

Short Communication

Electrochemically Grown Cadmium(II) Selenide Nanowires Coated by Au Nanoparticles: Photocatalytic Properties

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The control of the nanoparticles coating on the semiconductor nanowires and the photocatalytic processes can help to understand the importance for the potential application of nanostructures as photocatalysts. Here, Au nanoparticles-coated CdSe nanowires were successfully grown on indium tin oxide conducting glass substrate using a rapid electrochemically technique. The field-emission scanning electron microscopy image indicates a high-density array of CdSe nanowires in vertical alignment with an average diameter of <40 nm. A weak Au diffraction peak appeared in X-ray diffraction which confirm Au nanoparticles were coated on CdSe nanowires. UV–vis absorption spectra show the maximum absorption of Au coated CdSe nanowires is at 380 nm. The CdSe and Au coated CdSe nanowires were irradiated with UV light of 365 nm and the results of the photodegradation of Rhodamine B dye (RhB) were obtained. The results show 93.2% of RhB dye is degraded using the Au-coated CdSe nanowires after UV irradiation during 150 min, and the degradation rate of Au-CdSe nanowires is obtained to be 0.014 min^{-1} .

Keywords: Au-coated CdSe nanowires; Electrochemical technique; Photodegradation of Rhodamine B; UV–vis absorption; Photocatalytic activities

1. INTRODUCTION

Nanowires, the one-dimensional nano system, is one of the topics of increased interest in recent time as they have the ability to be used in nano level mechanical, electronic, sensing, and magnetic devices [1, 2]. CdSe is at the heart of interest for photovoltaics as a wide range of visible spectrum can be absorbed by its band-gap [3, 4]. Solution chemistry, mechanochemical reactions, chemical vapor deposition using the VLS mechanism are some of the methods that can be employed to synthesize CdSe nanomaterials in various forms like spherical particles, nanowires, nanotubes, nanobelts, nanorods and so on [5-7].

Noble metal (Ag, Au, or Pt)-coated CdSe is significant for photoelectron-transfer in the interface of CdSe semiconductors [8, 9]. The band structure and the Fermi level equilibration of CdSe are changing when the CdSe surface is coated with Au (Ag or Pt), as the photogenerated CdSe electrons are stored and shuttled to the receivers in a photocatalytic process. Therefore, noble metal deposition on the CdSe surface can enhance the efficiency of both photoelectric energy conversion and photocatalysis [10].

CdSe nanorods with metal nanoparticle deposition have been exhibited as catalysts for the reduction of methylene blue molecules. The CdSe nanorods absorb photon energy and the metal nanoparticles act as the catalytic active site. In electronic, photonic and bio-engineered applications, it is impossible to ignore the significance of Au nanoparticles due to their exclusive features.

The current work exhibits the significance of Au nanoparticle deposited CdSe nanowires in the enhancement of photocatalysis by increasing the charge separation efficiency and collecting energetic electrons in the Au nanoparticles. The nanowires were characterized to study the nanostructure and morphology using a transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray energy dispersion analysis (EDAX) and the photocatalytic activities were assessed by Rhodamine B dye.

2. MATERIALS AND METHOD

Two electrodes system was used for the electrochemical growth of CdSe nanowires. The working electrode, a pretreated indium tin oxide (ITO) conducting glass substrate, is at a parallel distance of 1 mm to the counter electrode, platinum (Pt) foil. The bath contained 0.05 mol L⁻¹ CdCl₂ and saturated elemental selenium in dimethyl sulfoxide (DMSO). The typical electrochemical parameters were maintained like Current density: 0.22 mA cm⁻², temperature: 147 °C, CdCl₂ and elemental Sd concentration: 10 mM and 5 mM, and stirring rate: 1000 rpm. CdSe nanowire samples obtained from the deposition were cleaned in acetone and DI water followed by annealing at 350 °C in an inert gas (N₂) atmosphere for 60 min to enhance photocatalytic properties.

Au nanoparticles are prepared by using 15 nm Au nanoparticles for the seed solution. 10 ml of seed solution was added to 90 ml DI water and was kept under stirring for 2 min at 320 rpm. The solution was stirred constantly for 5 minutes after adding Hydroxylamine hydrochloride, NH₂OH.HCl (1 mL, 0.2 M), followed by dropwise addition of gold (III) chloride (0.5 mL, 25.4 mM). The solution was mixed by stirring continually for another 5 minutes at 350 rpm. Spin coating at 2000 rpm for 2 minutes deposited the prepared Au nanoparticles on the CdSe nanowires.

