

Gold Nanorods for application in Plasmonic Luminescent Solar Concentrators

A. Sethi^{a, *}, S. Chandra^a, H. Ahmed^a and S. J. McCormack^a

^aDept. of Civil, Structural and Environmental Engineering, Trinity College Dublin, Dublin, Ireland.

*Corresponding author Email: sethia@tcd.ie Tel: + 353 1 896 2671

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Abstract

Luminescent solar concentrator (LSC) device is based on energy down shifting phenomenon with a primary goal of trapping, and concentrating solar radiation. The trapped light is guided to the photovoltaic cell through total internal reflection where it is absorbed and converted to electricity. LSC with its flexible design have the potential to find extensive use in the building integrated photovoltaics [1]. However, the optical efficiency of LSCs is limited by the properties of doped fluorescent materials. Plasmonic properties of metal nanoparticles (MNP) such as Gold (Au) and nanorods can be used for the enhancement of fluorescence of quantum dots (QDs), rare earth complexes and organic dyes in LSC devices [2]. The fluorescence enhancement of the luminescent species placed in the vicinity of MNP is dependent on spacing between the fluorophore-MNP, surface plasmon resonance (SPR) spectral overlap, and orientation. To maximize plasmonic coupling it is required to control spacing with the fluorophores and that can be achieved through concentration distribution of MNPs. The MNP-fluorophore composite in a polymer matrix material is required to have soluble and dispersion compatibility in this matrix material. Since, the wide range of MNPs synthesised using wet chemistry are functionalized with CTAB (hexadecyltrimethylammonium bromide) [3, 4, 5], that is insoluble in organic solvent hence in the polymer. This requires functionalizing MNPs and to make them soluble in organic solvent and polymer. Nanorods (NRs) were synthesized using the seed mediated wet chemical process, with the capping agent. The colloidal solution obtained has a high shape yield for the NRs as is evident by UV-VIS and SEM characterisation. The NRs were successfully separated from the by-products such as spheres and cubes.

Introduction

The ever-increasing global energy demands

can be met by the photovoltaic conversion of energy. Since 2008 there has been a huge decrease in the cost of the solar cell systems but for photovoltaics to become economic further cost reductions have to be achieved. Luminescent solar concentrators (LSCs) can concentrate both the direct and diffused sunlight [6] without the need of expensive solar tracking systems. This makes it easier for the LSCs to be integrated in the urban environment [7]. Silicon based PV cells remain relatively expensive (0.62 €/W for highly efficient crystalline module) [8] and limited in coloration and shape. LSCs consist of a slab of transparent plastic (PMMA) or glass in which luminescent species, originally organic dyes and now even quantum dots and rare earth complexes are dispersed. Light is absorbed by these fluorophores and is re-emitted at a longer wavelength. If the re-emitted light falls outside the escape cone it is trapped within the waveguide due to total internal reflection and is guided to the edge of the slab for conversion into electricity by the solar cells. The low conversion efficiency of the LSC design causes them to be uneconomic. The main deficiencies are: The non-unity quantum yield of the fluorophores results in non-radiative relaxation of the absorbed photon in the form of heat. The isotropic emission of photons by the fluorophores results in the loss of the light through the front surface of the waveguide. Re-absorption of the photons due to an overlap of the absorption and emission spectra of the fluorophores aggravates the escape cone and non-unity quantum yield losses for the LSC. Due to the limited spectral response of the fluorophores it is difficult to utilize the entire AM1.5 solar spectrum. Plasmonic interaction between metal nanoparticles (MNPs) and the fluorophores can help reduce these losses thus enhancing the optical efficiency of LSC. MNPs (Au, Ag) exhibit localized surface plasmon resonance (LSPR) with SPR wavelengths falling in the visible region. The LSPR results in a strong electric field enhancement that decays exponentially from the surface of the MNP. A

