) shows the SEM image of Pd NPs at 65°C for 60min. The average size is 46 nm. A grain structure for Pd nanoparticles and the size of grains are higher with increasing temperature of reaction compared with the particle size at 45^{o}C for 60min reaction time. This result is in agreement with that of H. Peng Choo et al [6].

The previous experiment work result confirmed by AFM images assures that the particles size increase as the temperature increase.

Figure 4 shows two-dimensional (AFM) images of Pd NPs that are prepared at room temperature (25^{o}C). The root mean square-value of roughness and grain size are calculated from the height values of the AFM image using the commercial software.

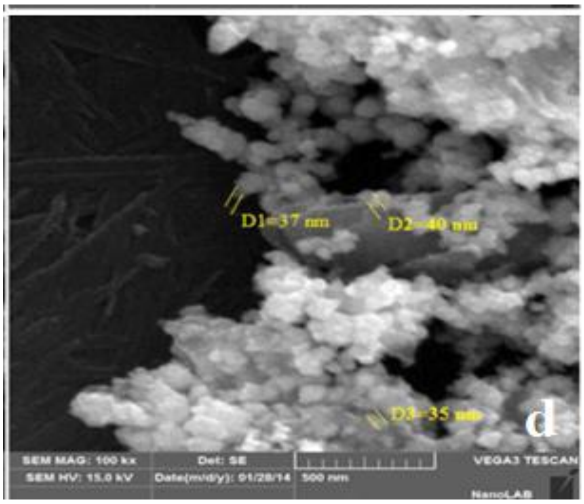


Fig. (3): The scanning electron microscopy for Pd NPs at 65 ^{o}C for 60-min reaction time.

The average diameter of the particle is 151.72 nm.

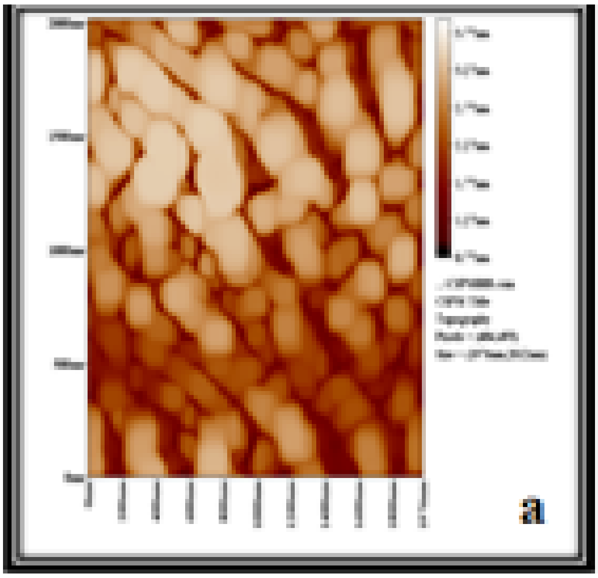
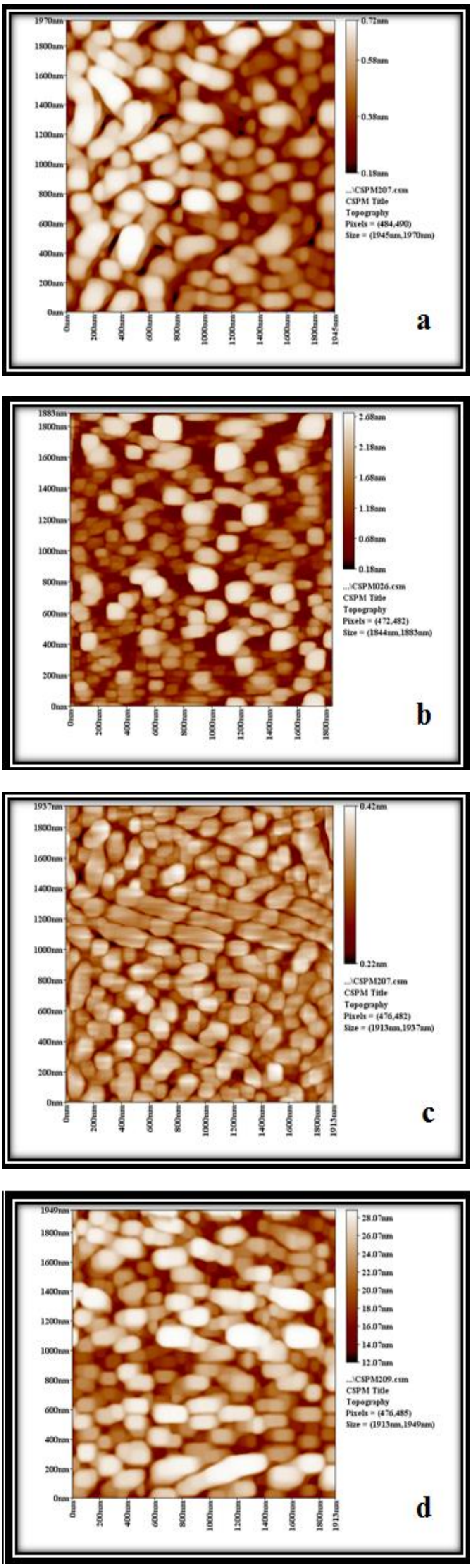


