

*Nonlinear optical signal enhancement cannot be achieved by using semiconductor materials alone. Here, we show that the recently discovered nonlinear optical behavior of plasmonic nanoparticles and hybrid nanowires enables an enhanced nonlinear optical response. A synthesis, characterization, and nonlinear optical response of synthesized hybrid nanowires structures were studied. The growth of gold nanoparticles (Au NPs) onto cadmium selenide nanowires CdSe NWs with different concentrations of gold nanoparticles coating prepared via an impregnation technique. Au nanoparticles in the CdSe/Au nanowires were uniformly dispersed on the CdSe nanowire surface. The surface morphologies and the propagation manner of hybrid nanostructures were used for transmission electron microscopy (TEM) to study the optical properties of pure and hybrid nanostructures. Dark-field scattering microscopy was used to characterize single CdSe NW and confirm the coating of hybrid CdSe/Au nanowires and characterize the concentration effect of gold nanoparticles. The dark-field scattering spectrum (DFSS) reference to the surface plasmon resonance of nearer Au NPs was observed at ca. 800 nm. By making a comparison between a single cadmium selenide with and without gold nanoparticles coating, hybrid CdSe/Au nanowires exhibit sufficient quality to produce second-harmonic generation stimulated with a pulsed, linearly polarized pump-light from a femtosecond Ti-sapphire laser. The estimated improvement of the second-harmonic generation signal is about ~ 1.8 times, ~ 5.5 times, ~ 6.9 times for low, moderate and full coating of gold nanoparticles, which was mainly due to the high quality of synthesis techniques and good dispersion of gold nanoparticles on CdSe nanowires*

**Keywords:** surface plasmon resonance, cadmium selenide, hybrid nanowires, gold nanoparticles, second-harmonic generation

# INVESTIGATION ON SYNTHESIS, STRUCTURAL AND NONLINEAR OPTICAL RESPONSES OF CADMIUM SELENIDE COATED WITH GOLD NANOPARTICLES INDUCED BY FEMTOSECOND LASER EXCITATION

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Received date: 16.02.2021

Accepted date: 10.05.2021

Published date: 25.06.2021

**How to Cite:** Jassim, N. M., Kareem, N. A., Ibrahim, N. I., Sumayyah, B. A. M. (2021). Investigation on synthesis, structural and nonlinear optical responses of cadmium selenide coated with gold nanoparticles induced by femtosecond laser excitation. *Eastern-European Journal of Enterprise Technologies*, 3 (5 (111)), 13–18. doi: <https://doi.org/10.15587/1729-4061.2021.231422>

## 1. Introduction

Because of unique electrical and optical properties as well as the potential applications in integrated nanophotonic devices, hybrid nanostructures have attracted great attention of scientific researchers [1, 2]. Nonlinear optical properties are considered an important part in nanostructures systems and second-harmonic generation is one of these properties, where photons create with half essential wavelength and double frequency. The relatively low conversion efficiency of coherent nanoscope light sources and integrated optical systems leads to the limitation of the second-harmonic generation in nanostructures, so the current work is concentrated on the second-harmonic generation signals improvement in nanostructures types. Specially, the nanostructures systems, which include semiconductor and metal nanostructures, have an important function because of nonlinear optical properties improvement due to the unique localized surface plasmon resonance (LSPRs) phenomena [2–5]. The goal of the work is to study and

investigate the improved SHG signal in single CdSe NWs coated with Au NPs using femtosecond laser pulses. The fabricated CdSe/Au nanowires exhibit enhanced second-harmonic generation (SHG) emission.

The relevance of the work is to get the nonlinear signal response by using hybrid nanowires, which are used in many applications such as bio-imaging, solar cells and biosensors.

## 2. Literature review and problem statement

Cadmium selenide material is one type of II-VI semiconductor nanowire for a bandwidth of 1.47 eV [1–5], which has unique chemical and physical properties of optoelectronic, optical devices system and optical microscopy applications [5].