fluorophore placed in the vicinity of the MNP is excited due to dipole–dipole interactions. The spacing between the fluorophore and the MNP can dramatically affect the fluorescence rate [9] and consequently the fluorescence quantum yield (FQY) [10], lifetime and Photoluminescence (PL) intensity. The plasmonic coupling depends on the orientation of the MNP with respect to the fluorophore, the enhancement is higher when the fluorophore dipole is along the main axis of the anisotropic NP [11]. Coherent excitation of surface plasmon takes place when Surface plasmon resonance (SPR) frequency overlaps with the frequency of the fluorophore and the spacing between them is greater or equal to 5 nm [12]. The MNP acts as a nanoantenna enhancing the strength of the dipole oscillator and thus enhancing fluorescence [13]. The SPR frequency is primarily the function of the size and shape of the Au NR. For this work, a precise control over the size of the NRs to match their wavelength with that of the fluorophores. Au NRs are crucial to align our fluorophores in the matrix to reduce the escape cone losses in the LSC design. In the past few years many Au NR synthetic strategies have been developed to achieve decent yields and monodispersity. This work focuses on the synthesis, purification and extraction of Au NR from the parent solution for a successful dispersion of the rods in organic solvent. CTAB was used as the capping agent for the seeds and the rods; CTAB capped seeds lead to the formation of single crystalline NRs as opposed to pentatwinned rods from citrate capped seeds. It is important to note that citrate capped seeds though more stable lead to the formation of various crystallographic habits and that is the main reason for a lower shape yield ~30% in the synthesis of pentatwinned rods. Despite the relatively higher yield of CTAB-Au NRs spheres and cubes are present as the by-product in the colloidal solution. Purification and shape separation was carried out using centrifugation by optimizing the centrifugal force and time for different aspect ratio (AR) NRs. The limitations imposed by the environment and the host material in a LSC require the NRs to be dispersed in a solvent that is compatible with the host material and does not change the shape of the NRs. QDs available in the market are usually dispersed in organic solvent such as toluene, to make the composite of the MNP with the QD need the NRs to be dispersed in toluene as well. Removal of excess CTAB is therefore imperative to ensure a successful phase transfer of the NRs from an aqueous to organic solution. Finding the amount of Gold Nanorods in the solution is important to optimize the

concentration of the MNPs in the MNP-fluorophore composite. An organic salt such as CTAB can hamper the results obtained for Au concentration from the inductively coupled plasma spectrometer (ICP-MS). This work will mainly focus on the synthesis, characterization, purification and shape separation of Au NRs.

Experimental section & Methodology

Au NR synthesis: An optimized seed mediated method was carried out to prepare an aqueous colloidal solution of Au NRs of aspect ratio ~4 and ~3.5. The seed solution was prepared by mixing 600 μ l of ice cold 0.01M NaBH₄ to the solution of 0.1M CTAB and 50mM HAuCl₄. It is important for an instantaneous addition of the reductant to the solution to achieve simultaneous production of all nuclei. CTAB capped seeds are relatively less stable than citrate capped seeds. Growth solution of NRs was prepared by mixing the gold precursor with CTAB at 27-30°C to form a complex between the Au salt and CTAB. After the addition of mild reducing agent AA the growth solution changed from dark yellow to colourless due to the reduction of Au(III) to Au(I). 40 μ l and 80 μ l of 5mM AgNO₃ was added to this growth solution. The presence of Ag⁺ ions is crucial for the formation of single crystalline rods as it hinders the formation of pentatwinned rods. Finally, 120 μ l of seed solution was added to the growth solution to complete the reduction of Au(I) to Au (0). The final NR solution was kept in the water bath at 27°C for 30 min to ensure the complete reduction of Au.

Optical characterisation: UV-Vis-NIR spectroscopy is one of the main tools required for the characterisation of the NRs. The full width at half maximum (FWHM), shape of the longitudinal LSPR band in the optical spectrum are a good indication about the size dispersion in the NR solution. The position of the plasmon band can give us an estimate of the average aspect ratio of the NRs. Presence of a shoulder in the transverse peak and the ratio between the transverse and longitudinal peak are an indication of by-products present in the solution.

Microscopic characterisation: Scanning Electron Microscope (SEM) Carl Zeiss Ultra was used to image the NRs. It can give good approximation of the size of the NRs. In lens detector is used to see the Au NR dispersed on a Si wafer. It is important to optimise the electron acceleration voltage as a higher EV can cause carbon deposition and damage the NRs while the image is being taken, a lower EV decreases the resolution of the image. TEM is

a better tool if a precise knowledge about the structure and dimension of the NRs is necessary.

Purification of Au NRs

Shape yield obtained after the seeded growth mechanism is usually very low to be sufficient for the targeted application. Wet chemical synthesis of the gold NRs inevitably contains spheres and cubes as the by-product. Therefore, post synthesis purification and separation is important to maximize the yield of monodisperse samples. Purification methods [14] including centrifugation [15], electrophoresis [16], depletion interaction forces [17] have been proposed in the separation of metal nanoparticles.

