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Enhanced photoelectric performance of nanorod TiO_2 film embedded with gold nanoparticles applied in dye sensitized solar cells studied by OptiFDTD

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ABSTRACT

We developed fundamental design principles to enhance absorption and power properties of nanorod TiO_2 photo-anode films in dye sensitized solar cells (DSSCs) over a broad wavelength range by embedding plasmonic gold nanoparticles (NPs). The plasmon-induced electric field distribution in nanorod TiO_2 photoanode film embedded with sphere gold NPs has been investigated using finite-difference time domain (FDTD) method based on Maxwell equation. The simulation was done for 500 and 1100 nm of incident plane wave wavelength. FDTD simulation indicates that by the localized surface plasmon resonance effect, the strong photo scattering took place and this increase the absorption path length towards near infrared region inside the active area (anode film) of the solar cell. Furthermore, the power absorption increases from the anode-films that embedded metal NPs of small diameter (40–60 nm) with large gap (10–18 nm) to that of the metal NPs of large diameter (100–150 nm) with small gap (2–6 nm).

1. Introduction

Since the industrial revolution that started around 200 years ago, humans have contributed more carbon dioxide to the atmosphere than Earth's plants can recycle, which has resulted in a global contaminate and temperature rise. To realize a low-carbon society, photovoltaic will play a key role in energy harvesting [1]. Dye sensitized solar cells represent one of the most promising emerging technologies for light-to-electrical energy conversion. The most attractive potential features of DSSCs are minimal capital costs for synthesis of component materials, and ease and economy of fabrication [2].

DSSCs are normally composed of a monocrystalline TiO_2 photoanode film, dye sensitizers, redox electrolyte and counter electrode [1]. Among all these different components, the photoanode plays a very important role in electron transmission, electrons collection from photo excited dye molecules, and it also determines the amount of dye absorption, which depends on its specific surface area, crystallinity, structure and morphology [3]. The structure and physical properties of the semiconductor oxide are predominant for the photoelectric properties of DSSCs. Some strategies have been attempted to optimize the structure of the photoanode films, by using TiO_2 photoanode films with various morphologies such as nanoparticles (NPs), ordered mesostructures, one-dimensional (1D) structures (nanorods, nanowires, and nanotubes). Because of their structures, the use of 1D electrode facilitates electron transfer up to the collection electrode, reducing the boundaries and decreasing the ohmic loss [4,5].

Solar cell efficiency is a key lever for PV cost reduction: For a given output power, higher cell efficiency directly translates into a smaller and therefore less expensive PV system, reducing the cost of electricity. But the efficiencies of DSSCs are still lower (11.9%) than other thin film technologies, and much lower than crystalline silicon solar cells [6]. One of the challenges for dye sensitized solar cells is the relatively high energy and narrow bandwidth associated with molecular absorption, which makes it difficult to harvest a wide range of solar spectrum. Researchers have tried a variety of methods to facilitate the optimal absorption of light in DSSCs, such as modifying TiO_2 structure, synthesizing different morphologies such as porous or one dimensional TiO_2 anode, nano-engineering of transparent conducting (TCO) glass substrate to improve the light harvesting through enhancing the light transmittance and scattering, use of modifying absorbing dye molecule, the use of dielectric and metal (surface plasmons) gratings and so on [7,8]. Among them, composite of photoanode film and plasmonic metal nanoparticles can be a better choice.

Embedding metal NPs in TiO_2 layer or ZnO layer typically employed in DSSC devices is a viable option for enhancing the light absorption. The commonly used synthetic dyes in DSSCs absorb primarily in the

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visible region, which is the reason why researchers mainly employ Au and Ag nanostructures in DSSCs because their surface plasmon resonance (SPR) can be tuned in the visible part of the electromagnetic spectrum [9,10].

Plasmons are created when incident light excites coherent oscillation of the free electrons in metal nanoparticles, typically composed of gold or silver. This phenomenon gives rise to unique property, such as an intense absorption feature and enhanced electromagnetic field [2]. The enhancement factor depends on the intensity of oscillating electric fields in the vicinity of the metal NPs. The electric field intensity is, in turn dependent on the metal species, the dye and interparticle spacing, the size and shape of NPs, and the dielectric environment [11,12]. Zhang et al. experimentally realized that the light scattering effect gradually strengthens as the size of Au NPs increase from 48 to 203 nm. The IPCE enhancement caused by the Au layer is more significant in the longer wavelength region, resulting in broadening of the action spectra [10].

These spheroidal metal nanostructures take advantage of the localized surface plasmon (LSP) effect to increase the light absorption. However, the effects of these spheroidal nanostructures are in local area and do little to increase light path and electrons transport in the photoanode [13,14]. Therefore, we need to find out the optimal existing state of metal NPs inside of the photo-anode film that can greatly improve the performance of DSSCs. Normally, the geometrical parameters to be optimized are diameter D of metal NPs and gap d among metal NPs.

The FDTD approach that is based on a direct numerical solution of time-dependent Maxwell's curl equations can be used to design, simulate and optimize surface plasmon base layout. This is due to its unique combination of features, such as ability to model light propagation and scattering effects. Moreover, the FDTD method allows for the effective and powerful simulation and analysis of sub-micro-devices with very fine structural details [15].

