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Optimizing non-radiative energy transfer in hybrid colloidal-nanocrystal/silicon structures by controlled nanopillar architectures for future photovoltaic cells

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To optimize colloidal nanocrystals/Si hybrid structures, nanopillars are prepared and organized via microparticle patterning and Si etching. A monolayer of CdSe nanocrystals is then grafted on the passivated oxide-free nanopillar surfaces, functionalized with carboxy-alkyl chain linkers. This process results to a negligible number of non-radiative surface state defects with a tightly controlled separation between the nanocrystals and Si. Steady-state and time-resolved photoluminescence measurements confirm the close-packing nanocrystal arrangement and the dominance of non-radiative energy transfer from nanocrystals to Si. We suggest that radially doped p-n junction devices based on energy transfer offer a viable approach for thin film photovoltaic devices. © 2012 American Institute of Physics. [doi:10.1063/1.3675634]

Silicon-based solar cells are still dominating the market, despite impressive progress in organic bulk-heterojunction systems that involve high photon absorption and cheaper production costs as compared with traditional crystalline Si-based technology. The primary issues faced by organic-based photovoltaic (PV) cells are their limited stability and poorly controlled interface quality, leading to insufficient carrier transport and collection. On the other hand, silicon-based PV cells suffer from weak absorption, requiring thick Si films.

A mechanism alternative to direct charge generation and separation is offered by non-radiative energy transfer (NRET) in hybrid nanostructures comprising of strongly absorbing components, such as organic molecules or inorganic nanocrystal quantum dots (NQDs) and highly conductive, ultra-thin and potentially flexible semiconductor (SC) layers. Light absorption in such structures is followed by longer-range energy transfer into SC layers,1,2 in which charge separation and collection are easily accomplished via the built-in electric fields, thus entirely avoiding interface charge separation issues inherent to traditional organic devices. In all cases, substrate nanostructuring improves the performance by providing a larger absorption due to the increased surface-to-volume ratio and benefits to enhanced exciton extraction. Several nanostructure architectures have been considered, such as one dimensional nanostructures (nanowires and nanorods).3–5 Particularly useful are PV nanodevices made in the form of nanopillars that can be fabricated by several methods, such as nanoimprinting (applicable to soft, organic based devices) or by controlled etching of the underlying inorganic substrate. Such nanopillars can be easily doped to form radial p-n junctions. These structures have been shown to have an advantage in carrier collection and device efficiency over planar devices because the shorter distance minority carriers must travel to reach p-n junction.6,7 Additionally, such structures have improved optical absorption through photon scattering/reabsorption within the nanostructured substrate as well as due to potential for light coupling in photonic structure. High concentrations of nanopillars would increase the effective absorption in both the active material (NQDs) due to higher concentration per unit area, and in the underlying thin Si substrate by efficient energy transfer into the thin film, ultimately increasing the light conversion efficiency.

Despite the potential advantages of one dimensional structures, light conversion efficiencies that are obtained with organic nanoimprinted solar cells are presently lower than their planar versions due to difficulties in controlling the surface passivation of the nanostructures, leading to exciton trapping and recombination.9 Further, ordinarily used drop-cast or spin-cast NQD films on unpassivated surfaces provide poor control of the placement at and chemical bonding to the surface.2 The situation is particularly difficult when the substrates are not well chemically passivated by a stable oxide (as is the case for oxide-free silicon). Yet, the attachment of NQDs on high quality surfaces with low interface state density is required for advanced applications. Methods for functionalizing and stabilizing defect-free surfaces have been developed,8–10 but surfaces may not always remain chemically stable during the NQD attachment process. Substrate oxidation and formation of trapping sites that occur on the outer NQD ligands11 may open an effective channel for electron scavenging that may hinder NRET related phenomena.