The paper [6] presents the results of research on synergistic effects on second-harmonic generation of hybrid CdSe-Au nanoparticles. The study of second-harmonic generation (SHG) in CdSe-Au hybrid nanoparticles in comparison with their components, using the “Hyper-Rayleigh scat-

tering” (HRS) method is shown. But there were unresolved issues related to the synthesis technique used. The reason for this may be the objective difficulties associated with the synthesis technique, cost part in terms of device of synthesis technique, which makes relevant research impractical, etc. A way to overcome these difficulties can be to use an easy synthesis technique. This approach was used in [2]. All this suggests that it is advisable to conduct a study on the cost of the synthesis technique.

The papers [7, 8] present the results of research on second-harmonic generation from bimetal composites doped with metal nanoparticles. The syntheses of Au-Ag nanoparticles and the nonlinear signals of bimetal are shown. But there were unresolved issues related to the type of materials used. The reason for this may be the objective difficulties associated with the type of materials, which makes relevant research impractical, etc. A way to overcome these difficulties can be to use another type of hybrid materials such as CdSe/Au nanoparticles. This approach was used in [3, 4]. All this suggests that it is advisable to conduct a study on enhanced second-harmonic generation by using semiconductors-metal nanostructures.

The papers [9, 10] present the results of research on the nonlinear optical properties of metal nanoparticles. The synthesis and nonlinear optical properties of metal nanoparticles are shown. But there were unresolved issues related to the improved signal responses. The reason for this may be the objective difficulties associated with the layer of materials, cost part in terms of layer of materials, which makes relevant research impractical, etc. A way to overcome these difficulties can be to use hybrid nanostructures to enhance nonlinear signal responses. This approach was used in [4, 8]. All this suggests that it is advisable to conduct a study on using semiconductors-metal nanostructures to study and enhance the nonlinear optical properties.

The papers [11, 12] present the results of research on second-harmonic generation in single semiconductor nanowires. The study of the nonlinear phenomenon of single semiconductor NWs is shown. But there were unresolved issues related to the type of materials used. The reason for this may be the objective difficulties associated with materials layer, cost part in terms of layers of materials, which makes the relevant research impractical, etc. A way to overcome these difficulties can be to use more layers of different materials to enhance nonlinear optical properties. This approach was used in [4]. All this suggests that it is advisable to conduct a study on the nonlinear phenomenon of semiconductor-metal nanostructures.

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### 3. The aim and objectives of the study

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The aim of the study is to present enhanced second-harmonic generation in single CdSe nanowires coated with gold nanoparticles.

To achieve this aim, the following objectives are accomplished:

- to investigate CdSe nanowires and hybrid CdSe/Au nanowires by using TEM microscopy;
- to study second-harmonic generation measurements and enhancement by hybrid nanowires at various gold nanoparticles concentrations;
- to study the dark-field scattering spectra to confirm the coating of hybrid nanowires;

– in practice the hybrid CdSe/Au nanowires will make as a simple platform for bio-imaging and biosensors applications.

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## 4. Investigation on materials and methods of CdSe and CdSe/Au hybrid nanowires

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### 4.1. Synthesis of CdSe and CdSe/Au hybrid nanowires

A hexagonal wurtzite CdSe structure belongs to the non-centro-symmetric crystal class of 6 mm [9, 11, 12] synthesized with a chemical precipitation technique. A mixture on top of high purity CdSe (cadmium selenide, powder, 99.995 % trace metals basis) and graphite powders (1:1 ratio weight) was used as a nucleus and was placed into a quartz cell that was put in the center of a tube furnace. Gold catalyses nanoparticles with a 30 nm diameter coated with Si (001) substrates were placed downstream of the origin matter. Oxygen gas at 5 sccm and argon gas at 100 sccm were utilized to quartz tube furnace flush. The tube furnace was heated to 950 °C for one hour and finally the tube furnace was cooled naturally to room temperature. The products synthesized of CdSe NWs were dispersed with ethanol transferred onto the quartz substrate for optical measurements and characterizations of material.

