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# Enhancing absorption in coated semiconductor nanowire/nanorod core–shell arrays using active host matrices

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ABSTRACT

In the present work, we investigated theoretically and experimentally the interaction of radiation field phenomena interacting with arrays of nanowire/nanorod core–shell embedded in active host matrices. The optical properties of composites are explored including the case when the absorption of propagating wave by dissipative component is completely compensated by amplification in active (lasing) medium. On the basis of more elaborated modeling approach and extended effective medium theory, the effective polarizability and the refractive index of electromagnetic mode dispersion of the core–shell nanowire arrays are derived. ZnS(shell)-coated by sulphidation process on ZnO(shell) nanorod arrays grown on (100) silicon substrate by chemical bath deposition (CBD) has been used for theoretical comparison. Compared with the bare ZnO nanorods, ZnS-coated core/shell nanorods exhibit a strongly reduced ultraviolet (UV) emission and a dramatically enhanced deep level (DL) emission. Obviously, the UV and DL emission peaks are attributed to the emissions of ZnO nanorods within ZnO/ZnS core/shell nanorods. The reduction of UV emission after ZnS coating seems to agree with the charge separation mechanism of type-II band alignment that holes transfer from the core to shell, which would quench the UV emission to a certain extent. Our theoretical calculations and numerical simulation demonstrate that the use of active host (amplifying) medium to compensate absorption at metallic inclusions. Moreover the core–shell nanorod/nanowire arrays create the opportunity for broad band absorption and light harvesting applications.



## 1. Introduction

One-dimensional nanostructures often exhibit fascinating physical properties that are not observed in their bulk counterparts [1,2]. Nanowire/nanorods photovoltaics (PV) has been the subject of research with a view to enhancing the energy conversion efficiency and reducing the material and fabrication costs compared with bulk and thin-film PV [3]. Core–shell nanowire/nanorod arrays are both an ideal platform for fundamental interfacial studies as well as a promising geometry for high and efficient optical absorption [4]. This occurs because of the core–shell geometry which increases the number of nearly degenerate resonances by largely removing the polarization dependence of 1*D* nanowires [5].

Interaction of light with nanocomposites exhibits novel optical phenomena which unrivalled optical properties of these materials. Since the optical properties of heterogeneous metal–semiconductor (core–shell) composites can be efficiently tailored by surface plasmon resonance (SPR), they are strongly dependent on the nanoparticles size, shape, concentration (filling factor) or spatial distribution and surrounding matrix [3]. Control over these parameters enables such composite core–shell to become promising media for development of novel non-linear materials, nanodevices and optical elements. Recent studies by Oener et al. [5] show that the utilization of metal–semiconductor core–shell nanospheres or nanorods for plasmon mediated charge carrier dynamics for photovoltaics and photocatalysis. Other group, Mann et al., [6], reported that core–shell geometry efficiently couples light normally reflected and scattered by the metal core into photonic resonances in the shell eliminating the so-called shadowing losses by embedding metal nanowires in an ultrathin semiconducting shell. The group used Finite-difference time-domain (FDTD) simulation to confirm that placing core–shell nanowires on low-index substrates like glass or plastic only leads to minor perturbations, primarily by increasing the radiative loss rate in the cavity and thus requiring a different shell thickness to maintain critically coupled resonances. This hybrid core–shell

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geometry makes semiconductor nanowire/nanorods an emerging and powerful class of materials for showing optimal absorption efficiency due to their unique electronic, optical, and chemical properties [7]. Among other fascinating applications, nanowire/nanorod core–shell are perhaps the most prospective materials for nanoscale sensors, light emitting diodes, solar cells, and so forth [8,9].

The core–shell geometry of nanowire/nanorod is thought to be able to enhance the efficiency of charge collection by shortening the paths traveled by minority carriers [10,11]. Specifically, ZnO/ZnS core–shell nanorod heterostructures have attracted a great amount of theoretical and experimental interests because of the typical type II band gap alignment that is of high benefit for the amelioration of photovoltaic and photocatalytic properties in comparison with the individual counterparts. Strong light confinement in nanowire/nanorod structures has enabled advances in diverse photonic applications from nanolasers to photovoltaic devices [12–15].

Considering available technologies, the use of cylindrical core–shell arrays structures is better suited for many optics and optoelectronics applications reported so far in Refs. [16–21]. Compared to spherical models, to understand the energy balance between absorption and scattering processes cylindrical model is very efficient, for instance in this kind of structures, the scattering of light is increased by three orders of magnitude [3]. Despite the fact that earlier studies [15] discussed the benefit of core–shell nanorod/nanowire arrays, the contribution of amplifying host matrices for optimal absorption was not explored.

In this work, the effect of active elements in composites having core–shell nanowire/nanorod arrays was investigated theoretically and experimentally. Indeed the theoretical calculations are compared with experimental work done on the growth of ZnO/ZnS nanorod core–shell arrays.