In this work, we controllably prepare large area, high aspect ratio Si nanopillar structures and demonstrate the grafting of dense monolayers of colloidal CdSe/ZnS NQDs positioned at well-controlled distances from Si interfaces.1 For oxide-free silicon surfaces, we show that grafting of a self-assembled monolayer (SAM) completely passivates the Si surface through the formation of a Si-C bond (i.e., prevents subsequent oxidation),5 as clearly demonstrated on flat silicon surfaces,10 and leads to an amount of interface states that remains negligible for most applications (i.e., comparable to what is typically seen with thermally grown silicon oxide),10 while providing functional headgroups for attachment of NQDs.1 In addition to passivating the interface, a linker-assisted deposition guides the creation of a single, tightly controlled monolayer of NQDs at pre-determined distances...
that densely covers the side facets of the Si nanopillars. High-resolution SEM analysis of nanopillars reveals a close packing of nanocrystals on the vertical sides on the nanopol-
lar with densities similar to those on planar Si surfaces. Using photoluminescence (PL) spectroscopy we register 
~35 fold increase of NQD surface coverage as compared to the planar Si/NQD structures. This increase is consistent with the increase in surface area obtained by forming the nanopillars and available for dense NQD monolayer grafting. Import-
antly, time-resolved PL measurements reveal that the NQD PL decay is much faster (~15 fold) compared to NQD/glass reference samples. Comparison with planar NQD/Si samples indicates that NRET into Si nanopillar substrate continues to be the dominant mechanism of energy transfer. The possible coupling of the NQD emitted light into the waveguiding modes within Si nanopillars and/or the change in the NQD radiative lifetime due to photonic crystal structure further contribute to the enhanced exciton depopulation dynamics.

Silicon nanopillars preparation is initiated by using polystyrene monodisperse microparticle 0.5 μm size in water (Sigma-Aldrich), following previously described procedures. Briefly, a mixture of ethanol/microparticle (1/1, v/v) is dispersed on a clean Si wafer by drop casting and drying. The layer of particles is then lifted off the wafer by inserting into a water bath containing a small amount of ammonium dodecylsulfate (ADDS) (60 μl @ 2% for a surface area of ~700 cm²). The layer is then transferred on a clean silicon substrate and left dry in ambient. Prior to deposi-
tion of 40 nm gold layer via e-beam evaporation the micro-
particle size is reduced using O₂ Reactive Ion Etching (RIE) plasma. The pillars are formed by leaving the structure for 10 min in a mixture of ethanol (98%), HF (49%) and H₂O₂ (30%) with a volumetric ratio of 1/1/0.01, then more of H₂O₂ is added to bring the ratio to 1/1/1 and left for 2 min. Finally, the gold is removed from the sample by using an aq-
ua regia solution (15 min) and the remaining micropar-
cles are washed away by using a piranha solution (20 min).

Surface functionalization is based on two approaches depending on the starting surfaces (oxide-free Si or pure glass) and is described elsewhere. Note that in the present study the slane used is 0.2% of triethoxysilyl undecanal (C11-Ald) instead of aminoundecyltrimethoxysilane due to the use of water soluble quantum dots. Water soluble colloidal NQDs are purchased from Invitrogen (Qdot 565 ITK amino (300 nm diameter, 35 fold) compared to NQD glass)

FIG. 1. (Color online) Digital camera picture and SEM top view imaging of Si nanorods.

To characterize the surface structure as well as the NQDs coverage, we performed scanning electron microsco-
py (SEM) imaging on the nanorodes using a Zeiss Supra-
pillars, thus increasing the proportion of the PL coming from the densely covered side surfaces vs. the flat substrate (see the inset to Fig 3(a)).