Gold nanoparticles Au with a 20 nm diameter, (NANO. COMOSIX COMPANY) were used for coating nanoparticles on the CdSe NWs by an impregnation method by dipping in gold nanoparticles solution several times to improve the SHG signal originated from CdSe NWs [3, 13], where the Au NPs solution was diluted with ethanol to three different concentrations (low, moderate and full), and silicon substrates with CdSe nanowires were prepared to suitable pieces. After that, the silicon substrates containing the nanowires were once immersed in the gold solution of three different concentrations. In the end, the gold nanoparticles-coated CdSe nanowires were dried in the air. And for optical measurements, the samples were dispersed on substrates made of quartz, the samples were marked, (A) represents bare nanowires, (B) represents bare nanowires with a low concentration of gold nanoparticles, (C) represents bare nanowires with moderate coating of gold nanoparticles and (D) represents bare nanowires with full coating of gold nanoparticles.

### 4.2. TEM Spectroscopy

Transmission electron microscopy was used to investigate CdSe nanowires and hybrid CdSe/Au nanowires at room temperature. (Abbreviated as TEM with the model number of Tecnai G2 20, the magnification of 25×–1100000× and resolution of 0.248 nm (point) and 0.144 nm (line)).

### 4.3. Second-Harmonic Generation Measurements

A mode – locked Ti sapphire femtosecond laser system (COHERENT, USA, 800 nm, 50 fs and 76 MHz) served as the pumping source was used to study the SHG properties of the samples at room temperature.

### 4.4. Dark-Field Scattering Spectra

The spectrum of dark-field scattering was obtained with microscopy of inverted Olympus I X 73, which included the dark-field condenser and a spectrometer of Andor Shamrock (193i).

5. Results of the research

5.1. TEM Spectroscopy Results

The TEM images of bare CdSe nanowires and hybrid nanowires are presented in Fig. 1.

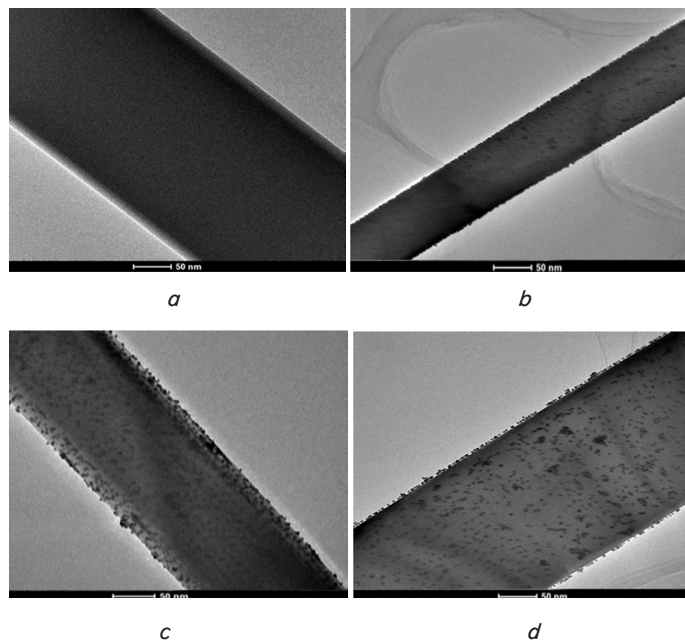


Fig. 1. TEM images of bare CdSe NWs and CdSe NWs coated with different concentrations of gold NPs:   
*a* – TEM image of bare CdSe NWs;   
*b* – TEM image of CdSe NWs with low coating of Au NPs;   
*c, d* – TEM images of CdSe NWs with moderate and full coating of gold NPs, respectively

Transmission electron microscopy (TEM) was used to characterize the surface morphologies and the propagation manner of hybrid nanostructures.