Fig. (4): (a) Two-dimensional atomic force microscopy images of Pd NPs prepared at room temperature (25) ^{o}C.

Figure 5a, 5b, 5c, 5d and 5e show two-dimensional (AFM) images of Pd NPs prepared at 45 ^{o}C for a reaction time (20, 40, 60 ,80 and 100) the corresponding average diameters are (117.37, 75.46, 73.21, 87.51, and 95.98) nm respectively.

With a reaction time of 20 min, it is clear that the maximum particles size are formed at initial stage, because the reaction time is not enough to complete the reduction, the particle became smaller after this reaction time the evolution process of Pd nanoparticles size gradually increases with time.



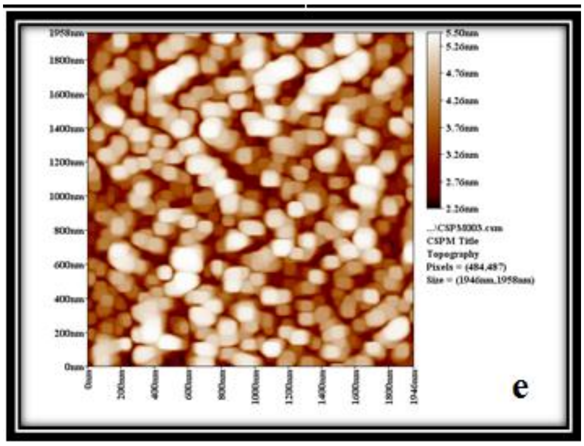


Fig. (5): Two-dimensional atomic force microscopy images of Pd NPs synthesized with different reaction times at 45 ^{o}C. (a) 20 min, (b) 40 min, (c) 60 min, , (d) 80 min and (e) 100 min.

Figures (6) shows two-dimensional (AFM) images of Pd NPs prepared at At (65, 100) ^{o}C for 40-min reaction time, we found that the average diameter of particles are (107.40, 127.77) nm.

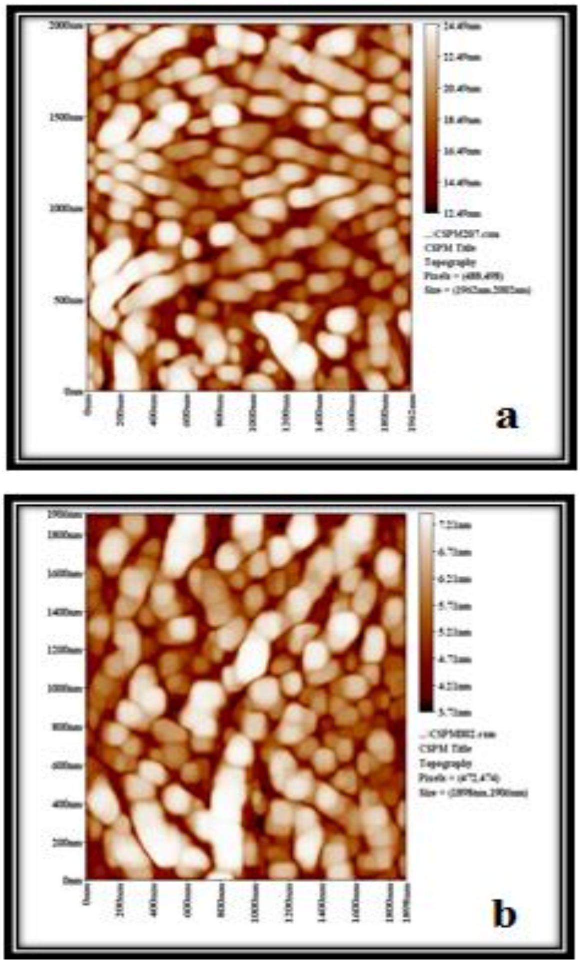


Fig. (6): Two-dimensional atomic force microscopy images of Pd NPs prepared at: (a) 65 ^{o}C, (b) 100 ^{o}C when the reaction time is (40 minute)

Figures (7) shows two-dimensional (AFM) images of Pd NPs prepared at (65 , 100) ^{o}C for 60-min, we found that the average diameter of the particle (79.74, 85.53) nm.

