

Plasmon enhanced heterogeneous electron transfer with continuous band energy model



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ABSTRACT

Photoinduced charge injection from a perylene dye molecule into the conduction band of a TiO₂ system decorated by a metal nanoparticles (MNP) is studied theoretically. Utilizing the density matrix theory the charge transfer dynamics is analyzed. The continuous behavior of the TiO₂ conduction band is accounted for by a Legendre polynomials expansion. The simulations consider optical excitation of the dye molecule coupled to the MNP and the subsequent electron injection into the TiO₂ semiconductor. Due to the energy transfer coupling between the molecule and the MNP optical excitation and subsequent charge injection into semiconductor is strongly enhanced. The respective enhancement factor can reach values larger than 10³. Effects of pulse duration, coupling strength and energetic resonances are also analyzed. The whole approach offers an efficient way to increase charge injection in dye-sensitized solar cells.

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1. Introduction

The dye molecule connected with the semiconductor material (such as TiO₂) with a porous structure through an anchor molecule is the main part of the dye-sensitized solar cell [1]. There is an ongoing interest in theoretical and experimental studies on improving the efficiency of charge transfer from the molecule to semiconductor.

A lot of evidences exist that surface plasmons of metal nanoparticles (MNPs) can greatly improve the efficiency of a solar cell [2]. Driven by an external field, the free electrons in the conduction band of MNP show collective oscillations known as the surface plasmon. In the resonance state, the energy of the external field is effectively converted to the plasmons. By means of the coupling to the dye molecule, the energy is further transferred to the dye molecule. MNP-molecule coupling have various forms, such as multi-layer structure model [3], core-shell nanoparticle model [4], nanocomposite films containing metal nanoparticles and molecules [5] and so on. There were numerous attempts described in literatures to achieve MNP induced efficiency enhancement of the dye-sensitized solar cell. Such as metal nano-structures combined with thin-film solar cells [6], photosensitization of bulk TiO₂ by embedded MNPs [7], TiO₂-nanostructures decorated with MNPs [8,9] and so on.

Currently, there are applications that employ metal nanoparticle plasmon resonance, for example, in the polymer solar cells [10–12], the devices with nanorod structures and sputtered metallic nanoparticles [13,14]. Irradiating metal nanoparticles with light at their plasmon frequency generates intense electric fields at the surface of the nanoparticle. The frequency of this resonance can be tuned by varying the nanoparticle size, shape [15], material, and proximity to other nanoparticles. We also have theoretical attempts on the enhancement effect of MNP [16,17], with the tight-binding model describing the TiO₂ semiconductor. The shortcoming of that is the wavefunction reflection on the boundary of the semiconductor, which strongly restricts us to calculate the bulk scale TiO₂ cluster and that requires more computational resources. Continuous band model of semiconductor used in Refs. [18,19] can effectively describe the quasi-continuous energy level of TiO₂, which introduced the Legendre polynomials expansion. We also note that the mirror charge effect can be ignored during the charge injection into the semiconductor [16]. Still, a two electronic level model [20,21] is used for dye molecule. The description of the dye-MNP system could be carried out on the basis of the inclusion of that part of the Coulomb coupling, which is responsible for excitation energy exchange [22]. Such a uniform description accounts for local field induced molecular absorption enhancement as well as for molecular excitation energy quenching [16]. Fig. 1 shows the energy level arrangement of the MNP decorated molecule-semiconductor system.

The paper is organized as follows. In the subsequent section we introduce the used model of the dye molecule TiO₂-semiconductor

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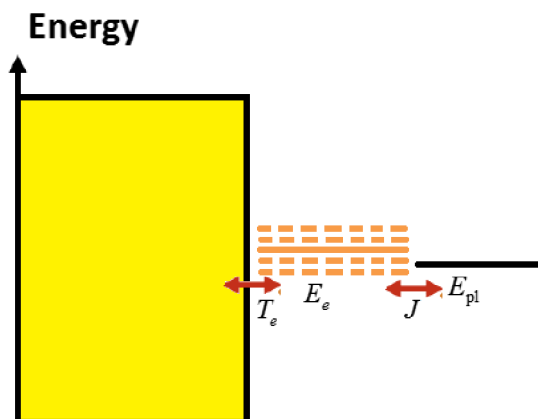


Fig. 1. Energy level arrangement displaying the energies which constitute the Hamiltonian, Eq. (1). The left rectangle symbolizes the energy band of the TiO₂. The molecular excited state with energy E_e (shown the orange lines) is coupled to the MNP dipole plasmon state with E_{pl} (shown the short black solid line) via the coupling J . Charge injection to the semiconductor conduction band is realized by the transfer coupling T_e . (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)

decorated by one MNP and the density matrix theory of charge injection. In Section 3 we present the results and corresponding discussions. Some concluding remarks are presented in Section 4.

2. Model and theory

The dye molecule, semiconductor, MNP system is treated as described in [16–18]. Therefore, an expansion is carried out with respect to system product states [17]. The ground-state φ_g does not contribute since the respective energy has been set equal to zero, cf. the energy sketch in Fig. 1. The remaining Hamiltonian reads

$$H(t) = H_{\text{mol}} + H_{\text{sem}} + H_{\text{mnp}} + H_{\text{mol-sem}} + H_{\text{mol-mnp}} + H_{\text{field}}(t). \quad (1)$$

The Hamiltonian of the excited dye molecule is

$$H_{\text{mol}} = \hbar \varepsilon_e |\varphi_e\rangle \langle \varphi_e|, \quad (2)$$

where $\hbar \varepsilon_e$ is the molecular electronic excitation energy (at the nuclear equilibrium configuration) and φ_e represents the product of the excited molecular state, the MNP ground-state and the empty semiconductor conduction band state.