5.2. Second-Harmonic Generation Measurement Results

Second-harmonic generation was measured by using femtosecond laser as a pumping source with an 800 nm wavelength; 76 MHz repetition rate and 50 fs pulse duration.

Fig. 2 shows the experimental graphic.

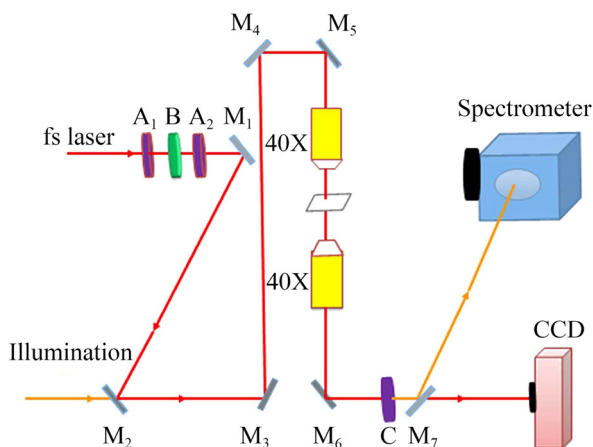
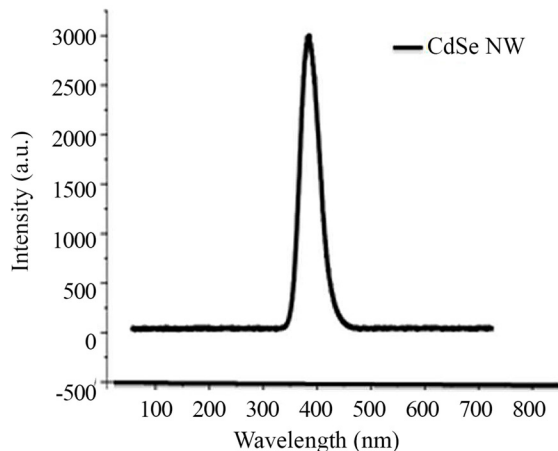
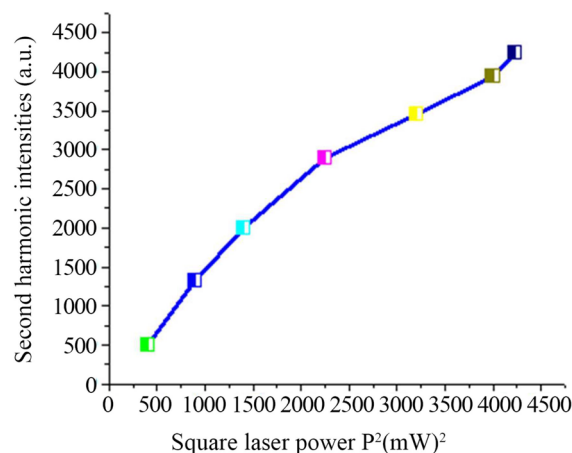


Fig. 2. SHG set up experiment

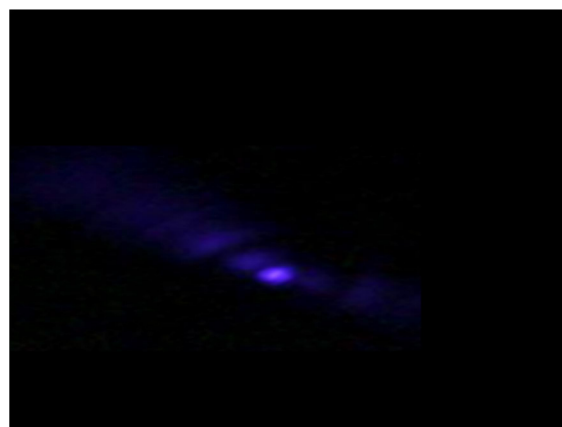
The intensity spectrum of CdSe nanowires and the relation between the second-harmonic generation intensities and the square laser power  $P^2$  and dark-field image of single CdSe nanowire are shown in Fig. 3.