Field-emission scanning electron microscopy (FESEM; FEI/Nova NanoSEM 450) was used to characterize the surface morphology of CdSe and Au coated CdSe. The morphology of the nanowires was characterized by High-resolution transmission electron microscopy (HRTEM) (TECNAI G2 20S-TWIN, FEI). Photoluminescence (PL) spectroscopy (Horiba Jobin Yvon Inc. Edison, NJ, USA) and a LABRAM-HR Micro-Raman spectrometer (Jobin-Yvon) at room temperature was used to investigate the optical properties. Electrochemical impedance spectroscopy (EIS) was utilized to study the recombination processes and charge transfer and with a potential of 20 mV at frequencies range of 0.1

Hz-0.1MHz. Au-coated CdSe nanowires grown on ITO conductive glass were utilized as the working electrodes. A platinum wire and Ag/AgCl were used as the counter and reference electrodes, respectively. 0.2 M Na₂SO₄ solution was used as the electrolyte in the experiment. Degradation of Rhodamine B dye under UV irradiation was used to study the photocatalytic performance of Au coated CdSe nanowires.

3. RESULTS AND DISCUSSION

Figure 1 shows the morphology and crystal structure of CdSe and Au nanoparticles coated CdSe nanowires fabricated in approved deposition conditions. The FESEM image of a high-density array of CdSe nanowires in vertical alignment is shown in fig 1a. The 2 μm long, straight CdSe nanowires grow in a direction perpendicular to the substrate. The FESEM images of 30 nm to 70 nm Au nanoparticles deposited on CdSe nanowires are shown in Fig 1b.

