Journal of Natural Sciences Research www.iiste.org
ISSN 2224-3186 (Paper) ISSN 2225-0921 (Online)
Vol.8, No.4, 2018

Second- Harmonic Generation Improved of ZnS/Au Core/Shell Nanomaterials

Nada Abdul Hadi Kareem[1] Nadia Mohammed Jassim[2]
1.Wuhan National Laboratory for Optoelectronics and School of Physics, Huazhong University of Science and Technology, Wuhan 430074, China, University of Qadissiya, College of Education, Department of Physics, Iraq
2.University of Diyala, College of Science, Department of Physics, Iraq

Abstract
we provide the synthesis and characterization of semiconductor nanowire attached with metallic nanoparticles. The wires consist of zinc sulfide (ZnS) attached with gold nanoparticles (Au NPs). The nonlinear optical properties of the semiconductor nanowires are combined with the plasmonic of metallic nanoparticles (Au NPs) and offer an improved optical signal in the near infrared spectral range. The plasmonic of a metallic (Au NPs) offers the effect of locally improving the electric field of the incident light on the nanowire and consequently inducing a much stronger second harmonic generation (SHG) signal. By comparing SHG signals measured from bare ZnS NWs and ZnS –Au hybrid nanostructures we obtain 6 time improvement of the SHG intensity It is demonstrated that is ZnS NWs is an ideal candidate for nanolasers, nanoprobes especially for the ultraviolet region, nonlinear optical microscopy and nanophotonic.
Keywords: plasmonic nanostructures. Chemical synthesis, ZnS NWs, Second - Harmonic generation (SHG).

1. Introduction

Nonlinear optical (NLO) harmonic generation play an important role in photonics[1], materials science[2] and bio sensing[3]. Second harmonic generation (SHG) is the lowest order frequency mixing nonlinear optical process where two photons create a single photon with half the incident wavelength [4]. This provides a convenient a practical means to obtain blue emission from a near- infrared laser. Practically, however NLO harmonic generation is generally inefficient at such a small scale. Plasmonic nanocavities are thus intriguing for the construction of more efficient coherent NLO light sources [5]. Surface-plasmon occurs, when light interacts with electron plasma waves at the metal surface. The electromagnetic field associated with these surface plasmons depends on the details of the nanostructure [6]. Localized surface-plasmon (LSP), in nanoparticle mediated emission has been proven as an efficient means to improve the quantum efficiency of light emitting devices [7] because of the strong coupling exciton effect between the surface-plasmons (SP) of the noble metal and the excitons of the semiconductors[8], the noble metal/semiconductor core/shell composite nanostructure has been one of the most promising composite nanostructures of the 21st century[9].Nanostructure plasmonic metal systems are known to greatly improve a variety of optical processes[10] including surface-plasmon enhanced photo catalysis, light-harvesting, and photo voltaic[11], surface-plasmon enhanced fluorescence[12], and forster resonance energy transfer[13], as well as the nonlinear optical properties of the semiconductors can be improved by the surface-plasmon[7], such as, second – and third- harmonic generation (SHG and THG)[14]. These have many potential uses in nanodevices for instance, nanolaser [15], and frequency doublers[16]. Semiconductor – metal hybrid nanostructures gives the basic information and improved optical properties on the optical coupling of the semiconductor and metal. Zinc sulfide (ZnS) is an important semiconductor with chemical stability and low toxicity, which has a wide range of potential applications[17], and its considered one of the most important materials in photonics because of its transmittance in the near- ultraviolet, visible and near- infrared regions with large refractive indices (n=2.3~ 2.5)[18]. ZnS is a direct wide band-gap semiconductor (3.72 and 3.77 eV for cubic and hexagonal structure, respectively, at 300K) with a large exciton binding energy of 40meV. In this paper, we reported the synthesis of ZnS NWs via chemical vapor deposition (CVD) method, the improved nonlinear optical SHG intensity from a ZnS NWs with attached Au NPs has been studied by localized surface plasmon. By comparing SHG signals measured from bare ZnS NWs and ZnS NWS attached with AuNPs, we obtain the improvement estimated of the intensity six times.

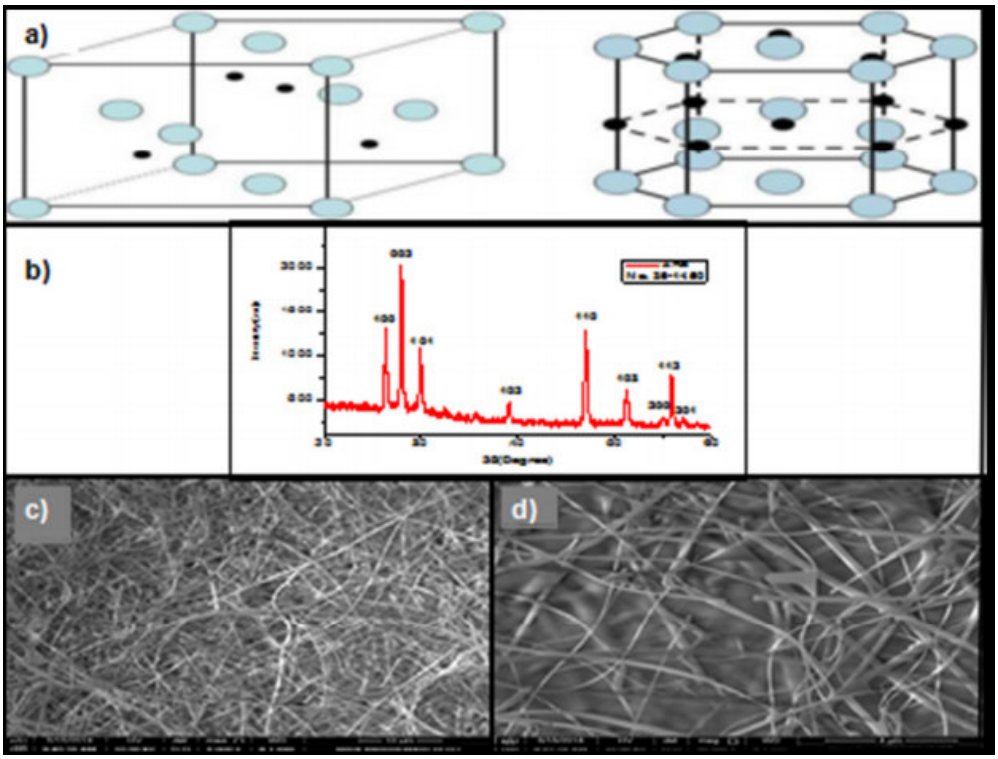
2.Experiment

ZnS nanowires were synthesized by chemical vapor deposition (CVD) using a simple conventional tube furnace with a 50 mm inner diameter quartz tube at 1050 Cº, High purity powder (Alfa Aesar, purity 99.99%) was used as a forerunner and was put in quartz boat that was placed in the center of a quartz tube furnace . Au, Gold catalyst nano particles, 30nm diameter coated silicon substrates were placed downstream of the source materials, serving as the deposition substrates. The quartz tube was purged with- high purity (H2) gas for one hour. After that, the source was heated to 1050 Cº at a rate of 30 Cº/min and maintained at the top temperature for one hour. During this process, the quartz tube was kept at a pressure of 0.03Mpa. with the high- purity H2 gas(carrier gas) introduced of a constant flow rate of 50 Sccm (Standard cubic centimeter per minute) .After the system was

cooled naturally, white wool- like products were deposited on the silicon substrates. The ZnS wires were coated with Au nanoparticles (10nm Citrate NanoXact Gold) by repeatedly dipping in Au colloidal solution. This Au colloidal solution was previous prepared according to NanoXact company. The ZnS wires were supposed to be covered with Au nanoparticles. A Single Au-nanoparticle coated ZnS wire was transferred on to the quartz substrate for the further optical measurements. The phase structure and purity of the obtained products were measured on X-ray diffractometer (XRD, X'Pert PRO, PANalytical B. V., Netherlands) using CuKα radiation at a scan speed of 15 *o*/min. The particles' size and morphology were observed by a scanning electron microscope (SEM, JSM-6701F and TEM, JEOL-4000EX), Energy Dispersive analysis of X-ray (EDAX) spectrum confirmed the formation of ZnS NWs and Au attached ZnS NWs . Second-harmonic generation measurements were recorded at room temperature , using a mode – locked Ti/Sappire laser with a wavelength of 810 nm as the excitation light source.

3. Results and discussion

The crystal structure of ZnS is typically found in the zinc blend crystal structure at room temperature.[17] The zinc blend structure is cubic, with four sulfur anions per unit cell located at the corners and centers of each face and with four zinc cations situated in half of the tetrahedral sites (the ¼, ¼, ¼ positions). At elevated temperatures, bulk ZnS can undergo a phase transformation from the cubic zinc blend structure to a hexagonal crystal structure known as the wurtzite structure. This transformation has been shown to occur at 1020°C. The zinc blend and wurtzite structures are very similar. The stacking sequence of the close-packed planes of zinc blend (the (111) planes) is represented by the ABCABCABCABC repeating pattern. However, if the closepacked planes stack themselves in the ABABABABAB repeating pattern, they would form the (0001) planes of the wurtzite structure. Both the zinc blend and the wurtzite structure are shown in Figure(1a). The products were characterized by X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V., Netherlands), field-emission scanning electron microscope (FESEM, Nova NanoSEM 450). A high and low magnified SEM images of the as- synthesized ZnS NWs on silicon substrates is shown in Figure 1(c,d). The XRD pattern of the sample shown in Figure 1b is in good agreement with JCPDS card no. 36-1450, indicating a hexagonal wurtzite structure of the ZnS NWs with the lattice constant of a=b=0.38nm and c=0.63nm.



Figure(1a), The zinc blende (left) and wurtzite (right) crystal structures of ZnS, (b) the XRD pattern of the ZnS nanowires, (c,d) high and low magnification of SEM images of the as-synthesized ZnS NWs on silicon substrates. To systematically investigate the nonlinear properties of the as-obtained ZnS NWs, Au nanoparticles were used to functionalize the wires via a solution process and the corresponding TEM image of a typical functionalized ZnS NWs is shown in Figure 2,From the TEM images, it can be seen that Au nanoparticles are randomly distributed on the surface of the wire with a different dimension along the long-axis .

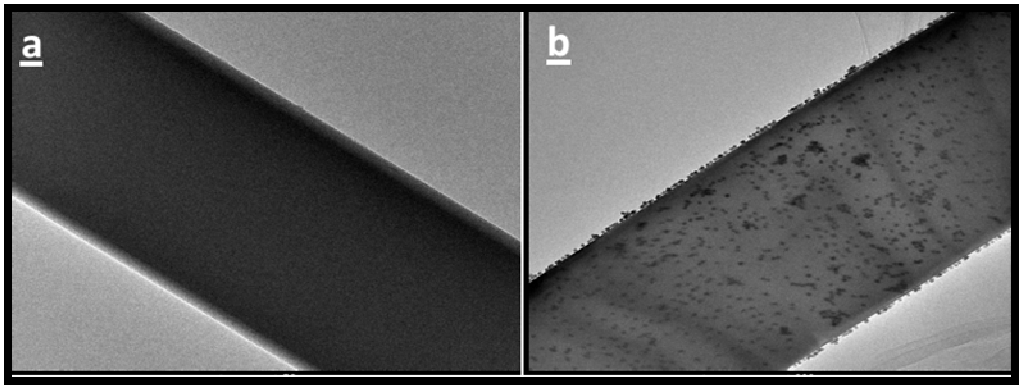


Figure2. Shows TEM images of bare ZnS NWs and ZnS –Au hybrid nanostructures. (a) TEM image of bare ZnS NWs,(b) TEM image of ZnS–Au hybrid nanostructures.

To study the nonlinear optical properties of ZnS NWs and ZnS –Au hybrid nanostructures, SHG experiment was carried out by a conventional confocal microscope system at room temperature., a conventional confocal microscope configuration shown in figure 3(a) was used for optical measurements at room temperature. A mode locked Ti/sapphire oscillator (spitfire, spectra-physics, 810 nm, 50 fs,76 MHZ) acted as the pumping source and a 40 X objective focused the beam to the sample with a laser a spot diameter of 4cm. A small pump spot contributes to a relatively large pumping power density since the laser power is limited in our experiment, leading to a high SHG signal for the precise determination. The transmitted signal was collected with the same objective and focused by a lens to the monochromator equipped with a photomultiplier (Hamamatsh CR131) and a look- in amplifier (SRS,SR 830). A750 nm short-pass filter was placed in front of the monchromator to flitter out the pumping laser light. A half-wave plate (A2).At 810 nm and a Glan prism (A3) were combined to measure the polarization properties of the surface second harmonic generation (SHG) .The signal spectrum in Figure 3b, presents a strong peak at 405nm, which is exactly the frequency doubling signal of the pumping laser. Figure 3c, shows the relationship between SHG and the square pumping laser power(p2). The quadratic dependency indicates the signal is generated from a second order nonlinear process. One can clearly see that the intensity increases linearly with the square pumping laser power (p2).

