Carrier Multiplication in PbS Quantum Dots Anchored on a Au Tip using Conductive Atomic Force Microscopy

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Carrier multiplication (CM) is the amplification of the excited carrier density by two times or more when the incident photon energy is larger than twice the bandgap of semiconductors. A practical approach to demonstrate the CM involves the direct measurement of photocurrent in the device. Specifically, photocurrent measurement in quantum dots (QDs) is typically limited by high contact resistance and long carrier-transfer length, which yields a low CM conversion efficiency and high CM threshold energy. Here, the local photocurrent is measured to evaluate the CM quantum efficiency from a QD-attached Au tip of a conductive atomic force microscope (CAFM) system. The photocurrent is efficiently measured between the PbS QDs anchored on a Au tip and a graphene layer on a SiO₂/Si substrate as a counter electrode, yielding an extremely short channel length that reduces the contact resistance. The quantum efficiency extracted from the local photocurrent data with an incident photon energy exhibits a step-like behavior. More importantly, the CM threshold energy is as low as twice the bandgap, which is the lowest threshold energy of optically observed QDs to date. This enables the CAFM-based photocurrent technique to directly evaluate the CM conversion efficiency in low-dimensional materials.

The solar energy conversion efficiency has been improved significantly by manipulating the excess energy of photo-excited carriers to minimize the thermalization loss. One of the key phenomena in the efficient conversion of solar energy is carrier multiplication (CM) that produces two or more carriers per photon with a CM threshold energy of two times the bandgap energy (2E₀) in semiconductors.[1–3] The CM quantum yield (QY) is expected to reach the maximum efficiency of single-junction solar cells (∼45%),[4] substantially exceeding the Shockley–Queisser limit (33.7%). The CM concept has been demonstrated in colloidal PbSe quantum dots (QDs) in 2004,[5] and extensive CM-based studies have been performed with various types of QDs in solution or device-grade film type samples.[6–8] The pump-probe technique is one of the CM evaluation methods based on carrier dynamic processes suitable for solution and homogeneous film samples.[9,10] However, this technique has limitations when used with optoelectronic devices owing to the insufficient optical density and limited spatial resolution of the probe-beam size.[11]

Recently, photocurrent has been directly measured via ultrafast spectrosopies in device-grade films with pump and probe pulses or pump and ultrafast oscilloscopes.[12] Photocurrent measurements are still limited to pump-probe optical techniques with poor spatial resolution and long carrier extraction pathway that often yield low CM efficiencies of the examined devices. Therefore, to directly evaluate the CM efficiency of photovoltaic devices, it is essential to develop innovative measurement techniques. The solar cell efficiency has been observed directly in QD films but with low solar cell efficiency and high CM threshold energy owing to high contact resistance and long carrier transfer length, although the high CM efficiency is achieved via optical approaches.[13] Therefore, it is essential to directly measure the photocurrent and CM efficiency by reducing the contact resistance and carrier transfer length.

This study demonstrates a unique method of investigating the CM via photocurrent measurements using a PbS-QD-decorated tip of a conductive atomic force microscope (CAFM) system. The QY estimated from the photocurrent measurement exhibits a step-like behavior. Effective carrier transport occurs in graphene because of its high electrical and thermal conductivity that minimize the electrical contact resistance and local heating around the QDs, respectively.

Figure 1a illustrates the decoration process of the PbS QDs on the Au-coated tip. The mean and ligand diameters of the PbS QDs (purchased from Evident Technology) were ∼5.4 and 4 nm, respectively, corresponding to a bandgap of 0.94 eV.[14] In order to decorate the QDs on the Au tip, we used a dielectrophoresis method. The QDs were first suspended in toluene solution to deionized water (1:5) to obtain opaque suspension. We prepared a large size of CVD-grown graphene film, which was transferred on SiO₂/Si substrate. The prepared opaque suspension was dropped onto graphene/SiO₂ film. The Au tip was immersed into the droplet on graphene film. A DC voltage was applied between the tip and the graphene film. No...
significant change occurred below 8 V. Applying DC voltage above 8 V with a few seconds, the opaque suspension immediately became transparent locally near the tip, indicating that the QDs were attached from the suspension to the tip (Figure 1a).