a



b



c

Fig. 3. SHG measurements: *a* – second-harmonic generation intensities spectrum;   
*b* – linear relationships between the second-harmonic generation intensities and the square laser power  $P^2$ ;   
*c* – dark-field single CdSe NW image

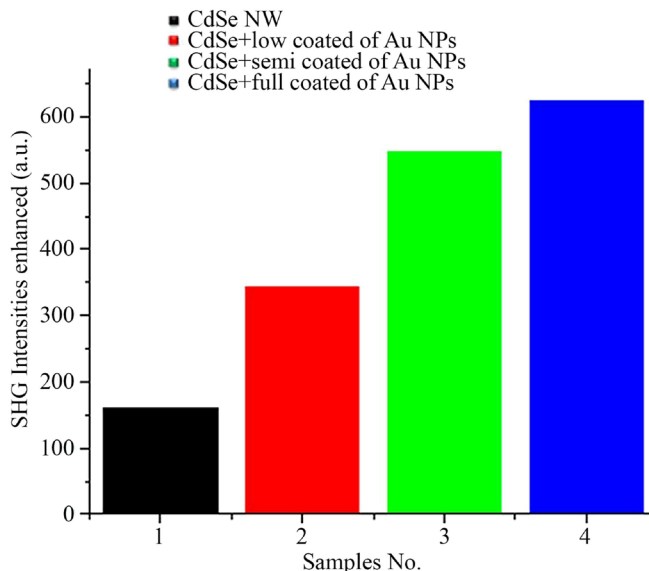


Fig. 4. Mean rate of SHG intensity as a function of samples number

The sample mark 1 points to CdSe nanowires, the sample mark 2 points to CdSe nanowires with low coating of gold nanoparticles, the sample mark 3 points to CdSe nanowires with moderate coating of gold nanoparticles and the sample mark 4 points to CdSe nanowires with full coating of gold nanoparticles. Table 1 shows the intensity peak of the samples number.

Table 1

Intensity peak of the samples number

Sample Number	SHG Intensity Peak
1	160
2	342
3	546
4	624

SHG intensities enhanced as a function of the gold nanoparticles concentration of the samples.

5. 3. Dark-Field Scattering Spectra Results

Dark-field scattering images of bare single CdSe nanowires and various densities of coated CdSe nanowires are shown in Fig. 5.

Dark-field scattering images showed the clear coating of gold nanoparticles with different concentrations.

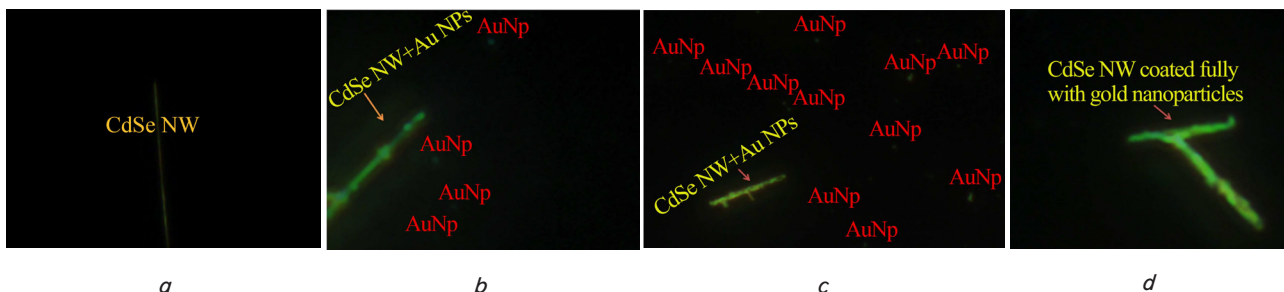


Fig. 5. Dark-field scattering images: a – single bare CdSe NW; b – CdSe NWs with low coating of gold nanoparticles; c – CdSe NWs with moderate coating of gold nanoparticles; d – CdSe NWs with full coating of gold nanoparticles

The dark-field scattering spectra of CdSe nanowires and CdSe/Au nanowires with different concentrations of gold nanoparticles were investigated to confirm the coating of hybrid nanowires (Fig. 6).