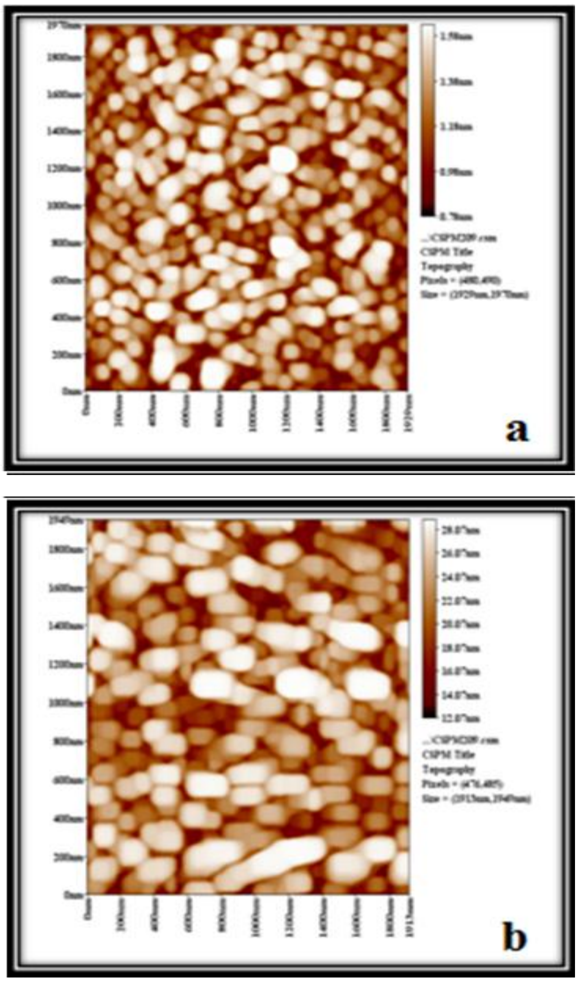


Fig. (7): Two-dimensional atomic force microscopy images of Pd NPs prepared at: (a) 65 ^{o}C , (b)100 ^{o}C when the reaction time is (60 min .

Figure (8) shows two-dimensional and three-dimensional (AFM) images of Pd NPs prepared at 65 and 100 ^{o}C for 80-min. It was found that the average diameter of the particle is 112.05 and 135.84 nm respectively. At the temperature ranges of 25-100 ^{o}C**.** it was found that at 25 ^{o}C there is a slowdown in the formation and growth reaction, which usually takes tens of hours to complete the reduced reaction, because there was no external force (heating) to break the binding between the molecules so that the particle size increases . At the temperature range of 45 to 60°C, the reaction rate increase, and the particle size increases as well. At high temperature (>60°C) the reaction was not investigated because at higher temperature, close to 100°C, ethylene glycol becomes more active in reducing Pd ions so the reaction became so fast for produced Pd NPs.