In the present work, the photo-electric performance of nanorod TiO_2 anode films embedded with sphere gold nanoparticles with different diameter and different gap applied in dye sensitized solar cells have been studied through FDTD simulations (Lumerical Inc., Lumerical.com). The aim of the work is to investigate the influences of interparticle spacing and size of sphere gold NPs to the photo-electric behavior of plasmonic TiO_2 anode films even in near infrared region while maintaining the spherical shape of gold NPs.

2. Experiment and numerical methods

2.1. Experiment

In accordance with our previous experiment work [16,17], the chemicals were reagent grade, using without further purification and the TiO_2 nanorod anode films were fabricated. To obtain the films modified with Au NP, the prepared photoanode films were firstly soaked in 1×10^{-3} mol L^{-1} of $HAuCl_4$ aqueous solutions for 1 min, followed by rinsing with deionized water, absolute ethanol, dying in ambient air. After total dry, the films were annealed at 500 °C for 30 min. The fabricated TiO_2 nanorod photoanode films and the films modified with Au NPs were soaked in N719 dye solution at 45 °C for 24 h, respectively. Finally, DSSCs were assembled after electrolyte diffusion. A Quanta 200 F Field emission scanning electron microscopy (FESEM), FEI Singshine Hongkong was used to check the films' morphology.

2.2. Simulation model

In this work, the photo-electric property simulation of the TiO_2 photo-anode film doped with gold NPs were performed base on the FDTD calculations using Lumerical simulation package code. For the simulation model, as shown in Fig. 1a, it is composed with indium tin oxide (ITO: 500 nm × 500 nm × 300 nm) substrate, TiO_2 nanorod with 80 nm diameter and 750 nm height for each (according to our previous research work [16]), uniformly distributed N719 dye molecules (10–20 nm diameter), spherical gold nanoparticles that embedded in the TiO_2 nanorod anode film with different diameters (40, 60, 100, 120 and 150 nm) and distances (2, 6, 10, 14 and 18 nm) among them.

2.3. Description of the concept

In this study, FDTD method was used to numerically solve Maxwell's equations in three dimensions.

Maxwell's equations for homogeneous medium are given in Eqs. (1) and (2):

$$\nabla x\overrightarrow{E} = -\mu\frac{d\overrightarrow{H}}{dt} \rightarrow \begin{cases} \frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z} = -\mu\frac{\partial H_y}{\partial t} \\ \frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = -\mu\frac{\partial H_y}{\partial t} \\ \frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = -\mu\frac{\partial H_z}{\partial t} \end{cases} \quad (1)$$

$$\nabla x\overrightarrow{H} = \varepsilon\frac{d\overrightarrow{H}}{dt} \rightarrow \begin{cases} \frac{\partial H_z}{\partial y} - \frac{\partial H}{\partial z} = \varepsilon\frac{\partial H_y}{\partial t} \\ \frac{\partial H_x}{\partial z} - \frac{\partial H}{\partial x} = \varepsilon\frac{\partial E_y}{\partial t} \\ \frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} = \varepsilon\frac{\partial E_z}{\partial t} \end{cases} \quad (2)$$

Each field components of electromagnetic wave is presented by E_x (i, j, k), E_y (i, j, k), E_z (i, j, k), H_x (i, j, k), H_y (i, j, k) and H_z (i, j, k). Here, both the permittivity and the permeability are complex function and relative to the frequency or wavelength [7].

2.4. FDTD simulation

The simulation was done in three steps. First, we build the layout and define the parameters of object such as refractive index, thickness, width and size of the sample. In this study, we use ITO as a transparent conductive substrate with refractive index of 1.92 and acts as an optimized anti-reflection coating. The active region (350 × 350 × 1500 nm) with 3D mesh grid of 1 nm spacing. The dielectric functions of Au and anatase TiO_2 were extracted from the data of Johnson and Christy (1972) and Jelison, Siefke et al., 2016, respectively. The time step of simulation was set up for 1500. The last process is analyzing the post data using OptiFDTD analyzer. In FDTD simulation, periodic boundary conditions (PBC) are used for the side boundaries to model the periodic nature of nanoparticles while perfect match layer (PML) boundary conditions are used for upper and lower boundary. The use of perfect match layer eliminates the reflection of light from the propagation direction. Symmetric and anti-symmetric boundary conditions are used to reduce the required memory size and computation time. To model the sunlight, a normally incident plane wave with a wavelength range from 500 nm to 1100 nm was used.

Second, we start the simulation for n-iteration. The H and E field were updated during simulation running. We record the electromagnetic fields, power and scattering cross sections, power absorption and short circuit current density for 100 equally spaced frequencies between λ = 500 nm and λ = 1100 nm.

In order to calculate the amount of absorption inside the active layer (photoanode), two power monitors were placed at the bottom and the top of the active layer to measure the power flow getting in and out of the layer, respectively. The power absorbed by the layer is obtained by calculating the power flow difference between the two monitors [8,18] as shown in Eq. (3).

$$P_{abs}(\lambda) = P_{in} - P_{out} \quad (3)$$

Where P_{abs} refers to power absorption inside the photoanode, P_{in} refers to power flow getting in the photoanode and P_{out} refers to power flow getting out of the photoanode.