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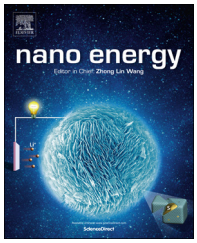

RAPID COMMUNICATION

Broadband efficiency enhancement in quantum dot solar cells coupled with multispiked plasmonic nanostars

Jiang Wu[a,b,c], Peng Yu[a], Andrei S. Susha[d], Kimberly A. Sablon[e], Haiyuan Chen[a], Zhihua Zhou[a,b], Handong Li[a,b], Haining Ji[a,b], Xiaobin Niu[a,b], Alexander O. Govorov[f], Andrey L. Rogach[d], Zhiming M. Wang[a,b,*]

[a]*Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, PR China*
[b]*State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, PR China*
[c]*Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom*
[d]*Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, PR China*
[e]*United States Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197, USA*
[f]*Department of Physics and Astronomy, Ohio University, Athens, OH 45701, USA*

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Abstract
We report a significant broadband enhancement of the external quantum efficiency of the quantum dot solar cell by coupling with plasmonic nanostars via a simple and scalable "boiling deposition" technique. The multispiked nanostars provide broadband scattering and absorption cross-sections, which can be engineered to dramatically boost the performance of the solar cells. The localized near field modes of nanostars result in an external quantum efficiency enhancement over 400% for short-wavelength light absorbed in the emitter, while plasmon light scattering causes distinct improvement in quantum efficiency (10–50%) in the long-wavelength region up to 1100 nm. Finite difference time domain method is adopted to explain the origin of the optical absorption enhancement in the quantum dot solar cells. The broadband light

*Corresponding author at: Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, PR China.
E-mail address: zhmwang@uestc.edu.cn (Z.M. Wang).

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concentration by plasmonic nanostars can significantly reduce the amount of quantum dot materials required for a solar cell and provide efficient utilization of the full solar spectrum.

Introduction

The global energy crisis and environmental problems have accelerated the demand for sustainable energy resources in the last few years. Solar energy, which is clean and abundant, is undoubtedly one of the most favored renewable energies. However, the deployment of solar energy requires further improvement in the cell efficiency to balance the cost of manufacturing solar cells with energy harvesting. To this end, a lot of efforts have been devoted to nanostructured materials, including nanowires [1,2], quantum dots (QDs) [3–7], and two-dimensional layered nanosheets [8,9], for enhanced solar energy conversion efficiency. Among these efforts, QDs with atom-like discrete density of states have attracted much attention due to their unique properties, and novel concepts, including multiple exciton generation [10], hot carrier transfer [11,12], and intermediate band assisted multi-photon absorption [13,14]. These concepts can potentially realize the so-called third generation solar cells with ultra high conversion efficiency via harvesting additional photons. For example, introducing a mid-bandgap energy band, referred to as intermediate band, can be helpful to collect photons of sub-bandgap energies. Through effective conversion of these otherwise wasted photons, intermediate band solar cells can potentially exceed the Shockley-Queisser limit of single junction solar cells [15]. Using self-assembled QDs, typically InAs/GaAs with non-optimized bandgap combinations of $\sim$0.30, 1.02, and 1.30 eV, the respective QD solar cells could achieve the efficiency limit of 51.6% under the condition of solar concentration ($\geqslant$1 sun), while the single junction solar cells could only achieve 36.7% [13]. However, most QD solar cells fabricated via self-assembly cannot provide a bulk intermediate band and the photon absorption in these cells is largely limited by the small QD absorption cross-section. The QD must be assembled into dense arrays to absorb enough photons, while strain accumulation from stacking multiple layers of QDs generates lattice defects and degrades device performance [16,17]. Despite widespread efforts in this field, the strain is intrinsic in the mainstream Stranski-Krastanov QD growth, while other strain-engineering techniques are still immature and require further optimization [16,18,19].

Plasmonic nanostructures, such as metal nanoparticles, are promising to address the issue of spectrally unbalanced photoabsorption in QD solar cells and achieve panchromatic solar energy conversion [20]. The rapid advances in the field of plasmon enhanced solar cells have significantly improved the performance of thin-film solar cells and nanostructured solar cells [21–23]. The metallic nanophotonic structures have demonstrated apparent advantages over conventional macroscopic surface textures for enhancing light absorption in solar cells over a broad spectral range [24]. The size and shape of metallic nanostructures play a critical role in achieving panchromatic photon absorption. For example, Mendes et al. proposed the use of the near-field of metallic nanospheroids to produce a dual-band absorption enhancement in QDs [25]. The resonance frequency of most of the spherical metallic nanoparticles is in the visible wavelength region, and thus located far away from the QD absorption peak wavelength [26]. Complex metal nanostructures, such as gold cages [27], gold nanostars [28,29], and hybrid metallic nanostructures [30,31], shift the plasmon resonance to the near infrared, which can potentially magnify the weak absorption of sub-bandgap photons in QD solar cells.

In this work, a broadband quantum efficiency enhancement in QD solar cells is demonstrated employing multispiked gold nanostars as a plasmonic absorber. The stars deposited on top of QD solar cells provide both near field coupling and light scattering to effectively enhance photon absorption arising from the localized surface plasmons. Efficient plasmonic enhancement in the QD solar cells requires both optimization in the design of plasmonic structures as well as the physical coupling between them and the active layers of solar cells. The current work provides a proof-of-concept demonstration of plasmonic enhanced nanostructured solar cells with small absorption volume. The broadband plasmonic enhancement demonstrated in this work will pave the way for realization of high efficiency QD based solar cells by solving the fundamental issues of weak absorption and non-radiative losses in QDs. Via balancing the absorption in different spectral regions mediated by the localized surface plasmon, high efficiency QD solar cells offer a promising next generation photovoltaic device architecture which fully utilizes the solar spectrum.

Material and methods

Fabrication of quantum dot solar cells

The QD solar cell structure was grown on a heavily n-doped GaAs (100) substrate by the molecular beam epitaxy. After a native oxide desorption step, a 100-nm n-type GaAs buffer layer was grown on the substrate with the doping level of 2.0×10^{18} cm^{-3} followed by a 400-nm n-type GaAs base layer with Si doping of 1.0×10^{18} cm^{-3}. Subsequently, an intrinsic region of 1000 nm undoped GaAs that contains 20 periods of InAs QDs was grown. The QDs were self-assembled in the Stranski-Krastanov (S-K) growth mode by depositing 2.1 monolayers of InAs. Each layer of QDs was separated by a 50-nm undoped GaAs spacer layer to avoid strain relaxation. Over the intrinsic region, a p-type GaAs emitter with Be doping of 1.0×10^{18} cm^{-3} was grown. Additionally, $Al_{0.45}Ga_{0.55}As$ window layer of 30 nm was deposited to prevent surface recombination. Finally, a 50-nm heavily doped p-type GaAs with Be doping of 5.0×10^{18} cm^{-3} was grown as a top contact layer.

Metal contacts were deposited on the top and rear of the solar cells (5.0 mm $\times$ 5.0 mm) by thermal evaporation and lift-off procedures using the standard photolithography proces-