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A Look into Plasmonic Energy Transfer in CIGS Solar Cells via Ultrabroadband Femtosecond Pump-probe Spectroscopy

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Abstract

This work has presented the merits of plasmonic energy transfer in CIGS solar cells by discussing the hot carrier relaxation via ultrabroadband femtosecond pump-probe spectroscopy.

1. Introduction

Plasmonics is a state-of-the-art approach for improving optoelectronic devices. The extraordinary optical properties originates collectively oscillation of triggered surface charges in nanostructures that is surface plasmon resonance (SPR), considerably enhances the photon-to-electron interaction. Recent research has revealed that SPR increases the scope of boosting high-efficient solar cells. Metallic nanostructures enable locally amplify the electromagnetic field and scatter incident light when placed on the surface or inside a photovoltaic device. In addition, plasmonic energy transfer is attracting an increasing research interest and also considered to overcome the Shockly-Queisser limit. Because it can transfer the radiative and non-radiative energies to exciting more electron-hole pairs. Although the CIGS TFPV efficiency enhancement via plasmonic Au nanoparticles was reported in our previous study [1]. But the mechanisms of plasmonic energy transfer still remains unclear and need to be manifested further. Hence, in this study, we elaborately investigated the hot carrier relaxation in plasmonic CIGS solar cells by using the ultrabroadband pump-probe spectroscopy and theoretical calculation to clarify plasmonic energy transfer mechanism.

2. Results and Discussion

Femtosecond pump-probe spectroscopy has been commonly used for investigation of ultrafast carrier dynamics [2]. The non-equilibrium carriers can be immediately generated while the pumping pulses exciting the semiconductors. And their ultrafast relaxation process are reflected on the transient differential absorption and recorded via each probing pulses. The measurement results of ultrabroadband pump-probe spectroscopy are shown in Fig. 1(a) and (b). It exhibit the transient differential absorption spectra at different probing wavelength in CIGS and plasmonic CIGS thin films, respectively. The negative parts of differential absorption in both spectrums are related to the photobleach (PB) mechanism which corresponds the photo-induced carriers are well excited from ground state even reach saturated. In contrast, the positive parts of differential absorption at longer wavelength attributed to photoinduced absorption (PIA) which arises from the excited carriers be further excited to higher energy level. The result indicates the photo-excited carriers in the CIGS thin films can be significantly increase and quenched in lower excited states while the Au NPs incorporated.

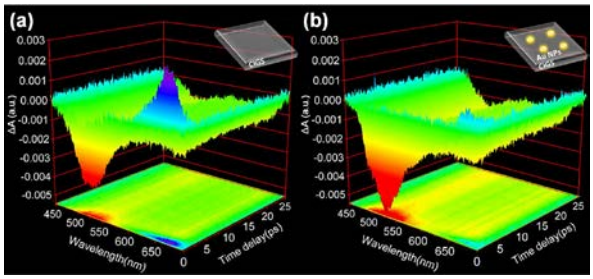

Fig. 1 The transient differential absorption spectra at different probing wavelength in (a) CIGS and (b) plasmonic CIGS thin films.

In order to elucidate the evolution of photoinduced species and plasmonic effect in more detail, we have extracted transient differential absorption spectroscopy at the 500 fs and 10 ps, respectively (see Fig. 2(a)). At 500 fs, the negative change in ΔA which is assigned to PB signal can be observed at both samples at shorter wavelengths (450~600 nm). That is attributed to the higher intensity region in probing spectrum located here. Much carriers were excited from ground states and reached saturated further. At longer wavelengths (> 600 nm), the positive change in ΔA which corresponds to PIA signal. It indicates the excited carrier were re-excited to the higher energy levels, that is free carrier absorption. It is worth noting that the PB and PIA signals in CIGS thin film were significantly enhanced and reduced at 500 fs while the Au NPs incorporated. The surface plasmon resonance (SPR) of Au NPs were triggered by the pulses and instantaneously generate a strong near-field in the vicinity (Fig. 2(b)). And the response of strong near-field quickly decay in short timescale through the surface plasma oscillation dephasing process. So that the more light-harvesting and excited carriers can generated via the

strong field at early time, and then the signals of ΔA are almost identical at 10 ps. In the other hand, SPR also obviously quench the PIA mechanism. That implies the heat loss from the hot-carriers relaxation will be effectively reduced. Besides, the evolution of PIA signal to PB signal at longer wavelengths was recorded. It features the process of hot-carrier population relaxation within few picoseconds.