To confirm the decoration of the QDs on the Au tip, we measured the $I$–$V$ characteristics of the decorated Au tip using a CAFM (Figure 1b). The top and bottom electrode in $I$–$V$ measurement is the decorated Au tip and graphene/SiO$_2$ substrate, respectively. The $I$–$V$ curve shows an ohmic behavior for the pre-decorated Au tip with a current jump near the zero-bias region. Meanwhile, the $I$–$V$ curve of the PbS-decorated Au tip exhibits a Schottky behavior with a smaller current, distinct from the ohmic behavior in Figure 1b. This confirms the strong adhesion of the PbS QDs onto the Au tip and the formation of a metal–semiconductor diode junction. In addition, scanning electron microscopy (SEM) images of the post-decorated tip reveal a tip curvature radius of ≈50 nm, which is significantly larger than that of the pre-decorated tip (Figure 1c). A single QD or several QDs could be decorated on the tip apex. Next, we demonstrate the effectiveness of graphene as a bottom electrode in the photocurrent measurement. A Au substrate was chosen as a reference electrode for comparison with the graphene electrode. Here, the photocurrent was measured under the internal built-in potential in an open circuit. Figure 1d presents the photon energy dependence of the photocurrent. The excited photocarriers were efficiently transferred to graphene by the low Schottky barrier height of the graphene/Au tip with asymmetric contact, compared to the symmetric Au tip contact (Figure 1e).

To measure the photocurrent and evaluate the CM efficiency, the CAFM system with the PbS-QD-decorated Au tip was equipped with a vacuum chamber with incident continuum white light (1 × 10$^{-5}$ Torr) (Figure 2a). The wavelength of incident light was selected using the bandpass filters (400–800 nm). This light was precisely focused at the PbS-QD-decorated Au tip end by a confocal microscope with a piezo-electric actuator beam scanner. Figure 2b presents the optical microscopy images of the light focused on the tip end at wavelengths of 460, 520, and 700 nm. Next, we investigate the $I$–$V$ characteristics between the PbS-QD-decorated tip and graphene electrode under darkness and illumination at 440 and 780 nm (Figure 2c). No appreciable photovoltaic effect was observed in the $I$–$V$ curve with the Au tip without PbS decoration under illumination (Figure 2c, inset). Both the short-circuit current ($I_{SC}$) and open-circuit voltage ($V_{OC}$) were higher at shorter wavelengths. The higher $I_{SC}$ at higher photon energy is ascribed to the CM, and the higher $V_{OC}$ is a signature of the hot carrier effect owing to the early emergence of charge transfer from the excited photocarriers of the PbS QDs to graphene at high energy.

Next, we measured the photocurrent with the photon energies of few PbS QDs attached to the Au tip of the CAFM. The photocurrent was measured with a white light laser equipped with a bandpass filter having a bandwidth of 10 nm (Figure 3a). The photocurrent is averaged over ≈10–15 s and moved to the next photon energy by repeating 21 steps for photon energies ranging from 400 to 800 nm.
(1.6E_g < E < 3.3E_g). The photocurrent initially increases gradually to be saturated at over 2.5 eV, and is reduced at higher photon energy regime due to low laser excitation power density (Figure 3b). As well as with the photon energy, the photocurrent is also modulated with the laser power density as illustrated in Figure 3c. Figure 3d shows the absorbance of the PbS QDs dispersed in toluene. The absorption peak near 0.94 eV is identified from the PbS QDs.