## 2. Theoretical consideration

### 2.1. Background

The concept of an effective permittivity is useful to describe the optical response of a metamaterial molded into arbitrary shapes, rather than having to deal with the detailed arrangement of particles. Theoretically, the permittivity and refractive index have been calculated from polarizability of the core–shell arrays by considering the wavelength outside cylindrical core–shell composite, which is larger compared to cylindrical diameters. Metal/Semiconductor composite core–shell at the resonant frequencies, close to the plasma frequency of the coated shell, shows strong anomalous dispersion even at comparatively small volume fractions of the inclusions and a very high level of losses. The losses in the composites can be considerably reduced by introducing gain elements into the host matrix of the composites or by using alternative layers of composite and gaining medium. The literature reports that an array of nanowire/nanorods can exhibit superb absorptivity even at a fairly sparse arrangement [3,9,22], therefore to explain these properties the rigorous solution of the Maxwell equations is imperative.

Formally, the effect of active elements in composites can be described by introducing a negative part in the dielectric function of the host matrix [23–26]. For instance metamaterials can be synthesized by embedding artificially fabricated inclusions in a specified host medium or on a host surface, this provides the designer with a large collection of independent parameters (or degrees of freedom), such as the properties of host materials, the size, shape, and composition of the inclusions [27]. By depositing a layer of shell on the nanowires to fabricate core/shell nanowires, the surface states of the core will be modified [28–31], the band gap of the core material can be tailored, and as a result, the properties including photoluminescence (PL) of the core will be improved.

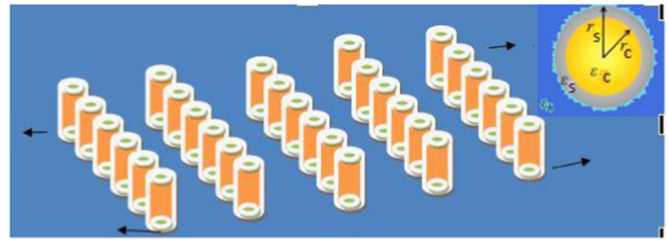

Fig. 1. Structural model for cylindrical core–shell nanowire under consideration together with the relevant parameters.

### 2.2. Electrodynamic analysis

To gain greater insight into how the shape and array of the core–shell nanorod/nanowire distribution influences the effective dielectric response, the discussion starts with presenting core–shell nanowire as cylindrical geometry for theoretical discussion and nanorod for experimental comparison.

Let us consider core–shell cylindrical nanowire/nanorod with radius $r_c$ coated by metallic nanoshell of radius $r_s$ centered at the origin and extending along the $z$-axis to infinity, embedded in a homogeneous dielectric environment (host medium) with permittivity $\varepsilon_h$ where $r_c < r_s$ (see Fig. 1). The nanowire/nanorod is illuminated by a uniform, quasi-static electric field, $E = E_0 e^{i(kx-\omega t)}$ where $k$ is the complex wave vector given by $k = \frac{n\omega}{c}$ and has form $k = k' + k''$, [25]. In the model retardation effect is neglected and only dipolar interaction is under consideration: diameter of the nanowire/nanorod is much smaller than the wavelength of the excitation field. The incident electric field is assumed not to vary spatially over the dimensions of the nanowire while maintaining its time dependence.

The dielectric functions (DFs) of the core, shell, and host matrix are denoted as $\varepsilon_c$, $\varepsilon_s$, and $\varepsilon_h$, respectively. The distribution of the potential in a cylindrical core–shell arrays embedded in a dielectric host matrix in an external constant electric field can be written as:

$$\phi_h = -E_h\left(r - \frac{D_n}{r^{n-1}}\right)\cos\theta, \quad r \geq r_2. \tag{1}$$

where $E_h$ is the applied field, perpendicular to the axis of the nanorod/nanowire, the local field in these arrays can be considerably enhanced if a frequency of the incident radiation is close to the surface plasmon frequency. The local field $E$ in the semiconductor core of the inclusion can be obtained with the help of the relation $E = AE_h$ where $A$ is an enhancement factor discussed in Refs. [1,32]. Here $n$ is the dimension of the problem: $n$=3 for the spherical (quantum dot) and $n$=2 for the cylindrical inclusion (nanorod/nanowire), respectively:

$$D = \beta r_c^2, \quad \beta = 1 - 2\frac{\delta}{\Delta} \tag{2}$$

where $\Delta$ is given by

$$\Delta = \varepsilon_c^2 + q\varepsilon_c + \epsilon_s\varepsilon_h, \quad \delta = \varepsilon_h\left[\left(\frac{2}{p} - 1\right)\varepsilon_c + \varepsilon_d\right] \tag{3}$$

$p = 1 - (r_c/r_s)^2$ is the metal fraction of cylindrical core–shell nanowire/nanorod: