Tailoring Optical and Plasmon Resonances in Core-Shell and Core-Multishell Nanowires for Visible Range Negative Refraction and Plasmonic Light Harvesting: A Review

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[Received 1 October 2014; Received in revised form 13 January 2015; Accepted 13 January 2015]

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Semiconductor nanowires (NWs) are sub-wavelength structures which exhibit strong optical (Mie) resonances in the visible range. In addition to such optical resonances, the localized surface plasmon resonances (LSPRs) in metal-semiconductor core-shell (CS) and core-multishell (CMS) NWs can be tailored to achieve novel negative-index metamaterials (NIM), extreme absorbers, invisibility cloaks and sensors. Particularly, in this review, we focus on our recent theoretical studies which highlight the versatility of CS and CMS NWs for: 1) the design of negative-index metamaterials in the visible range and 2) plasmonic light harvesting in ultrathin photocatalyst layers for water splitting. Utilizing the LSPR in the metal layer and the magnetic dipole (Mie) resonance in the semiconductor shell under traverse electric (TE) polarization, semiconductor-metal-semiconductor CMS NWs can be designed to exhibit spectrally overlapping electric and magnetic resonances in the visible range. NWs exhibiting such double resonances can be considered as meta-atoms and arrayed to form polarization dependent, low-loss NIM. Alternatively, by tuning the LSPR in the TE polarization and the optical resonance in the transverse magnetic (TM) polarization of metal-photocatalyst CS and semiconductor-metal-photocatalyst CMS NWs, the absorption within ultrathin (sub-50 nm) photocatalyst layers can be substantially enhanced. Notably, aluminum and copper based NWs provide absorption enhancement remarkably close to silver and gold based NWs, respectively. Further, such absorption is

polarization independent and remains high over a large range of incidence angles and permittivity of the medium. Therefore, due to the tunability of their optical properties, CS and CMS NWs are expected to be vital components for the design of nanophotonic devices.

Key words: **Nanowires, Core-shell, Core-multishell, Negative refraction, Metamaterials, Scalable plasmonics, Plasmonic light harvesting, Solar hydrogen**

1. Introduction

In the recent years, nanostructures consisting of both semiconductor (or dielectric) and metal components have drawn considerable attention owing to their unique tunable optical properties. For instance, semiconductor nanowires (NWs) exhibit strong diameter dependant optical (Mie) excitations in the visible and infrared range^[1–3]. This intriguing response of semiconductor (or dielectric) nanomaterials can be used to tune their absorption for energy applications^[1–7], as well as to provide natural magnetic dipole resonances for the design of negative-index metamaterials (NIM)^[8–15]. On the other hand, metal nanostructures exhibit plasmon resonances which can be utilized to spatially confine optical fields in the nanometer scale, act as waveguides, enhance absorption, increase light scattering, resonantly transfer energy to generate electron-hole pairs in the surrounding semiconductor, provide hot electrons and drive the electrolysis of water^[16–24]. Combining the optical excitations in semiconductor layers with the localized surface plasmon resonances (LSPRs) in metal layers of the same core-shell (CS) and core-multishell (CMS) nanostructure enables unique photonic applications such as cloaking^[25,26], negative refraction^[27–30] and extreme absorption^[31–35].

This mini-review is primarily focussed on such hybrid CS and CMS NWs that exhibit highly tunable optical and plasmon resonances. Here we highlight the results of our recent theoretical studies focusing on two very diverse applications, namely, visible range NIM (Ref. [30]) and scalable plasmonic photoelectrodes (Ref. [33] © 2014 ACS, Ref. [34] © 2014 SPIE). The results presented here show that by identifying simple design parameters, such as the geometry, core diameters, shell thicknesses, and materials, CS and CMS NWs can be utilized in a diverse range of nanophotonic applications. In particular, such coaxial nanostructures show great potential towards scalable, high efficiency solar energy harvesting.

2. Theory and Calculations

The optical response of single NWs coated with multiple shells under plane-wave incidence can be calculated accurately using Mie formalism where Maxwell's equations are solved in cylindrical coordinates and the NWs are assumed to be infinitely long. The total scattering, absorption and extinction efficiency can be expressed as infinite summations of contributions from each angular momentum channel^[30,32,33,36–39]. Fig. 1 is a schematic depicting oblique plane-wave incidence on a CMS NW. Unpolarized light incident on the NW can be resolved into Case I and Case II where the magnetic and electric fields are perpendicular to the NW axis, respectively. When the incidence is normal to the NW axis, Case I and Case II correspond to transverse magnetic (TM) and transverse electric (TE) polarizations, respectively.

2.1. Absorption efficiency of single NWs

The absorption efficiency within the core and shells of CMS NWs can be individually computed from the ratio of the absorbed power to the incident power as follows^[32,33]:

$$\eta_i^{(\text{TE})} = \frac{k_0}{2r_0\epsilon_0 E_0^2} \iint \text{Im}\{\epsilon(r)\} \left| \left(E_r^{(\text{TE})} \right)^2 + \left(E_\phi^{(\text{TE})} \right)^2 + \left(E_z^{(\text{TE})} \right)^2 \right| r dr d\phi \quad (1)$$

Here, $\eta_i^{(\text{TE})}$ is the absorption efficiency under TE illumination where $i=0, 1, 2$ or 3 corresponds to the medium surrounding of the NW, outer shell, intermediate shell and core, respectively, k_0 is the wave-number of the incident light in the medium, r_0 is the total radius of the nanowire, $\epsilon(r)$ is the dielectric function of the NW, ϵ_0 is the dielectric constant of the medium, E_0 is the amplitude of the incident light and $E^{(\text{TE})}$ is the electric field within the NW. Similarly, the absorption efficiency under TM illumination can be calculated. The absorption efficiency for unpolarized illumination is obtained from $\eta_i = \frac{1}{2} \left(\eta_i^{(\text{TE})} + \eta_i^{(\text{TM})} \right)$.

2.2. Integrated photon flux absorbed

The photon flux absorbed within individual layers of the NW is calculated assuming an unpolarized air mass 1.5 global (AM 1.5G; 1-sun) illumination incident perpendicular to the

NW axis. The photon flux absorbed is integrated over the range of interest which is over 300 and 1000 nm for solar water splitting. The integrated photon flux absorbed is given as follows:

$$\phi_{\text{abs},i} = \int_{\lambda_1}^{\lambda_2} \frac{\lambda}{hc} I_{\text{AM1.5G}}(\lambda) \eta_i d\lambda \quad (2)$$

where, $I_{\text{AM1.5G}}(\lambda)$ is the intensity of AM 1.5G illumination, h is the Plank's constant and c is the speed of light. Assuming ideal charge generation and forward injection, the ideal photocurrent density is obtained from $J = q\phi_{\text{abs},i}$. For all subsequent calculations presented, we utilize the dielectric functions interpolated from experimental data for thin films^[40,41].

2.3. Magnetic and electric polarizability of NWs under transverse electric polarization

The magnetic and electric polarizability per unit length can be obtained from the magnetic and electric moment, respectively, and the magnitude of the incident field (H_0 and $\epsilon_0 E_0$)^[30]. The magnetic polarizability normalized to the area of cross section (A) is as follows:

$$\alpha_m = \frac{-i\omega}{2AH_0} \int_A (\epsilon_i - \epsilon_0) \{xE_y - yE_x\} dA \quad (3)$$

The electric polarizability normalized to the area of cross section is as follows:

$$\alpha_e = \frac{1}{A\epsilon_0 E_0} \int_A (\epsilon_i - \epsilon_0) \{E_y\} dA \quad (4)$$

3. Core-multishell Nanowire Arrays for Visible Range NIM

Metamaterials which exhibit both negative refraction as well as phase reversal have been studied with increasing interest due to their potentially unique applications towards sensing and sub-diffraction limit imaging^[42,43]. Most typical NIM designs consist of an array of sub-wavelength resonant units called meta-atoms which exhibit a spectrally overlapped magnetic and electric resonance—a double resonance. Several breakthroughs have been made in the design and fabrication of visible range NIM using metallic nanowires embedded in a dielectric matrix^[44,45], fishnet structures^[46–48], metal-dielectric stacks/sandwiches^[49–51], planar waveguides^[52] and metal-insulator-metal coaxial waveguides^[53,54]. However, losses arising from the design as well as large material absorption in the visible range requires the use of active materials to compensate for these losses in order to achieve NIMs with a high figure of merit, $\text{FOM} = |\text{Re}(n_{\text{eff}})| / |\text{Im}(n_{\text{eff}})|$. In particular, the losses arising from the NIM design can be minimized by using Mie resonances in semiconductor/dielectric nanostructures^[8–15]. A high FOM has been achieved in NIMs based on metal-semiconductor heterostructures such as

Ag-GaP hybrid rods^[55], Ag-Si core-shell (CS) nanospheres^[27] and nanowires^[28]. For instance, in the Ag-Si CS structures, the natural magnetic dipole resonance in the semiconductor shell is coupled to the LSPR in the metal core and hence has been found to substantially reduce the design based losses. A refractive index of -1 and a FOM of 85 in the near infrared range was predicted for NIM consisting of Ag-Si CS NWs under TE illumination^[28]. Notably, the anisotropy of NWs leads to stronger coupling with light and higher FOMs when compared to nanospheres. In order to shift the working range of such NIMs into the visible range, the meta-atoms should be scaled down. However this also leads to reduction in the resonance strength and poor FOMs. The use of an intermediate low-permittivity layer between the metal and semiconductor has been explored in order to shift the double resonance into the visible range^[29]. Alternatively, plasmon hybridization in semiconductor-metal-semiconductor CMS NWs has been shown as a simple and effective route towards achieving high FOM in the visible range^[30].

3.1. Plasmon hybridization and visible range double resonance in CMS NWs

The intermediate metal shell of semiconductor-metal-semiconductor CMS nanowire can support both cavity and surface plasmon resonances. Depending on the thickness of the metal shells, these plasmon resonances can hybridize to form symmetric and anti-symmetric plasmon resonances similar to the plasmon hybridization in metal nanoshells, nanowires and nanotubes^[56–61]. Fig. 2(d) is a schematic of plasmon hybridization where the cavity (ω_c) and the surface (ω_{NW}) plasmons hybridize to form a lower energy symmetric (ω_-) and a higher energy anti-symmetric (ω_+) plasmons as compared to the energies of the cavity and surface plasmon resonances. This difference in the energy of the hybridized plasmon resonances enables high tunability without the need for a large change in the diameter.

Utilizing the higher energy anti-symmetric plasmon resonance, Si-Ag-Si CMS NWs can be designed to exhibit double resonance in the visible range. E.g., a CMS NW with a 80 nm diameter Si core, 20 nm thick Ag intermediate shell and a 30 nm thick Si outer shell exhibits double resonance around 660 nm as seen from the scattering efficiency plotted in Fig. 2(a). This is further confirmed from the electric and magnetic near-field plots (Fig. 2(d)) for the NW under 660 nm TE illumination. The electric and magnetic polarizability (Fig. 2(b) and c) are negative around 660 nm which is essential for the NW to behave as a meta-atom for a NIM with both negative refraction and phase reversal. It is interesting to note that increasing the Si outer thickness alone increases the energy of the anti-symmetric plasmon and decreases the

energy of the symmetric plasmon resonance. Reducing the core diameter also shifts the anti-symmetric plasmon to smaller wavelengths. However, shrinking the core diameter is accompanied by a reduction in the dipole strength which is unfavorable for the design of NIMs. Si cores with diameters lower than 80 nm have been found to exhibit weaker dipole moments and hence limit the double resonance tunability of NW meta-atoms achieved by reducing the diameters. A similar trend is observed for Ag shells, where thinner shells shift the anti-symmetric plasmon to lower wavelengths accompanied by weaker dipole strength. For Si–Ag–Si CMS NWs, a Ag shell of about 20 nm has been found to provide the best balance between the tunability and resonance strength.