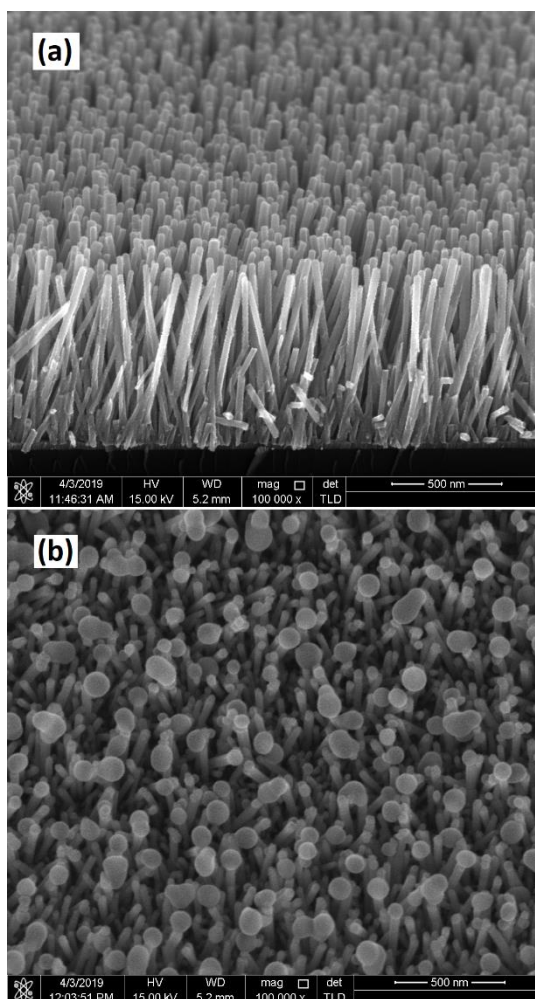


Figure 1. FESEM images of CdSe and Au nanoparticles coated CdSe nanowires

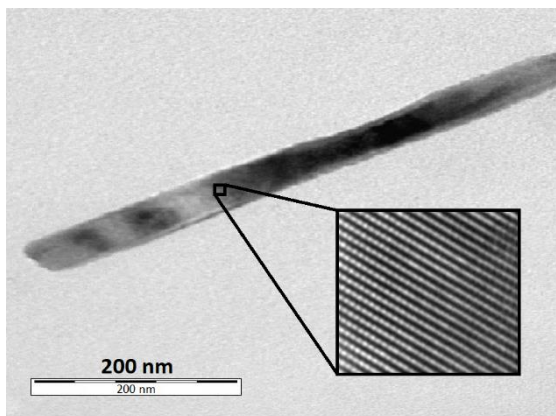


Figure 2. Low magnification TEM image of CdSe nanowires. Inset shows the HRTEM

A huge amount of particles was deposited on the substrate as the same volume while the spin coating was used. The CdSe nanowires with an average diameter of <40 nm and many outgrowths on the surface are shown in low magnification TEM images in Fig 2. The length and diameter ratio is more than 55. The estimated lattice spacing and the direction of growth are pointed out. HRTEM was used to find interplanar spacing as 0.69 nm, from which it is clear that CdSe nanowire is a single Wurtzite structured crystal with [0001] growth direction.

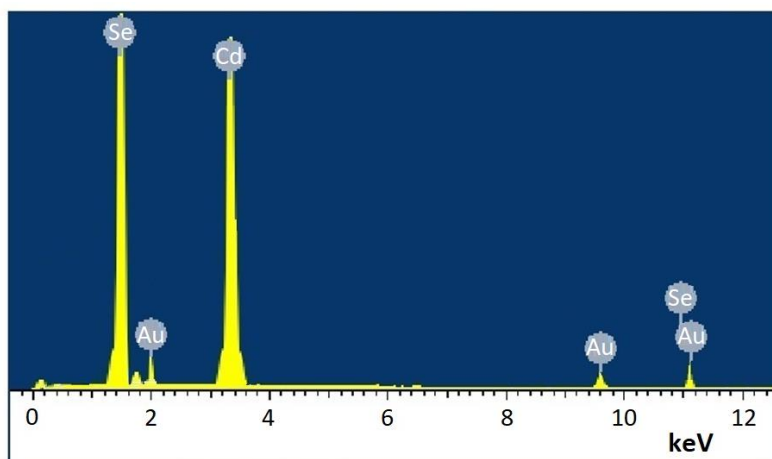


Figure 3. EDX of Au-coated CdSe nanowires

A common spectrum of chemical composition was obtained by EDX for the sample (Fig. 3). The spectrum consisted only of Gold, Cadmium, and Selenium. The gold peak starts from the tip where Au nanoparticles are present. 48.76%Se, 46.32% and Cd 4.92 Au were analyzed and found to be unison within the experimental errors.

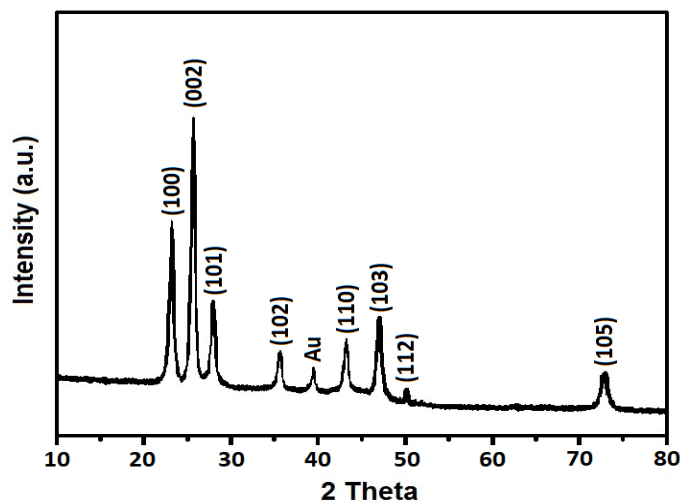


Figure 4. XRD pattern of CdSe nanowires

Figure 4 shows the XRD pattern of CdSe nanowires before deposition. The crystal plane (002) in the hexagonal Wurtzite crystal is of 25.55. The diffraction peaks counter with the bulk CdSe Wurtzite crystal with lattice constants $a = 4.299 \text{ \AA}$ and $c = 7.010 \text{ \AA}$. Furthermore, a weak Au diffraction peak from catalytic Au nanoparticles was detected.