The semiconductor conduction-band Hamiltonian takes the form [16]

$$H_{\text{sem}} = \sum_{\mathbf{k}} \hbar \varepsilon_{\mathbf{k}} |\varphi_{\mathbf{k}}\rangle \langle \varphi_{\mathbf{k}}|, \quad (3)$$

with \mathbf{k} as the quasi-wave vector. The $\hbar \varepsilon_{\mathbf{k}}$ are the conduction band energies (including the energy necessary to remove the electron from the dye and put it into the TiO₂ lattice; cf. [17]). For further discussion, we write $\hbar \varepsilon_{\mathbf{k}}$ as $E_c + \hbar \omega_{\mathbf{k}}$, with the lower band-edge E_c and with $\hbar \omega_{\mathbf{k}}$ running over the conduction band. $\varphi_{\mathbf{k}}$ denotes the product states which include the electron in the semiconductor, the cationic dye state, and again the MNP ground-state.

The Hamiltonian of the excited MNP has the form [17]

$$H_{\text{mnp}} = \sum_I \hbar \varepsilon_I |\varphi_I\rangle \langle \varphi_I|, \quad (4)$$

with the dipole plasmon energy $E_{pl} = \hbar \varepsilon_I$. I counts the three degenerated dipole plasmon ($I = x, y, z$ indicates excitations in the three directions of a Cartesian coordinate system). The state φ_I covers the excited MNP state, the dye molecule ground-state and the state referring to the empty TiO₂ conduction band.

The molecule-MNP coupling Hamiltonian is written as

$$H_{\text{mol-mnp}} = \sum_I J_{Ie} |\varphi_I\rangle \langle \varphi_e| + H.c., \quad (5)$$

and the coupling matrix element J_{Ie} can be approximated as an interaction between molecular and MNP transition dipole moments. Such an interaction of the excitation energy transfer type is of minor importance between the MNP and the TiO₂ system since interband transitions of the latter lie in the UV.

The Hamiltonian of the molecule-semiconductor interaction reads [18]

$$H_{\text{mol-sem}} = \sum_{\mathbf{k}} T_{\mathbf{k}e} |\varphi_{\mathbf{k}}\rangle \langle \varphi_e| + H.c., \quad (6)$$

where charge injection from $|\varphi_e\rangle$ into the manifold of states $|\varphi_{\mathbf{k}}\rangle$ is realized by the transfer coupling $T_{\mathbf{k}e}$.

The Hamiltonian of interaction between the system and external applied laser field takes the form [16]

$$H_{\text{field}}(t) = -\mathbf{E}(t) \cdot \hat{\boldsymbol{\mu}} = -\mathbf{E}(t) \cdot \left(\mathbf{d}_{eg} |\varphi_e\rangle \langle \varphi_g| + \sum_I \mathbf{d}_{I0} |\varphi_I\rangle \langle \varphi_g| + H.c. \right), \quad (7)$$

where \mathbf{d}_{eg} and \mathbf{d}_{I0} are dipole moments of molecule and plasmons respectively, they have the form of $\mathbf{d}_{eg} = d_{eg} \mathbf{e}_z$ and $\mathbf{d}_{I0} = d_{pl} \mathbf{e}_I$, $\mathbf{E}(t)$ is the time-dependent electric field strength of a pulsed optical excitation with the following form

$$\mathbf{E}(t) = \mathbf{e} E(t) \exp(-i\omega_0 t) + \text{c.c.}, \quad (8)$$

here, \mathbf{e} is the unit vector of field polarization (here we set that the direction of \mathbf{e} is consistent with that of \mathbf{d}_{eg}) and ω_0 is the carrier frequency. The envelope $E(t)$ has the Gaussian shape

$$E(t) = E_0 \exp(-2(t - t_p)^2 / \tau_p^2), \quad (9)$$

with amplitude E_0 , pulse center at t_p and duration τ_p . All the used parameters can be found in Table 1 (for motivation see also our earlier work of Refs. [16–19]).

The injection process is described in the framework of open system dynamics with density matrix theory, and the related density matrix reads

$$\rho_{\alpha\beta}(t) = \langle \varphi_{\alpha} | \hat{\rho}(t) | \varphi_{\beta} \rangle, \quad (10)$$

where α and β label the different states introduced beforehand, $\hat{\rho}$ is the reduced density operator. To account for energy relaxation and dephasing an application of the standard quantum master equation is appropriate. Due to fast plasmon decay we may take a version where the dissipative part of the equations does not couple populations and coherences [16]

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{\alpha\beta}(t) = & -i\tilde{\omega}_{\alpha\beta} \rho_{\alpha\beta}(t) - \frac{i}{\hbar} \sum_{\gamma} (v_{\alpha\gamma} \rho_{\gamma\beta}(t) - v_{\gamma\beta} \rho_{\alpha\gamma}(t)) \\ & - \delta_{\alpha,\beta} \sum_{\gamma} (k_{\alpha \rightarrow \gamma} \rho_{\alpha\alpha}(t) - k_{\gamma \rightarrow \alpha} \rho_{\gamma\gamma}(t)), \end{aligned} \quad (11)$$

Table 1

Parameters introduced in Refs. [16–19] and used here (for explanation see text).

d_{eg}	3 D
d_{pl}	2925 D
$\hbar \gamma_{\text{mol}}$	3 meV
$\hbar \gamma_{\text{pl}}$	28.6 meV
r_{mnp}	10 nm
$\hbar \Delta \omega$	3 eV
$\tau_p(t_p)$	10 fs (15 fs)
E_0	5×10^5 V/m
$\hbar \varepsilon_e$	2.6 eV, 2.4–2.9 eV
$\hbar \omega_I$	2.6 eV
$\hbar \omega_0$	2.6 eV, 2.4–2.9 eV

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