3.2. Effective refractive index and figure of merit

As discussed in the previous section, CMS NWs exhibit a strong and tunable double resonance in the visible range and hence are ideal meta-atoms. Such meta-atoms can be arranged in an array to form a slab that behaves as a low-loss, visible range NIM under TE polarized incidence. E.g., a slab consisting of Si(80 nm dia.)–Ag(20 nm)–Si(30 nm) CMS NWs arranged in a hexagonal lattice (Fig. 3(a) inset) with a separation of 200 nm between the centers of neighboring NWs behaves as a NIM in the 620–730 nm range. Using full numerical simulations performed with COMSOL and S parameter retrieval method^[62,63], the real part of the effective refractive index and FOM was found to be about -1 and 17 , respectively, around 660 nm (Fig. 3(a) and (b)). In such CMS NW arrays, it is important to note that the standard S parameter retrieval method works well for extracting the imaginary part of the effective refractive index. As shown in Fig. 3(c), the oscillations in the imaginary part die out as a function of the NIM slab thickness. The oscillations in the real part however do not die out and hence cannot be accurately extracted from S parameters. It can, however, be determined graphically using Snell's Law since the incidence is polarized. The isotropy of the NIM can be studied from the transmission through the slab as function of the incidence angles. From Fig. 3(d), the transmission is fairly constant up to 20° or 30° and then undergoes a dip and then remains fairly constant above 40° incidence angles. This increased absorption in a small range of incidence angles is due to Fabry–Perot like resonances^[28]. This range of angles is dependent on separation between centers of neighboring NWs as seen in Fig. 3(d).

The FOM predicted for Si–Ag–Si NIM is among the highest for NIM in the visible range with designs not employing active materials for loss compensation. The FOM can be improved further by minimizing the separation between NW surfaces without contact. However, this is

limited by the fabrication methods used to achieve the NW arrays. Alternatively, the FOM can be improved by using a semiconductor/dielectric with a permittivity lower than silicon. For instance, GaP–Ag–GaP NW with same dimensions as the Si–Ag–Si NW exhibits a double resonance around 590 nm. At this wavelength, the real part of the effective refractive index and FOM of a NIM slab consisting of such GaP–Ag–GaP NWs is about -1 and 25 , respectively.

4. Plasmon Enhanced Light Harvesting in Nanowire Photoelectrodes

The use of earth abundant materials in photoelectrodes for splitting water has been studied intensively over the past few decades. In order to achieve high solar-to-hydrogen (STH) conversion efficiencies, the photocatalytic material should have the right bandgap for absorbing visible light, right band alignment to drive the reactions, good reaction kinetics, high conductivity and stability in electrolytic medium^[64,65]. Furthermore, the use of earth abundant materials would ensure scalability of the photoelectrodes and enable an inexpensive route for the production of renewable hydrogen. The photocatalytic properties of semiconductors, metal oxides and chalcogenides have been explored extensively^[66–76]. However, most material candidates face one or more challenges such as high bulk recombination, poor visible range absorption, poor reaction kinetics, surface states and stability in the electrolytic medium. For instance, in hematite (α -Fe₂O₃), the short minority carrier diffusion (~ 20 nm) limits the maximum thickness of the active layer to sub-50 nm layers leading to insufficient absorption^[41,77,78]. Additionally, the conduction band edge of hematite is lower than the reduction potential of water and recombination at the hematite-electrolyte interface is substantially high. Several photocatalyst material specific strategies have been developed to address the interface recombination, poor conduction and the large overpotential and those strategies include improving the quality of hematite deposition^[79–84], doping^[84–90], surface state passivation^[91–94], co-catalysts^[89,94–96] and ‘dual absorber’ system^[93,97–102]. The tradeoff between large bulk recombination in thick layers and poor absorption in thin films is a fundamental challenge common to most photocatalytic as well as photovoltaic materials. This challenge can be potentially addressed by growing or patterning nanowires^[66,67,72,73,75,89,103–106], plasmonics nanostructures^[41,102,107–110], opal scaffolds^[83,96], resonant light trapping in thin films^[41] and photonic nanostructures^[111]. An STH efficiency of 6%, a third of the theoretical potential of hematite, has been reported for Si–Fe₂O₃ CS NW arrays decorated with Au nanoparticles^[102]. This plasmonic absorption enhancement achieved using nanoparticles can be improved further through metal-semiconductor CS NWs^[31,32] and nanocones^[35]. In such NWs,

the absorption in ultrathin semiconductor shells can be found to be above the bulk limit. However, precious metals have been typically employed in most of the photoelectrode designs, making them infeasible for sustainable and large scale devices.