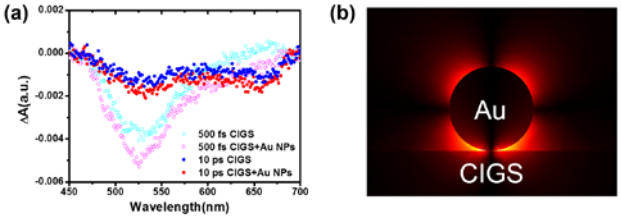

Fig. 2 (a) Transient absorption spectroscopy at the 500 fs and 10 ps in CIGS and plasmonic CIGS thin films. (b) The enhanced electromagnetic field distribution while SPR was triggered, which is calculation result by finite element method.

The value of zero momentum is related to the amount of excited carriers, and its evolution also features the thermalization process in carrier relaxation. Fig. 3(a) exhibits the calculation result of zero momentum for CIGS and plasmonic CIGS thin films in PB dominating region. The μ0 of CIGS at t = 0 can be increased to ~1.5 times while Au incorporated. It indicates more carriers were excited from ground state via the plasmonic effect. And the decay time constant of μ_0 is the hot carrier relaxation time. However, the relaxation time of plasmonic CIGS is faster than CIGS. This result is will corresponding to the PIA mechanism can be quenched while Au NPs presents. The less excited carriers will re-excited to higher energy level in plasmonic CIGS thin films so that the hot carrier relaxation is much fast to reach thermalization. Resonant energy transfer (RET) mechanism is a frontier of SPR energy transfer which researchers are paying attention to explore. It presents that the electromagnetic field can be a medium of plasmonic energy transfer in the form of nonradiative mechanism. By comparing to enhanced local electromagnetic field (LEMF) mechanism increases the interband transitions rate of carriers in the semiconductor via the enhanced local EM field (Fig.2 (b)). The resonant energy transfer (RET) process is another approach to induced charge separation in semiconductors via nonradiative mechanism. The electron−hole pairs in the semiconductor can be nonradiatively excited through the relaxation of the localized surface plasmon dipole (Fig. 3(b)). Plasmon-induced RET in the near field is analogous to Förster resonance energy transfer (FRET), whereas the LSPR dipole substitute for the fluorescent system.

To shed light on the RET from Au NPs to CIGS thin film, we conducted the theoretical calculation. The LSPR of Au NPs triggered by the incident electromagnetic wave and the collective oscillation of charges can be treated in the form of dipole moment behavior. And the enhancement of carrier transition probability arises from nonradiative RET interaction of μ_{LSPR} and the semiconductor can elaborately obtained by quantum electrodynamics (QED) theory.

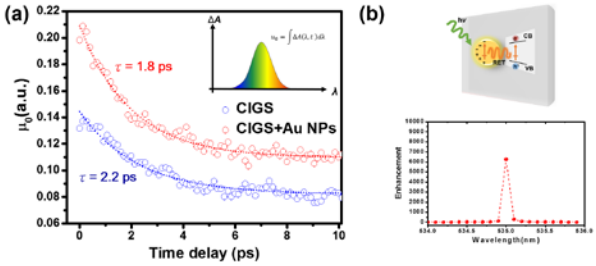

Fig. 3 (a) Evolution of zero momentum for CIGS and plasmonic CIGS thin films. (b) Resonant energy transfer (RET) mechanism and RET-induced enhancement of carrier transition rate.

3. Conclusions

In summary, we have performed the ultrabroadband femtosecond pump-probe spectroscopy of CIGS with and without Au NPs incorporation, and conducted elaborative analysis of the lifetime and zero momentum for hot carrier relaxation. The enhanced photobleach (PB) and quenched photoinduced absorption (PIA) phenomena by LSPR of Au NPs were observed in transient differential absorption of CIGS thin films. The result has suggested the carriers can be considerably excited from ground state to lower energy levels, and the hot carriers can reach thermalization much fast while the LSPR triggered. That implies the heat loss can be effectively reduced by LSPR of Au NPs and the direct electron transfer (DET) is a viable method to enhance photocurrent of CIGS solar cells. And improvement of the electrical transport while LEMF reduced the surface recombination also be confirmed. Finally, the theoretical calculation for enhancement of RET-induced probability of exciting electron-hole pairs was conducted and the result is well corresponding to the enhanced PB peak of transient differential absorption in plasmonic CIGS.

Acknowledgements

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