The PL spectra of the CdSe and Au-CdSe nanowire arrays are shown in Figure 5. The near-band-edge emission (NBE) of CdSe lies between 530nm to 650nm. The uniform distribution of nanowires is confirmed by the narrow PL emission peaks (FWHM~ 40nm). And also, the input of defect sites to the overall emission were revealed by a broad peak due to the deep defect level (DL). The DL emissions appear from surface defect states recombination. It is known that gold nanoparticles influence the interfacial charge transfer processes, transfer of an electron from CdSe to Au is the reason for the observable reducing PL emission in Au-CdSe nanowires [11].

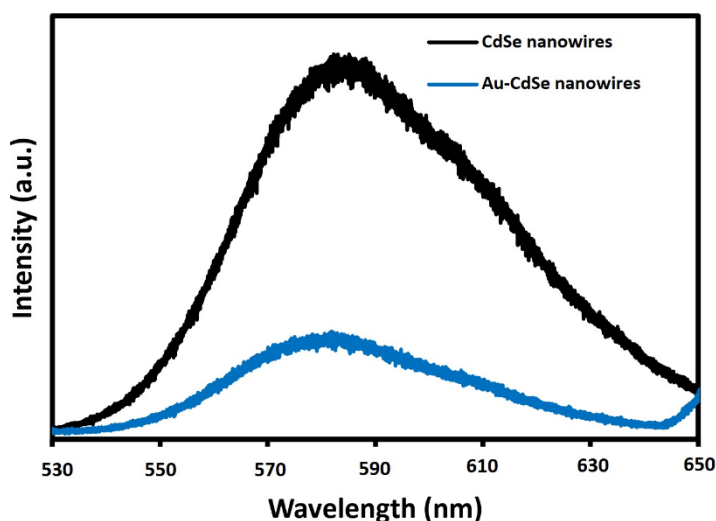


Figure 5. PL spectra of the CdSe and Au-CdSe nanowire

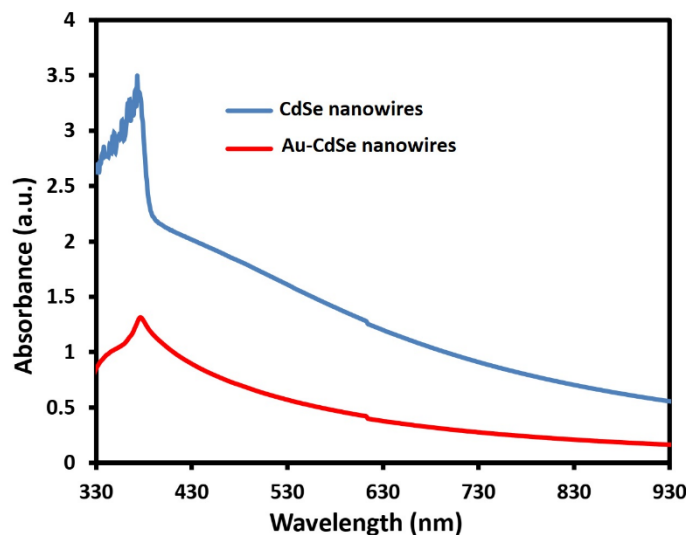


Figure 6. UV–vis absorption spectra of CdSe and Au-CdSe nanowires

UV–vis absorption spectra of CdSe nanowires and Au-CdSe nanowires are shown in figure 6. The transfer of electrons from the valence band to the conduction band forms the absorption band at 380 nm. From this, it is clear that Au-CdSe nanowires compared to bulk CdSe, are under spatial excitonic confinement. The maximum absorption of Au coated CdSe nanowires is at 380 nm.

CdSe nanowires triggered with 514.5 nm Ar^+ ion laser shows Raman Spectrum relating to longitudinal optical (LO) and its overtone (2LO) at 206.6 cm^{-1} and 411 cm^{-1} (Fig. 7) [12]. The wide range of nanowires represents the existence of strain influences phonon spectra of nanowires in opposition to the confinement effect [13]. A common low-frequency shoulder LO peak relating to small size nanowire is seen due to the surface optical (SO) vibrations input and phonon confinement effect. In comparison to the CdSe nanowires, the ones coated with Au has an extra peak at around 280 cm^{-1} .

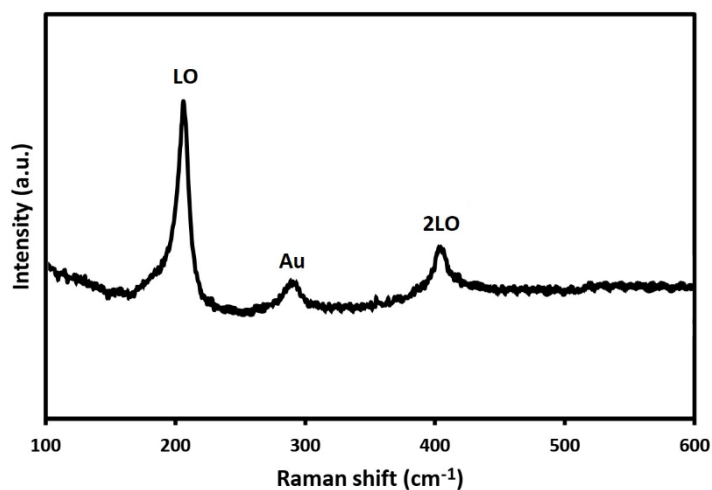


Figure 7. Raman Spectrum of Au coated CdSe nanowires

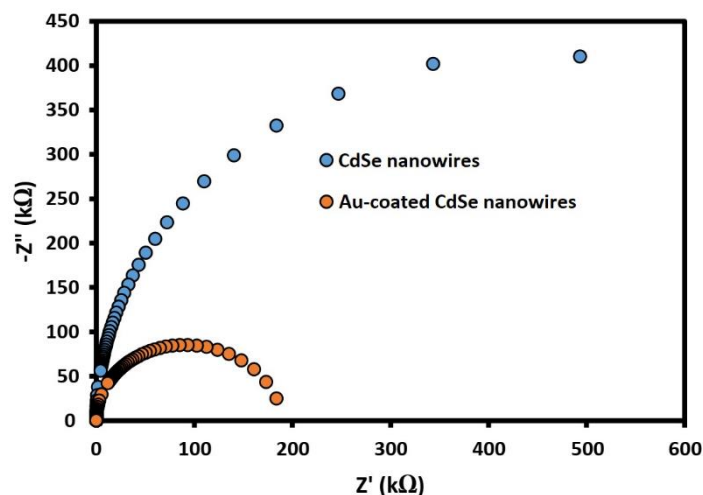


Figure 8. Nyquist plots of CdSe nanowires and Au-coated CdSe nanowires in 0.2 M Na₂S O₄ electrolyte solution.

In order to understand the charge transfer and efficiency interface properties of samples, CdSe nanowires and Au-coated CdSe nanowires were analyzed using EIS technique [14]. Figure 8 indicates Nyquist plots between an imaginary and real impedance for CdSe and Au-doped CdSe nanowires. The arc radius shows the interface layer resistance at the surface of electrode. As the efficiency of charge transfer is decreased, the arc radius increases. The Au particles decrease the interface layer resistance, indicating the advanced interfacial charge-carrier separation and charge transfer efficiency on the CdSe nanowires. These results reveal that the Au particles on CdSe nanowires can lead to higher free-electron carriers that accelerate charge transfer and reduce the resistance, it is helpful for the improvement of the CdSe photocatalytic activity.

The CdSe and Au coated CdSe nanowires were irradiated with UV light of 365 nm and the results of the photodegradation of Rhodamine B dye (RhB) were obtained as in Figure 9a. In aqueous solution, RhB dye reveals the main absorption at 525 nm. As the UV radiation time increased, absorption decreased slowly for the coated CdSe sample and the process was slower for pure nanowires. Figure 9b shows the RhB dye decomposition rate with UV irradiation time. Both the samples were tested under the same conditions for 150 minutes. It was observed that the degradation of RhB dye in the coated and uncoated samples was 93.2% and 17.2% respectively. Hence it is negligible. First order kinetics model is followed by the photodegradation of RhB dye, as indicated by the linear correlation between $\ln(C_0/C)$ and irradiation time (t) shown in figure 8b. The CdSe and Au-coated CdSe nanowires had 0.0019 and 0.014 min⁻¹ rate constants as kinetic evidence, respectively. The Au coating enhances the photocatalytic activity as seen from the results. The improvement is due to the enhancement of photogenerated electron-hole pairs as a result of varied potential energy between CdSe and Au.