Alternatively, we have demonstrated that “poor” plasmonic materials, such as aluminum and copper, can be utilized in metal-photocatalyst CS and semiconductor-metal-photocatalyst CMS NWs to effectively enhance absorption in ultrathin photocatalyst layers^[33,34]. Using hematite as the photoanode, copper(I) oxide as the photocathode and silicon as the scaffold, plasmonic photoelectrodes can be fabricated as shown in Fig. 4. Here aluminum layer thickness can be optimized to exhibit strong visible range plasmon resonance^[112,113]. Silicon can potentially behave as a secondary absorber to provide the overpotential required to drive the hydrogen evolution. By integrating both the anode and cathode onto the same wafer, it is possible to realize a complete, efficient photoelectrochemical cell. It is critical to note that in this work the absorption predicted is valid only for single NWs and hence does not quantitatively translate to the performance of a large area device directly. However, an array of such optimized CS and CMS absorbers is expected to provide a substantial enhancement in the absorption leading to an overall improvement in the STH efficiency.

4.1. Absorption efficiency of CS and CMS NWs with hematite shells

Considering the short minority carrier diffusion length of about 20 nm in hematite, the maximum thickness of the active layer is restricted due to recombination. For instance, assuming a simple exponential model, less than 10% of the charges generated on one end of the hematite layer are expected to reach the other end for a layer thickness of 50 nm. Hence, it is meaningful to consider the absorption within sub-50 nm hematite shells of CS and CMS NWs in comparison to a homogenous hematite NW. Further, absorption in such ultrathin layers ensures that the photo-generated charges are sufficiently close to the photocatalyst-electrolyte interface to drive the reaction without substantial recombination in the bulk. This is expected to provide a significant boost to the internal quantum efficiency of the photoelectrodes.

Fig. 5(a) plots the absorption efficiency of a 50 nm radius hematite NW in a medium of air under TE, TM and unpolarized incidence normal to the NW axis. The optical resonance around 430 nm in the TM polarization leads to a large absorption enhancement while the absorption under TE polarization is substantially lower. The highest solar irradiance (for AM 1.5G) occurs in the range of 500–600 nm and hence tuning the optical resonance into this range would result in a large enhancement in the photon flux absorbed. However, this requires substantially larger

diameter NWs which leads to larger bulk recombination. A simple solution could be the use of Si-Fe₂O₃ CS NW where, by the addition of a silicon core, the optical resonance can be shifted to around 500 nm as shown in Fig. 5(c). This shift provides a substantial improvement to the photon flux absorbed as will be shown in the next section. Furthermore, the charge collection in the CS structures is in the radial direction as compared to the axial direction in homogenous NWs which substantially reduces recombination and improves the efficiency. Further, the silicon core behaves as a secondary absorber albeit for lower wavelengths where the AM 1.5G solar irradiance is very weak. However, in a NW array, the silicon cores and the wafer together could behave as efficient absorber and thereby reducing the overpotential required to drive the reaction^[93,98,100–102].

Employing a semiconductor core does boost the absorption under TM polarization, however, the absorption under TE polarization remains substantially smaller in comparison. Instead of silicon, a metal core such as aluminum (Fig. 5(b)) or silver (Fig. 5(e)) can be used to substantially improve the absorption under TE polarization. Here the core diameters have been chosen to tune the LSPR into the visible range in order to overlap with both the absorption spectrum of hematite as well as the AM 1.5G illumination. Specifically, the LSPR in the metal core under TE illumination enhances the fields within the hematite shell around 500 nm thereby improving the absorption substantially. Although silver exhibits substantially lower absorption as compared to aluminum, the absorption within the hematite layers is very similar.

