Blending quantum emitters and nanoresonators into the perfect metamaterial downconverter for increased solar cell efficiency

Antonio Capretti, Arnon Lesage and Tom Gregorkiewicz

Van der Waals-Zeeman Institute, University of Amsterdam Amsterdam, The Netherlands

Summary. Downconversion holds great promise for reducing thermalization and front-surface recombination losses in solar cells. In the simplest configuration, a thin layer of luminescent emitters is placed on the front-surface of a cell with bandgap E_g (~1.11 eV for Si), turning 1 high-energy photon of sunlight (with energy $E>2E_g$) into 2 photons of lower energy ($2E_g>E>E_g$). This can be achieved by utilizing photoluminescent (PL) materials, which feature forms of carrier multiplication, resulting in a quantum yield (QY) > 100%. A number of emitters are being investigated for this purpose, including rare-earth ions, organic molecules and semiconductor quantum dots, with a focus on maximizing their QY.

However, the QY is not the only relevant parameter, and a practical downconverting layer has to satisfy strict requirements on its absorption spectra, in order not to introduce additional losses to the solar cell. Specifically, an ideal downconverter layer features:

i) total absorption of photons with energy $E>2E_g$ (which requires a large layer thickness),

ii) zero absorption of photons with energy $2E_g>E>E_g$ (requiring a layer as thin as possible).

Clearly, a planar downconverting layer is not be able to satisfy both conditions simultaneously, because absorption follows the simple Beer-Lambert law. Here, we tackle these spectral requirements by using a metamaterial approach. We propose a hierarchical metamaterial as shown in Figure, where each scale is optimized for a different task:

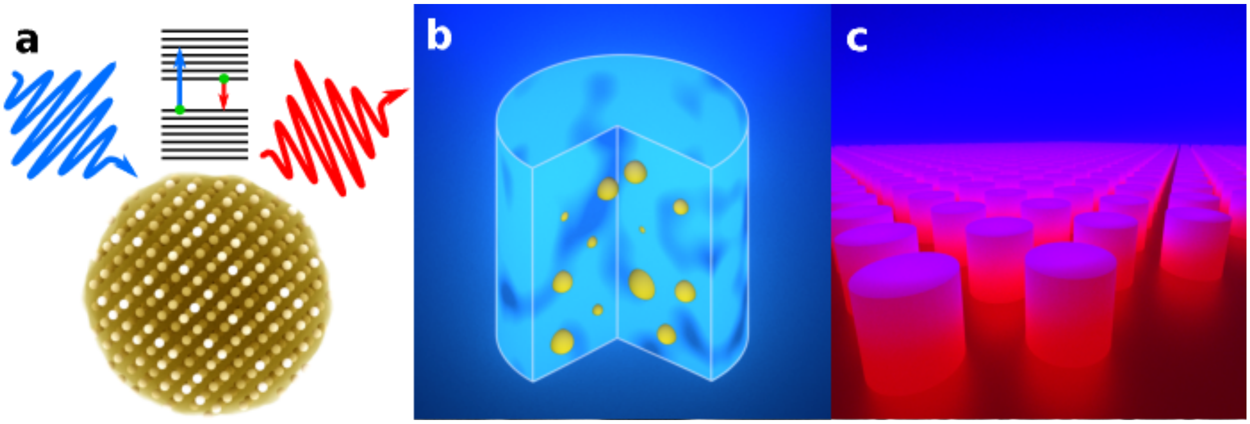

Figure. a) Quantum emitter, b) nanoresonator and c) 2D array.

a) Quantum emitters in a matrix (with size < 10nm) provide the optical transitions to enable photon absorption at $E>2E_g$ and emission at $2E_g>E>E_g$. They are optimized for maximal QY.

b) The emitters in a matrix compose the nanoresonators, whose size and shape are optimized to support Mie modes, resulting in nanocylinders with diameter of 100nm-300nm.

c) The nanoresonators are arranged in a 2D lattice with spacing designed to support grating modes. At the emission wavelengths (> 700nm), the layer is optically homogeneous.

Both Mie and grating modes, whose spectral position is independently controlled by the nanocylinder diameter D and spacing S, allow for absorption peaks at energies $E>2E_g$, thus satisfying the spectral requirement I) above. The nanocylinder height can be kept at a few hundreds *nm*, thus addressing the requirement ii).

In order to prove the validity of our concept, we choose a specific material platform and fabricate hierarchical metamaterials where the quantum emitters are silicon nanocrystals (Si-NCs) and the matrix is SiO_2. This choice is strongly motivated by the fact that all the material components are based on Si (envisioning the use of this downconversion scheme on Si solar cells) and by the ease of nanopatterning. Moreover, ensembles of Si-NCs support carrier multiplication in the form of a process named space-separated quantum cutting (SSQC). However, a substantial improvement of the Si-NC PL QY (currently at 35%)) is necessary for applications. We fabricate three sets of metamaterials with nanocylinder height 100nm, 300nm, and 450nm. In each set, the nanocylinder diameter varies from D=164nm to 420nm.

The metamaterials show broad extinction spectra in the 350 - 600 nm wavelength range. The amplitude of the extinction bands is maximized for the set of metamaterials with height 300nm. By extracting the 0-th order transmission from the scattering background, we clearly detect extinction peaks throughout the visible range. The metamaterials with nanocylinder diameter from 215nm to 372nm show both Mie and grating peaks, whose spectral position is tuned throughout the visible spectral range. We perform rigorous electromagnetic calculations and show that extinction peaks up to 100% are supported by a free-standing metamaterial configuration, corresponding to 50% absorption. Total absorption can be achieved by using a dielectric metamaterial with a back-reflector, as recently proposed in literature.

In order to prove that the metamaterial Mie and grating modes determine enhanced absorption in the Si-NCs, we measure the PL enhancement per average Si-NC (PL_{enh}), defined with respect of an equivalent planar layer. The metamaterials with height 300 nm show a significant PL_{enh}, in contrast to the metamaterials with non-optimized height. We measure the PL enhancement as function of the excitation wavelength, and show that is it maximized in correspondence of the Mie and grating resonances. Remarkably, our metamaterials show up to +30% more intense light emission than a planar film, achieved with less than half the number of Si-NCs. This result translates into a 3-fold PL enhancement. It is worth to remark that this result has been obtained without using plasmonic components, which are well-known to introduce losses by Joule heating. It is important to point out that the nanopatterning could modify the reflection and transmission coefficients at the emission wavelengths, or the photonic density of states and affect the Si-NC radiative lifetime. We perform all the relevant experiments and find that these properties are not altered with respect to the homogeneous reference film.

This results show that we have successfully integrated quantum-confined Si-NCs into SiO_2 nanocylinders, arranged into a 2D array. This hierarchical metamaterial inherits the optical and electronic properties of its building blocks and shows boosted performances than the individual components. This metamaterial concept with spectrally-selective absorption will find direct use as a downconverting layer for solar cells.