Broadband Up-Conversion at Sub-Solar Irradiance[1]

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Abstract Summary: Molecular chromophores that undergo triplet-triplet annihilation (TTA) have recently shown promise for efficient up-conversion at low irradiance, an effect that can be useful for some types of solar cells. However, the molecular systems that have exhibited the highest up-conversion efficiency to date are ill suited to broadband light harvesting, reducing their applicability. We will discuss the potential to overcome this limitation by combining an organic TTA system with highly fluorescent CdSe semiconductor nanocrystals. The resulting nanocrystal-boosted system shows a doubled light-harvesting ability, which allows a green-to-blue conversion efficiency of ~12.5% under 0.5 suns of incoherent excitation. This record efficiency at sub-solar irradiance demonstrates that TTA-boosting by light-emitting nanocrystals can potentially provide a general route for up-conversion for different photovoltaic and photocatalytic applications.

Introduction: The efficiency of photovoltaic and photocatalytic devices is limited by the electronic properties of the light-harvesting layer. For example, in semiconductor solar cells, the band gap leads to fundamental losses when photons with energies below the band gap are not be absorbed. For single-crystal silicon solar cells, this means that infrared (IR) photons with wavelengths longer than ~1000 nm are not harvested. In organic and dye-sensitized solar cells, which typically have wider band gaps, a bigger fraction of the solar spectrum, *e.g.* starting in the near-IR (700-1000 nm), cannot be utilized. Other solar-conversion devices, such as photocatalytic cells for splitting water into hydrogen, exhibit even higher losses. Typically in those devices, the active material absorbs mainly in the ultraviolet (UV) and only a few percent of the incoming solar radiation is utilized.[2,3]

To reduce such light-harvesting losses, different strategies have been pursued. Multi-junction solar cells, which incorporate several semiconductors with different band gaps, are the most advanced, but they also suffer from high fabrication costs. Another strategy is to utilize materials that shift the energy of the incoming photons higher, a process known as up-conversion (UC).[4,5] This permits the recovery of low-energy sub-band-gap photons that would otherwise not be absorbed by the light-harvesting layer. Up-conversion can, in principle, lead to performance improvements of 50 and 100% for photovoltaic and photocatalytic devices, respectively.[6,7] However, traditional up-conversion methods rely on multiphoton processes (*e.g.* second-harmonic generation in nonlinear crystals or two-photon absorption in materials doped with rare-earth elements).[8] These require high light intensities (MW to GW per cm^2) that are well outside the working range of conventional solar cells.

Sensitized Triplet-Triplet Anihilation Up-Conversion: For low-power up-conversion, pairs of organic chromophores have recently been investigated.[9-12] Briefly, a light-harvesting molecule, called the sensitizer, absorbs a low-energy photon and transfers its energy to the metastable triplet state of another molecule, called the emitter. Through a process known as triplet-triplet annihilation, two excited emitters then combine their energy yielding one emitter in a high-lying singlet state. When this molecule fluoresces, a high-energy photon is produced. The overall process, known as sensitized triplet-triplet annihilation up-conversion (sTTA-UC), has led to quantum yields as high as 20% at irradiances of only a few suns and can work under incoherent excitation.[13-18] It has also been used to enhance the light-harvesting efficiency of photovoltaic and photocatalytic cells. In this case, the sTTA-UC layer is placed after the sunlight passes through the device (Figure 1c) to recapture some of the sub-band-gap photons. However, the improvement offered by these low power up-converting systems has so far been limited by the narrow absorption bands (15-20 nm) of the employed sensitizers.[19]

Nanocrystal-Boosting: Here we will discuss a simple strategy to overcome this limitation by combining state-of-the-art sTTA-UC chromophores with CdSe nanocrystals. In general, colloidal nanocrystals have unique optoelectronic properties that have been explored for many applications. This includes the use of doped nanocrystals[8,20-23] and nanocrystal heterostructures[24] as up-converting chromophores. However, here we take a completely different approach. We demonstrate their utility as a "booster" for sTTA-UC. Because semiconductor nanocrystals have broadband absorption as well as efficient, narrow-band fluorescence that is tunable with nanocrystal size, they can be engineered to absorb light lost by the sTTA-UC system and return the energy back to the sensitizer. This enhances the population of excited emitters, allowing the maximum TTA yield to be reached at lower irradiance. The tunability of the optical properties of the nanocrystals also makes this technique extremely versatile. We demonstrate a 2-fold improvement in the light-harvesting ability of two benchmark sTTA-UC systems, achieving a record green-to-blue conversion efficiency of 12.5% at 0.5 suns of incoherent excitation. The resulting systems can therefore provide efficient broadband up-conversion at sub-solar irradiances for photocatalytic solar cells, which typically absorb wavelengths below 500 nm.[2] More generally, nanocrystal-boosted sTTA-UCs have the potential to aid other solar cells including conventional photovoltaic devices.

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