The advantages of the absorption in silicon and the LSPR from the metal can be combined together in Si-Al-Fe₂O₃ and Si-Ag-Fe₂O₃ CMS NWs as shown in Fig. 5(c) and (f), respectively. The absorption enhancement due to LSPR in such CMS NWs is similar to the metal-hematite CS NWs, while the absorption within the silicon core is negligible. However, in a CMS NW array, the silicon wafer and the NW cores could potentially behave as an effective secondary absorber as seen in the Si-Fe₂O₃ CS NW arrays^[93,98,100–102]. In addition to the absorption, the Si NWs behave as a robust scaffold for the deposition of metal and hematite layers. It is interesting to note that the silver based CMS exhibits plasmon hybridization as seen from the two distinct absorption peaks within the silver shell under TE illumination (Fig. 5(f)). However, aluminum based CMS NWs do not show such plasmon hybridization for the aluminum shell thickness considered due to the large screening effect. As a result, the absorption in hematite layer of aluminum based CS and CMS NWs is nearly identical whereas hematite absorption in silver based CMS NWs show a slight decrease as compared to the CS NW.

4.2. Integrated photon flux absorbed in various NWs

Absorption efficiency plots provide a clear understanding of the role optical and plasmon resonances playing in the enhancement of absorption. Using this absorption efficiency and assuming an AM 1.5G illumination, the photon flux absorbed integrated over 300–1000 nm range can be computed. Assuming ideal charge injection, the ideal photocurrent density can be computed from the integrated photon flux absorbed which is a good metric to compare between various NWs. Fig. 6 plots the integrated photon flux absorbed and the corresponding ideal photocurrent density for various CS and CMS NWs as a function of the photocatalyst layer thickness. Here, the photocatalysts considered are hematite and copper(I) oxide. In each plot, the plasmonic metals considered are aluminum, silver, copper and gold. The grey dashed line corresponds to the theoretical maximum photocurrent of bulk photocatalyst in air. All calculations assume the NWs to be immersed in a medium of water with a constant permittivity of 1.77 which is valid for typical aqueous electrolytes.

In Fig. 6(a), the photocurrent densities of metal-hematite CS NWs are plotted in comparison with homogenous hematite NWs. Clearly the CS NWs exhibit a tremendous enhancement. For instance, Al(120 nm diameter)–Fe₂O₃ (50 nm) NW is predicted to exhibit an ideal photocurrent density of 12 mA/cm² (i.e. ideal STH of 14.75%) which corresponds to about 95% of the bulk maximum. Notably, the photocurrent densities achieved in aluminum based wires is very close to that of silver based wires. Fig. 6(b) plots the photocurrent densities of silicon-metal-hematite CMS NWs in comparison with silicon-hematite CS NWs. Here, silver and aluminum based CS and CMS NWs show a strong improvement over Si–Fe₂O₃ CS NW, however, copper and gold based NWs provide only a slight enhancement in the photocurrent density. This can be attributed to the copper and gold LSPRs which occur at wavelengths larger than the hematite absorption edge at about 600 nm.

A similar absorption enhancement for various metal based NWs with a copper(I) oxide shell as seen in Fig. 6(c) and (d). It is interesting to note that the absorption within sub-50 nm copper(I) oxide layers is higher than that in the theoretical bulk maximum. More significantly, aluminum, copper and gold based NWs show nearly identical photocurrent densities. This is primarily due to the broader absorption range of copper(I) oxide which not only improves the absorption, but also enables the use of LSPRs in copper and gold occurring beyond 600 nm to enhance the absorption. Hence, both aluminum and copper are effective plasmonic materials to enhance absorption in photocatalyst with a broad absorption range over 300–1000 nm.