The dark-field scattering spectra of single bare CdSe NW and CdSe NWs coated with three different concentrations of gold nanoparticles are shown in Fig. 6.

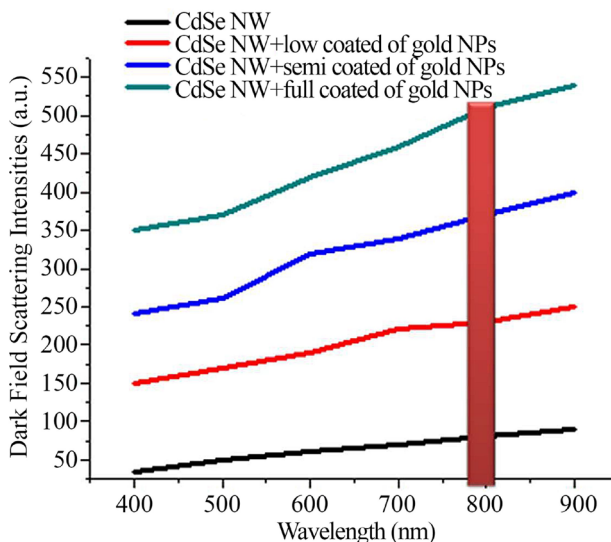


Fig. 6. Dark-field scattering spectrum of bare CdSe NWs and hybrid CdSe/Au NWs

6. Discussion of the results of the study of second-harmonic generation in single CdSe nanowires coated with gold nanoparticles

Cadmium selenide nanowires were prepared with various densities of plasmonic gold nanoparticles coated as a platform to measure the impacts of plasmon on the second-harmonic generation signals. Analysis of the results obtained (results of transmission electron microscopy, second-harmonic generation measurements and dark-field scattering spectroscopy) showed the following enhances in the second-harmonic generation properties of hybrid CdSe/Au nanowires. An increase in the concentration of gold nanoparticles leads to an increase in the coating on the CdSe nanowire surface and a decrease in the gold nanoparticles concentration leads to less coating of gold nanoparticles on the CdSe nanowire surface. The results are consistent with the research [4, 6].



From Fig. 1 TEM images, irregular distribution of gold nanoparticles on the cadmium selenide nanowires surface can be seen. A microscopy system was used to study the non-linear characteristics of the samples, where titanium-sapphire femtosecond laser was used with the parameters of 800 nm wavelength, 50 femtosecond pulsed width and 76 MHz repetition frequency rate. Laser energy was focused by a 40× objective. This objective was used to collect the reflected intensity of second-harmonic generation. The laser energy was filtered by a 700 nm short-pass filter. The measurement of the polarization-dependent second-harmonic generation response of the single CdSe NWs was done by rotating the polarization direction of the pumping laser with the half-wave plate (A2). Fig. 2 showed the experimental graphic.

An intense peak at 400 nanometers indicates the intensity spectrum of second-harmonic generation. Fig. 3 shows that the wavelength at half the original wavelength that represented 800 nm generated from the samples is the intensity of second-harmonic generation. Moreover, Fig. 3, *b* shows the linear relationships between the second-harmonic generation intensities of the samples as a function of the square laser power  $P^2$ . The dark-field image of a single CdSe nanowire is shown in Fig. 3, *c*.