Further, we recorded time-resolved PL dynamics for (i) the Si/NQD nanopillar sample, (ii) the planar Si/NQD sample, and (iii) the NQDs grafted on a glass substrate, used as a reference. All samples were prepared using the same starting NQD concentration (i.e., 15 nM) for grafting to ensure similar surface coverages. The NQD PL dynamics (recorded at the peak position, i.e., $\lambda = 570$ nm) differ greatly, with those on the Si-nanopillar sample being the fastest as seen in Fig. 3(b). A monolayer of NQDs deposited on glass has a monoexponential PL transient with decay time $\tau_{\text{glass}} = 21$ ns, attesting to the high quality of the commercial NQDs. The NQD dynamics on the planar Si/NQD sample also exhibit a nearly monoexponential decrease, with much faster dynamics, $\tau_{\text{Si}} = 3.5$ ns, as compared to the reference on glass. In our recent work, we characterized the PL decay rates for NQDs grafted at well-defined distances from planar Si surfaces. The large observed difference in PL dynamics is fully described by modification of the radiative and non-radiative decay rates for an emitting dipole placed near high refractive index ($n_{\text{Si}} \sim 4$), weakly absorbing ($\text{Im}(\varepsilon) \sim 0.3$) Si surface. The observed ratio of total decay rates $\Gamma_{\text{Si}}/\Gamma_{\text{glass}} = (21 \text{ ns}/3.5 \text{ ns}) = 6$ is in excellent agreement with the theoretical calculations that predict (i) the NRET contribution accounting for a factor of 2.5, and (ii) the change in the radiative rate due to presence of highly polarizable Si substrate accounting for a factor of 2.4.

The PL decays recorded for NQDs grafted on Si-nanopillar samples are considerably faster than for those grafted on planar Si surfaces and are distinctly biexponential. The fit produces two components, $\tau_{\text{fast}} \sim 1.5$ ns and $\tau_{\text{slow}} \sim 3.5$ ns with relative weights $A_{\text{fast}} / A_{\text{slow}} \sim 0.15$ as seen in Fig. 3(b). Based on their decay times and relative amplitudes, we attribute the fast PL component to NQDs attached to the side facets of the nanopillars (region B on the inset to Fig. 3(a)). The slow component that exactly matches the lifetime of PL emission from planar Si/NQD sample is therefore attributed to the NQD emission from “planar” surfaces, i.e., top facets (region A) and trenches between nanopillars (region C) parts of the sample.

The observed fast decay component $\tau_{\text{fast}} \sim 1.5$ ns is, therefore, indicative of additional/enhanced decay channels that are responsible for exciton depopulation when NQDs are placed on nanopillars. Two possible mechanisms are possible: (1) further modification of NQD radiative rates when placed in the photonic crystal structure, and (2) coupling of the NQD emission into quasi-waveguide modes of the nanopillars, thus further reducing the PL decay times. The former mechanism has been extensively studied in different photonic structures for both colloidal NQDs as well as for epitaxial quantum dots grown in situ in microcavities (so called Purcell effect). The later mechanism has been recently discussed in the context of the plasmonic-based light coupling. Further optical experiments are currently being performed to clarify these mechanisms in Si nanostructures.

In summary, we have prepared large-area, regular arrays of 3D Si nanopillars and grafted monolayers of colloidal CdSe/ZnS quantum dots. Such 3D nanopillar structures gave

![Fig. 2](https://example.com/fig2.jpg)  
**Fig. 2.** (a)-(c) SEM cross-sectional images of Si nanorods’ structure at different magnifications after functionalization and attachment at high concentration of NQDs. Well resolved individual NQDs are seen on panel (c).

![Fig. 3](https://example.com/fig3.jpg)  
**Fig. 3.** (Color online) (a) PL spectra of NQDs grafted on glass, planar Si and Si-nanopillars for similar starting NQD concentrations. Inset: Schematic of nanopillar structure (b) PL decays for the same set of samples. Dashed lines are fits to monoexponential decays (top and middle curves) and to biexponential decay (bottom curve).
an effective increase in surface area of ~20 fold without compromising the interface quality and without detectable evidence of surface states (if created) that typically hamper the performance of composite nanostructured devices. We have clearly demonstrated that in such hybrid architecture, NQDs’ grafting still produces close to ideal monolayer coverage similar to what is achieved on planar Si substrates. PL spectroscopy measurements have revealed considerable acceleration of the PL dynamics of NQDs positioned on the nanopillars due to the combined effects of the non-radiative and radiative energy transfers. Such a photon harvesting architecture would potentially allow the combination of effective exciton collection from NQDs to Si via energy transfer mechanisms and improved carrier extraction via built-in electric fields of radially doped p-n junctions. This approach may prove useful for the development of thin-film, flexible Si solar cells with power conversion efficiencies approaching the efficiencies of thick, crystalline Si devices, but at much lower production costs and higher throughput.

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