4.3. Effect of the permittivity of the medium

It is critical to study the effect of the relative permittivity of the medium on the absorption within the NW to provide a more realistic estimate of the ideal photocurrent density at working condition. From Fig. 6(a) and (b), hematite thicknesses that exhibit the highest photocurrent densities can be identified. Using these NW dimensions, the ideal photocurrent densities of various CS and CMS NWs as a function of the medium's permittivity is plotted in Fig. 7. All NWs show a monotonic decrease in absorption as a function of increasing permittivity. It is interesting to note that, in both CS and CMS NWs, the slope of the curve for silver based NWs is larger than aluminum based NWs. This indicates that aluminum based NWs are slightly more robust to variations in the electrolyte (medium) as compared to the silver counterparts. For typical aqueous electrolytes with permittivity in the range of about 1.6–2.0, aluminum based NWs exhibit a large photocurrent density (around 12 mA/cm²). Hence, aluminum is a good alternative to silver for plasmonic light harvesting in photoelectrodes.

4.4. Effect of polarization and the angle of incidence

One of the fundamental advantages that nanospheres have over NWs is that their optical response is independent of the polarization and angle of incidence. However, metal-semiconductor CS NWs have been reported to exhibit polarization independent absorption under plane-wave illumination incident normal to the NW axis^[32]. This along with the stronger optical coupling due to their large lengths gives NWs a substantial advantage over nanospheres. It is also essential to consider the effect of the incidence angles on the absorption within NWs. Fig. 8 plots the ideal photocurrent density (blue curve) of a Si(40 nm diameter)–Al(50 nm)–Fe₂O₃(40 nm) CMS NW as a function of the incidence angles. The ideal photocurrent density remains fairly large up to an incidence angle of about 45°. Hence, the NW arrays are expected to exhibit fairly consistent photocurrent densities irrespective of the illumination angle during operation. Notably, the ratio of the photocurrent densities plotted in Fig. 8 (red curve) under Case I (denoted as TM) and Case II (denoted as TE) is nearly constant ($J_{TM}/J_{TE} \approx 1$) over a large range of incidence angles. This implies that the integrated absorption is polarization independent and hence, the critical challenge posed by the anisotropic absorption of non-plasmonic NWs can be overcome by metal based CS and CMS NWs.

5. Conclusions and Outlook

In conclusion, our recent theoretical studies on metal and semiconductor based CS and

CMS NWs as modular components for nanophotonics have been reviewed. Such structures exhibit size dependent, highly tunable optical (Mie) and surface plasmon resonances in the visible range. This unique optical response can be used to achieve negative refraction and efficient light harvesting. In particular, plasmon hybridization in semiconductor–metal–semiconductor CMS NWs is an effective route to achieve visible range double resonance without the need for large changes in the size of the NW meta-atoms. The NIM consisting of such meta-atoms exhibits high FOM in the visible range. In metal-photocatalyst CS and semiconductor-metal-photocatalyst CMS NWs, the field enhancement around the plasmon resonance can be utilized to substantially boost the absorption within ultrathin photocatalyst layers. Notably, such NWs exhibit polarization independent absorption despite being highly anisotropic structures. Further, aluminum and copper are excellent alternatives to silver and gold respectively for plasmon enhanced light harvesting in such NWs which enables the design of scalable plasmonic photoelectrodes. These CS and CMS NWs are predicted to show high photocurrent densities when working with typical aqueous electrolytes with relative permittivity in the range of 1.5–2. The versatility of CS and CMS architecture combined with the strong optical coupling of NWs in the visible range makes such NWs ideal nanophotonic elements for applications beyond NIM and photocatalysis such as photovoltaics, sensors, lasers and optical switches.

Amongst the various possible applications, we believe, such coaxial nanostructures have a tremendous and immediate role in solar energy harvesting devices. In such devices, variations in the NW diameters and randomness in their position and height typically leads to broader absorption range which could further improve the device performance. In addition, this relaxes the need for developing complex fabrication strategies often necessary for nanophotonic devices. In this review, the optical response of only a single NW has been considered. To obtain the true device characteristics, the coupled optical and electrical response of nanowire arrays must be evaluated. Furthermore, the absorption improvement here is only due to field enhancement around the plasmon resonance. However, plasmon resonance mediated resonant energy transfer, direct electron transfer as well as hot carriers in metal layers are expected to provide a substantial boost to the photocurrent density. Hence, carefully tuning the plasmon resonance and the nanowire size can potentially provide enhanced absorption as well as carrier generation beyond the absorption edge. We believe that through better understanding of such plasmon mediated phenomena and combining them with optical resonances will enable the design and fabrication of a new generation of high efficiency, scalable photoelectrodes and solar cells.