Fig. 4 shows the mean SHG intensity as a function of the gold nanoparticles density of the samples. Several NWs were measured corresponding to the same sample, and the mean values of these NWs' average SHG intensity were evaluated to be the final rate [10, 11]. It is clear from Fig. 4 that the average SHG intensity increases with the increased attach of the gold nanoparticles on the cadmium selenide nanowire surface. The second-harmonic generation enhancement of the samples is evaluated by calculating the rate of the SHG of nanowires and the SHG of hybrid nanowires. The SHG improvement of low, moderate and high density of gold nanoparticles coated on the nanowire surface was 1.8 times, 5.5 times and 6.9 times, respectively. But it is worth noting that, under a high NPs density situation, the extra plasmonic waves could be generated due to the plasmonic wave coupling of the NPs. An increase in the concentration of gold nanoparticles solution leads to an increase in the coating of the nanowire surface and enhanced second-harmonic generation.

The observed improvement can be attributed to the localized surface plasmon of Au NPs. The plasmonic resonance of the metallic Au NPs locally improves the electric field of the incident fundamental light near the CdSe NWs [3, 10, 12]. The SHG signal improvement, semiconductor/metal hybrid nanostructures have a some merit such as controlling the times improvement by controlling the coating density and the distance between the metal and semiconductor is not needful with the charge transfer.

Dark-field scattering microscope was used to confirm the coating of single cadmium selenide nanowires with various concentrations of gold nanoparticles and the effect of the densities of gold nanoparticles is shown in Fig. 5, where *a* shows the dark-field scattering image of bare single CdSe nanowires and *b–d* show the gradual increase of the gold nanoparticles

concentrations of coated CdSe nanowires, the full coating was obtained with high density of gold nanoparticles shown in *d*.

Fig. 6 points to the black line that represents the bare CdSe nanowires, which shows a frequently gradual curve. With the coating of the gold nanoparticles on the surface of CdSe nanowires, the related scattering spectra change. The full scattering intensity is quite enhanced with sundry characteristic bands. Precisely, the powerful scattering band about 500 nm matches the electric dipole oscillation from single Au NPs, as shown in the curve of sample 2. While Au NPs tend to aggregate and form Au NP clusters. Because the effect of pairing nanoparticles a cluster open new band in the near-infrared region and the size of gold nanoparticles grows and the scattering intensities of hybrid samples are stronger than the scattering intensities of the bare sample. CdSe nanowires coating with gold nanoparticles leads to the enhancement of optical signal, because localized surface plasmon resonance of the gold nanoparticles. Overlap between wavelength pumping laser with 800 nm and scattering bands of near-infrared spectrum leads to powerful local field with resonance case.

In contrast to the well-known works, the research results cover a wide range of enhancement of second-harmonic generation signal obtained by hybrid CdSe/Au nanowires, but it is worthwhile to understand that the ideal homogenous distribution of gold nanoparticles on the surface of a single nanowire leads to strong and enhanced second-harmonic generation signal. This is considered an inherent limitation in terms of the experiments of this study. Therefore, more extensive research is needed to find them. It is also necessary to continue research in the direction of using more hybrid semiconductor/metal nanowires and varying their concentrations.

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## 7. Conclusions

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1. TEM images show that gold nanoparticles are assembled on the CdSe nanowire surface as a cluster.
2. Second-harmonic generation of CdSe nanowires was measured and the enhancement of second-harmonic generation factor was got, with different concentrations of gold nanoparticles and bare CdSe nanowires, ~1.8 times for low coating of gold nanoparticles, ~5.5 times for moderate coating of gold nanoparticles and ~6.9 times for full coating of Au NPs. High enhancement of second-harmonic generation was got with the near-resonant condition.
3. The dark-field scattering spectrum of CdSe nanowires with and without gold nanoparticles showed the surface plasmon of gold nanoparticles was red shifted, interfacing with pumping laser wavelength at 800 nm.

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## Acknowledgments

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The authors have no funding from any professional official institution. The research was funded at the self-expense of the authors.

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