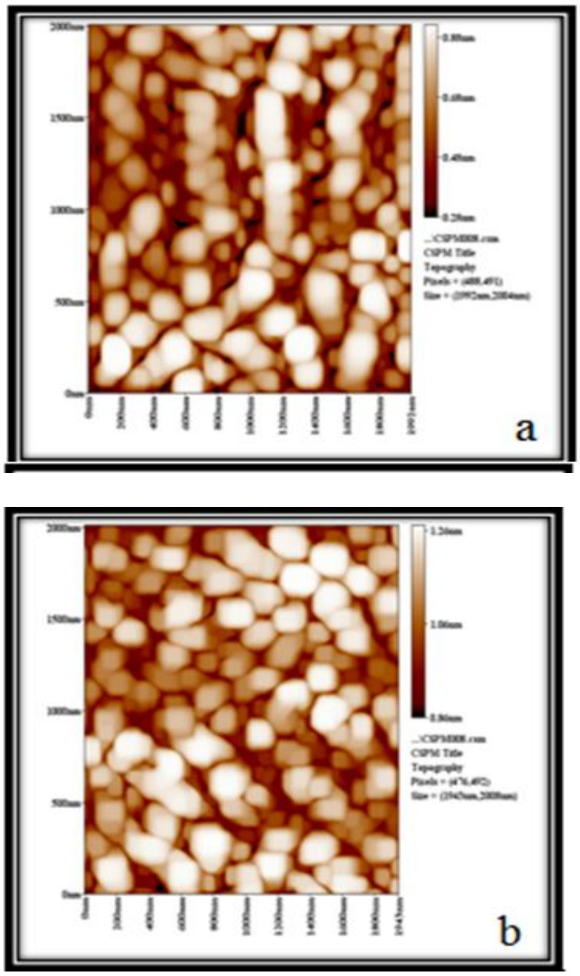


Fig. (8): Two-dimensional atomic force microscopy images of Pd NPs prepared at: (a) 65 ^{o}C , (b) 100 ^{o}C when the reaction time is (80 minute).

Optical Limiting Behavior

The limiting behavior of Pd NPs was studied. The results were investigated for Pd NPs of 532nm Nd:YAG laser at different incident energies. From Fig. 9, the values of E_L (Limiting threshold) and E_D (Damage threshold) for palladium nanoparticles can be extracted. The output energies increases as the incident energies increased until the limiting threshold energy where the output energy stays unchanged. The results showed that Eclamping value is low value and the D.R values are low. The values of EL, ED, Eclamping and D.R (Dynamic range) are 51.3,63, 46.3 mJ, and 1.22 respectively.

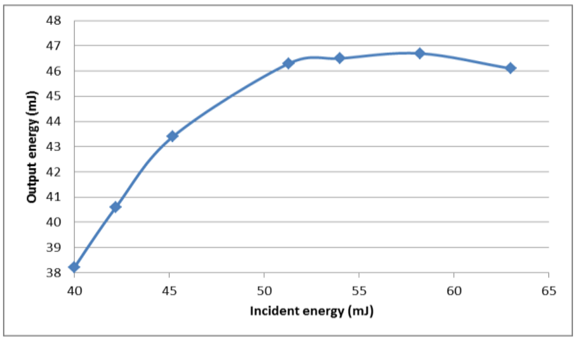


Fig. (9): Optical limiting behavior of Pd NPs at 532 nm.

To study the NLO response of the Pd NPs, the energy-dependent light measurements was done on the sample under the same conditions. This behavior is shown in Fig. 10.

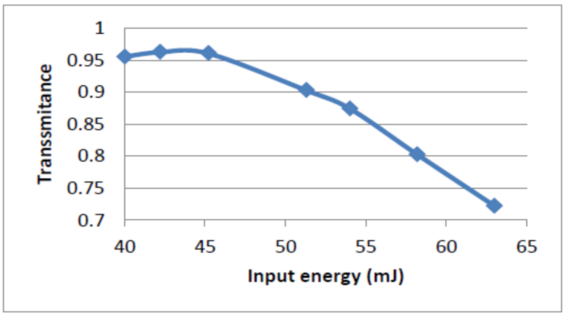


Fig. (10): Transmittance output of optical limiter as function of the input energy of Pd NPs at 532 nm.

The energy value of 51 mJ represents the optical limiting threshold energy for the sample, over which the sample may be damaged. The sample damage threshold is 61 mJ. This result is matches well with the result reported by G. Fan[8].

Conclusions

Pd NPs have been successfully synthesized in pure ethylene glycol (E.G) via a Polyol method by changing the temperature and the time of reaction. It was found that the reaction temperature and time play a key role in particles growth and sizes controlled. The particles sizes distribution was determined by AFM, SEM. This experiment shows that the best conditions for preparing palladium nanoparticles at temperature of 45^0C and reaction time of 60-minute reaction time. Finally this achievement shows the possibility of using the palladium nanoparticles as an optical limiter.

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المحدد البصري للدقائق النانومترية للبلاديوم

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الخلاصة: تم تحضير دقائق البلاديوم النانومترية بالتحلل الحراري. وتم دراسة الصفات التركيبية للشريحة المحضرة بأستخدام تقنية (المسح بالمجهر الالكتروني) ، تقنية (المجهر الذري) ووجد ان حجم هذه الدقائق تتناسب طرديا مع درجة الحرارة وزمن التفاعل. الظروف القياسية لتحضير اصغر قطر للدقيقة عند 45م وبزمن 60 دقيقة . اصغر قطر للدقائق يساوي 25 نانومتر. وقد تم دراسة صفات المحدد البصري ووجد ان العينة تعمل كمحدد بصري مثالي.