Acknowledgement

S. Ramadurgam thanks the support from the National Science Foundation ECCS 1118934.

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Figure and table captions

Fig. 1 Schematic of CMS NWs under oblique polarized incidence. Magnetic field and electric field perpendicular to the NW axis in Case I and Case II, respectively. Adapted with permission from Ref. [33]. © 2014 ACS.

Fig. 2 (a) Total scattering efficiency and contributions of the first (magnetic) and second (electric) Mie coefficients of a Si (80 nm dia.)–Ag (20 nm)–Si (30 nm) CMS nanowire under TE illumination. Inset: schematic representation of the CMS nanowire structure. (b) and (c) are the corresponding normalized electric and magnetic polarizability, respectively. The shaded grey region represents the spectral region of double resonance. (d) Schematic of plasmon hybridization in CMS NW. (e) Magnetic and electric near-field contours at 660 nm. Reprinted from Ref. [30].

Fig. 3 (a) Real part (green curve) and imaginary part (blue curve) of the effective refractive index, (b) corresponding FOM of a slab of hexagonally packed Si (80 nm dia.)–Ag (20 nm)–Si (30 nm) nanowire array under TE plane-wave illumination ($\alpha = 20^\circ$). The error bars in the real part of the refractive index (green curve) are estimated based on the $\pm 2^\circ$ error assumed while measuring the refracted angle. Inset: schematic of the slab based on CMS nanowires arranged in a hexagonal lattice. (c) Imaginary part (green curve) and $m = 0$ branch of the real part (blue curve) of the effective refractive index plotted as a function of number layers in the NIM slab simulation. Also plotted is the corresponding transmission (red dashes) through the NIM slab. (d) Transmission through the NIM slab for two different pitch lengths as a function of the angle of incidence. Reprinted from Ref. [30].

Fig. 4 Schematic of a standalone CMS NW water splitting device.

Fig. 5 Absorption efficiency plotted for individual core and shell layers of various nanowires with core diameters and shell thicknesses chosen to maximize absorption within sub-50 nm thick layer of hematite. Reprinted with permission from Ref. [33]. © 2014 ACS.

Fig. 6 Absorbed photon flux integrated over 300–1000 nm and ideal photocurrent density within the

photocatalyst layer as a function of its thickness for (a) metal-hematite CS NWs compared with hematite NW, (b) silicon-metal-hematite CMS NWs compared with silicon-hematite NW, (c) metal-copper(I) oxide CS NWs compared with hematite NW and (b) silicon-metal- copper(I) oxide CMS NWs compared with silicon-hematite NW. Here, an unpolarized 1-sun illumination incident normal to the NW axis and water as the electrolytic medium is assumed. The grey dashes show the theoretical maximum absorption in the photocatalyst bulk. The insets show the cross-section of CS NW in (a) and (c) and, CMS NW in (b) and (d). Adapted with permission from Ref. [34]. © 2014 SPIE.

Fig. 7 Ideal photocurrent density within the hematite shell plotted as a function of the relative permittivity of the medium (electrolyte) for (a) metal–hematite nanowires compared with hematite nanowire and (b) silicon-metal-hematite nanowires compared with silicon–hematite nanowire. An unpolarized 1-sun illumination incident normal to the nanowire axis is assumed. Reprinted with permission from Ref. [34]. © 2014 SPIE.

Fig. 8 Ideal photocurrent density (blue) obtained by integrating the flux absorbed over 300–590 nm and the ratio of the photocurrent density under perpendicular polarizations (green) as a function of the incidence angle within the hematite shell of a Si(40 nm diameter)–Al(50 nm)–Fe₂O₃(40 nm) nanowire. Inset: Schematic of CMS nanowire under oblique incidence. Note: here, TM (Case I) and TE (Case II) refer to polarizations where the magnetic field and electric field are perpendicular to the NW axis, respectively. Reprinted with permission from Ref. [33]. © 2014 ACS.

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