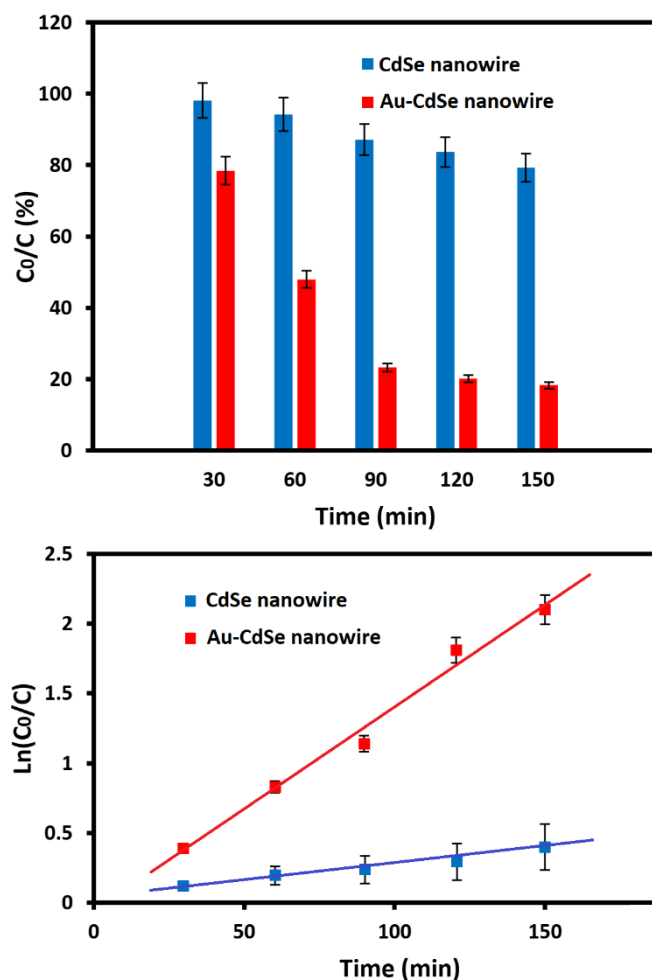


Figure 9. (a) Photodegradation and (b) Rate of photodegradation of RhB in CdSe and Au-coated CdSe nanowires

Table 1. Overview of the various semiconductor nanostructures with their synthesis methods and photocatalytic performances

Dopant	Synthesis method	Pollutant	Time (min)	Deg. (%)	Ref.
CdS nanowires	Solvothermal method	RhB	180	~90	[15]
CdS/ZnO heterostructure	Hydrothermal method	RhB	480	~85	[16]
TiO ₂ -PDMS sponge	Sacrificial template method	RhB	180	~80	[17]
AgIO ₃ /WO ₃ heterojunction	Hydrothermal and chemical precipitation methods	RhB	120	~50	[18]
Au-coated CdSe nanowires	Electrochemical method	RhB	150	93.2	Present work

Table 1 indicates different photocatalysis influence on the photodegradation of RhB dye according to previous researches [15-18]. In comparison to previous reported works, Au-coated CdSe photocatalyst in this research has the highest photocatalytic activity under UV light. According to Table 1, Au-coated CdSe nanowires can be a good choice for photocatalytic activity.

4. CONCLUSIONS

Au-coated CdSe nanowires were successfully synthesized on ITO substrate using a facile electrochemically method to evaluate photocatalytic properties of CdSe nanowires. The FESEM image indicates a high-density array of CdSe nanowires in vertical alignment with an average diameter of <40 nm and height of 2 μm . HRTEM was used to find the interplanar spacing as 0.69 nm, from which it is clear that CdSe nanowire is a single Wurtzite structured crystal with [0001] growth direction. A weak Au diffraction peak appeared in XRD results which confirm Au nanoparticles were coated on CdSe nanowires. The CdSe and Au coated CdSe nanowires were irradiated with UV light of 365 nm and the results of the photodegradation of Rhodamine B dye (RhB) were obtained. The results show 93.2% of RhB dye is degraded using the Au-coated CdSe nanowires after UV irradiation during 150 min, and the rate of degradation for Au-CdSe nanowires is obtained to be 0.014 min^{-1} .

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