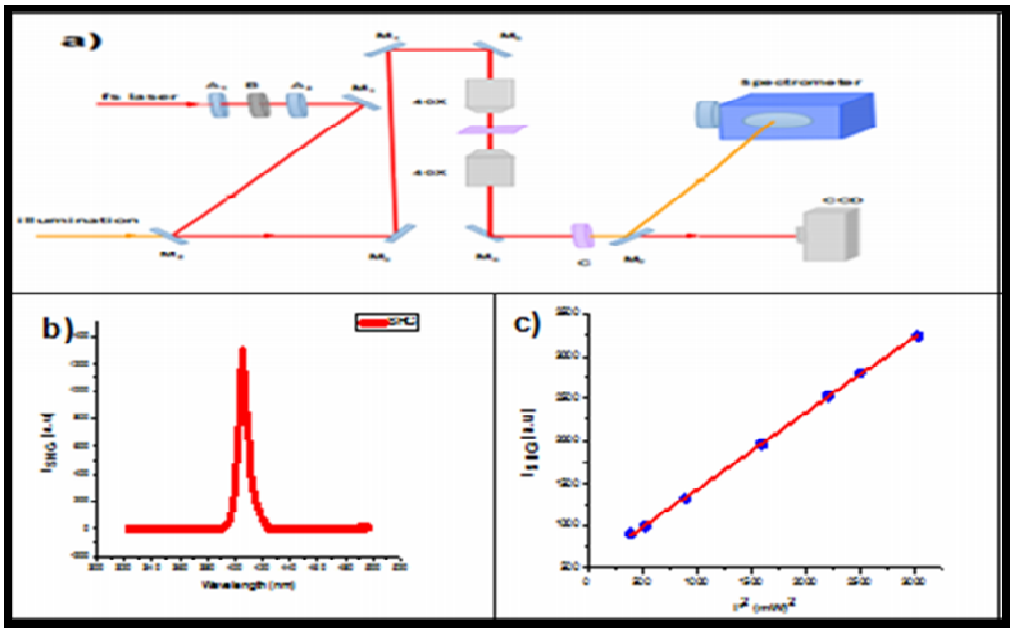
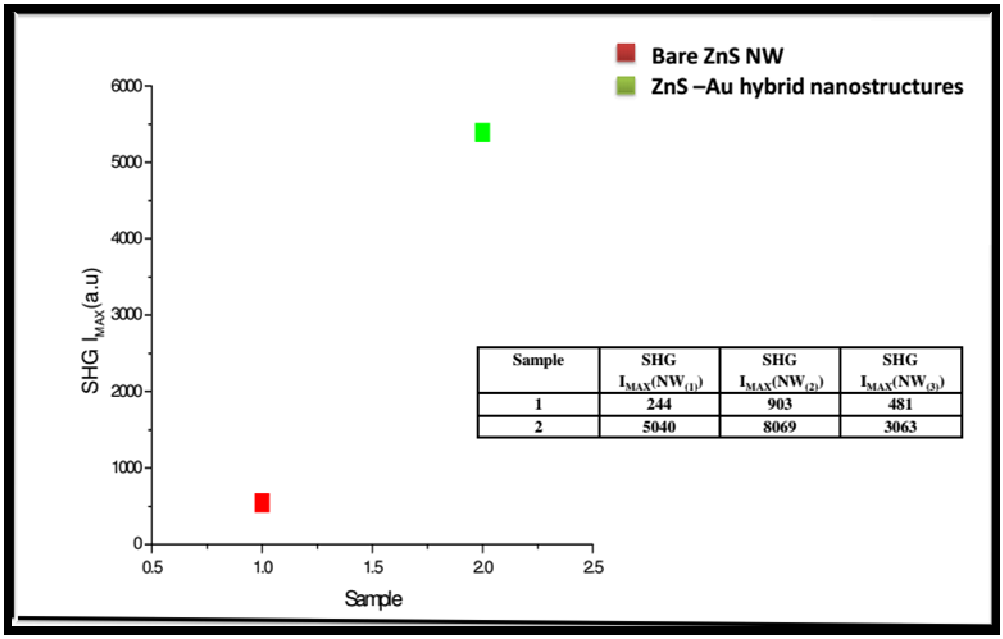


Figure3a. SHG experiment setup. The signal spectrum of the SHG was shown in Figure 3b, and Figure 3c, show the relationship between SHG intensity I and the square of the pumping power (P2). The improvement of the SHG is calculated by observing the ratio between the SHG signal with and without the plasmonic attachment. Au NPs attached ZnS NWs performed on three various NWs exhibit maximum SHG intensity. The improvement of the SHG intensity is observed to be six times Au NPs attached ZnS NWs, Figure 4. Shows the relationship between the SHG intensity max and the (bare ZnS NW, ZnS –Au hybrid nanostructures) samples. Its clear from this figure, the second- harmonic generation intensity (IMax) increased with ZnS-Au hybrid nanostructures.