Because we are interested in the CM in QDs, the photocurrent is normalized by the photon density and absorbance. Relatively low photocurrent largely fluctuates below ≈1.8 eV and then increases after ≈1.8 eV to saturate up to ≈2.7 eV. The photocurrent increases abruptly at photon energies above ≈2.7 eV, implying the emergence of carrier multiplication. Figure 3f shows the photocurrent as a function of the power density in terms of photon energy. The linearity in the fluence regime is preserved within a power density of 20 mW cm⁻², which is maintained for the photocurrent measurement to avoid unnecessary complexity of nonlinear carrier–carrier interactions. The linear slope of the photocurrent increases with the photon energy, which implies the occurrence of CM.

Figure 4 presents a comparison between the QYs of the PbS QDs measured in this study and those measured via optical approaches reported in previous studies. Because the normalized photocurrent of the PbS QDs clearly exhibits step-like behavior near the 2E_g and 3E_g levels, a 100% QY is defined as an ideal 2E_g of photon energy. A step-like behavior at 3E_g is clearly observed, together with the referenced 2E_g. Furthermore, the CM efficiency[15] is ≈99%, which is considerably higher than those of PbS with other forms such as colloid, sheet, and bulk.[16–19] The high CM efficiency of the PbS QDs with a step-like feature in our Au tip-assisted photocurrent measurement is attributed to the ultrashort channel length that allows the efficient extraction of photoexcited carriers by the CAFM probe. The rapid charge transfer to graphene in our measurements is essential to suppress the overwhelming electron-phonon scattering in conventional QDs.[20] A similar rapid charge transfer was observed in a layered MoTe2 thin film with an ideal 2E_g.[21] Another merit of this technique is the high spatial resolution of the photocurrent measurement by near-field detection that is helpful in investigating the CM in one QD or multiple QDs at the very apex of the Au tips.

In summary, we observed a nearly ideal CM efficiency with the lowest threshold energy of twice the bandgap energy in PbS QDs by using tip-assisted photocurrent measurement. The highly efficient CM is attributed to the efficient photoexcited charge extraction from the short channel of the PbS QDs anchored on the Au tip. The prevention of the electron-phonon scattering in QDs owing to the fast charge transfer of photoexcited carriers to graphene also contributes to the high efficiency. Therefore, the combination of the tip-assisted CAFM with photocurrent measurements is a robust approach for evaluating the CM effect in low-dimensional materials.

**Experimental Section**

The CAFM-assisted photocurrent measurements were performed with an AFM-Optics hybridized system (NT-MDT, Russia). The light energy
was obtained from a white light continuum source (Energetiq, USA) with a bandpass filter (400–800 nm) (Thorlab, 10 nm bandwidth). The laser was focused on the end of the CAFM tip with an objective lens with a long working distance (N.A. 0.7, ×100, Mitutoyo, Japan). The Au-coated tip (NT-MDT, VIT P/Au) in the CAFM was used with a curvature radius of 25 nm and electrical resistivity of 0.025 Ω cm with a current resolution limit of 1 pA. The photocurrent measurement was carried out under vacuum environment (1 × 10⁻⁵ Torr). The quantum yield is calculated with below formula

\[
\text{Quantum yield} = \frac{\text{Normalized photocurrent}}{\text{Photons absorbed}}
\]

\[
\text{Photons absorbed} = \text{Number of photons} \times \text{Absorption cross section}
\]

\[
\text{Number of photons} = \left( \frac{J}{s \cdot \text{cm}^2} \right) \times \left( \frac{6.24 \times 10^{18} \text{ eV}}{1 \text{ eV}} \right) \times \left( \frac{1}{\hbar} \right) \times \left( \frac{1}{\lambda} \right)
\]

\[
\text{Absorption cross section} \left[ \text{cm}^2 \right] = \ln(10) \times \frac{10^2}{N_A} \times \varepsilon = 3.823 \times 10^{-21} \varepsilon,
\]

\[
\varepsilon: \text{molar attenuation coefficient}
\]

The normalized photocurrent value at two times the bandgap energy of QDs is set to 100% and others are normalized with this value.
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Conflict of Interest
The authors declare no conflict of interest.

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carrier multiplication, conductive atomic force microscopy, lead sulfide quantum dots, photocurrent measurement

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