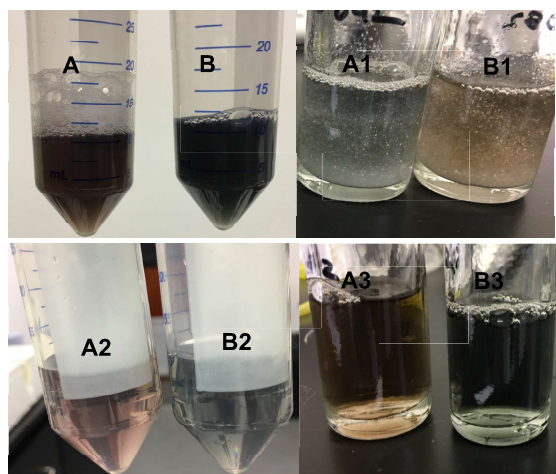


Figure 1: A, B (top left): Au NPs containing 80 μ l and 40 μ l respectively re-dispersed in DI water after the first centrifugation cycle at 12,000g/30min. A1, B1 (top right): Supernatant after the first centrifugation cycle, it mainly consists extra CTAB as is evident by the crystallization of the CTAB within a few hours. A2, B2 (bottom left): Au NPs left in the pellet after the second centrifugation cycle re-dispersed in DI water. A3, B3 (bottom right): Supernatant after the second centrifugation cycle, containing mainly the NRs.

Centrifugation was used to separate the NRs from the spheres and cubes. Although there are scattered reports in literature to use centrifugation-assisted sedimentation but there was difficulty to achieve efficient separation reproducibly. Small differences in concentrations, centrifugation parameters and size of the NRs can lead the NRs to either sediment out or remain in the solution after centrifugation. It is difficult to separate Au NRS with low AR<4. We perform two-step centrifugation; the first step involves the

isolation and purification of all the Au nanoparticles from the excess CTAB. Excess CTAB can affect the phase transfer of the NRs into an organic solution, and centrifugation temperature below 20°C causes the crystallization of CTAB and hinders the purification of the NR solution as can be seen in Figure 1.

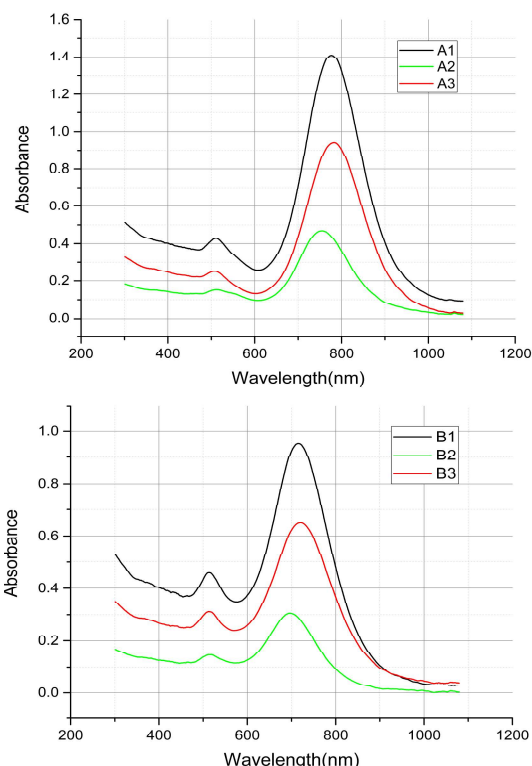


Figure 2: (top): UV-Vis spectra of aforementioned (Figure 1) solution of NRs containing 80ul of AgNO₃. (bottom): Absorption spectra of Au NRs containing 40ul of AgNO₃ thus lower AR NRs.

Results and Discussion

Au NRs were synthesised of different AR by changing the no. of Ag⁺ ions in the growth solution. For single crystal rods higher concentration of Ag⁺ ions will increase the AR of the rods [18].

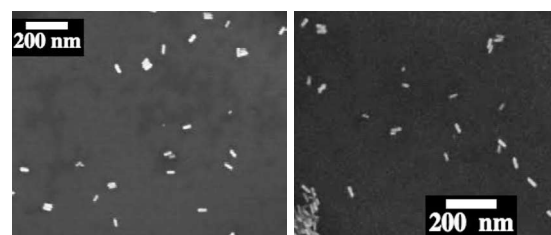


Figure 3: SEM images of A3 NR solution, containing NRs with L~40nm and W~10nm.

Figure 1 shows the apparent colour change of the NR solution after the second centrifugation cycle. A2, B2 and A3, B3 are the pellet and supernatant, the latter containing longer NRs and the former containing mainly the spheres, cubes and the shorter NRs. This is confirmed by the UV-vis spectra in Figure 2. There is a blue shift in the longitudinal peak for A2, B2 (green) spectrum indicating the presence of smaller NPs than the supernatant. Figure 3 shows the SEM image of the NRs having an AR ~ 4 for the 790 nm longitudinal peak. A successful synthesis, purification (removal of excess CTAB), shape separation of the NRs have been achieved. The NRs are stable for long periods of time. The next step is to extract the NRs from aqueous to organic solvent for research in PLSC.

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