Sample	SHG $I_{MAX}(NW_{(1)})$	SHG $I_{MAX}(NW_{(2)})$	SHG $I_{MAX}(NW_{(3)})$
1	244	903	481
2	5040	8069	3063

Figure 4. Shows the relationship between the SHG intensity and the(bare ZnS NW, ZnS –Au hybrid nanostructures) samples. sample 1: bare ZnS NWs ; sample 2 : ZnS –Au hybrid nanostructures) samples. Inset: table Shows the SHG intensity max for three nanowire with the number of sample.

4. Conclusions

In conclusion, we have shown great improvement of the second harmonic generation of ZnS NWs by incorporating Au nanoparticles and strongly modified by the interaction between excitons in ZnS NWs and surface plasmons in the metal component. Second -harmonic generation SHG improvement is due to the local electromagnetic field improvement from the metal surface plasmons and the estimate the improvement of second - harmonic generation in a nanowire due to the attachment Au NPs. we obtain the improvement of the SHG intensity is observed to be 6 times. It is demonstrated that is ZnS NWs is an ideal candidate for nanolasers, nanoprobes especially for the ultraviolet region, nonlinear optical microscopy and nanophotonic.

References

1. Berger. V. Nonlinear photonic crystals, Phys.Rev.Lett.1998,81,4136-4139.
2. S. I. *et al.* Supramolecular materials: self-organized nanostructures. *Science* 276,384–389 (1997)
3. Campagnola .P.J. and Loew. L.M.,. Second –harmonic imaging microscopy for visualizing bio molecular arrays in cells, tissues and organisms. Nat. Biotechnol.21,1356(2003).
4. Franken, P.A., Hill, A.E., Peters, C.W., Weinreich, G. Generation of optical Harmonics, Phys. Rev.Lett. 1961, 7, 118-119.
5. Nakayama. Y. et *al.* Tunable nanowire nonlinear optical probe. *Nature* 447, 1098–1102(2007).
6. Maier. S.A, Plasmonic field enhancement and SERS in the effective mode volume picture. Opt. .Express 14, 1957(2006).
7. Kauranen.M , and Zayat A.V. , "Nonlinear plasmonics,"NATURE PHOTONIC. 244(6).(2012).
8. Haglund . R. F. , Jr., B. J. Lawrie, and R. Mu, Coupling of photoluminescent centers in ZnO to localized and propagating surface plasmons, Thin Solid Films 518, 4637 (2010).
9. J. T. Jiu, M. Nogi, T. Sugahara et al., "Ag/TiO2 core-shell nanocables prepared with a one-step polyol process," J. Nanopart. Res. 14, 1241 (2012).
10. Ming Fu, Kai Wang, Hua Long, Guang Yang, Peixiang Lu, Frederik Hetsch, Andrei S. Susha, and Andrey L. Rogach , Resonantly enhanced optical non linearity in hybrid semiconductor quantum dot – metal nanoparticle structures, APPLIED PHYSICS LETTERS 100, 063117 (2012).
11. Komarala, V. K. Bradley A. L., and et al, Surface plasmon enhanced Förster resonance energy transfer between the CdTe quantum dots Appl. Phys. Lett. 93, 123102 (2008).
12. Gong .H. M., and et al, Optical nonlinear absorption and refraction of CdS and CdS-Ag core-shell quantum dotsJ. Chem. Phys. 125, 024707 (2006).
13. Long. J. P., and et al "Far-field imaging of optical second-harmonic generation in single GaN nanowires," Nano Lett. 7, 831–836 (2007).
14. Chen R., and et al, "Lasing: room temperature excitonic whispering gallery mode lasing from high-quality

hexagonal ZnO microdisks," Adv. Mater. 23, 2199–2204 (2011).
15. Nakayama. Y., and et al, "Tunablenanowire nonlinear optical probe," Nature 447, 1098–1102 (2007).
16. Fang, X. S.; Wu, L. M.; Hu, L. F. ZnS nanostructure arrays: a developing material star, Adv. Mater. 2011, 23, 585-598.
17. Moore, D.; Wang, Z. L. J, Growth of anisotropic one-dimensional ZnS nanostructures. Mater. Chem. 2006, 16, 3898-3905.
18. Bieniewski, T. M.; Czyzak, S. J. J.Refractive indexes of single hexagonal ZnS and CdS crystals,"Opt. Soc. Am. 1962, 53, 496-497.