

# Study on Surface Plasmons of Core-shell Type Particles for Enhanced Energy Conversion Efficiency of Dye Sensitized Solar Cells

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## Introduction

While dye sensitized solar cells (DSSCs) have several advantages that potentially offer an alternative to currently dominant Si-based photovoltaics, there are still problems that need to be solved to make DSSCs as efficient as other semiconductor-based photovoltaics. In particular, a single type of a dye material used in DSSCs cannot absorb a full range of the solar spectrum due to the mismatch between the solar spectrum and the light absorption spectrum of dyes. To address this issue, we incorporate plasmonic nanostructures in DSSCs to control the passage of photons. Surface plasmons are oscillations of charge density that can exist at the interface between two media with electric permittivities of opposite signs.<sup>1</sup> The coupling of the surface plasmons with incoming light amplifies local field intensity in the vicinity of nanostructures and enhances absorption and scattering cross-sections.

Recently, we have explored the influence of dielectric core - metallic nanoshell particles on solar energy conversion in DSSCs. The plasmonic behavior of the core-shell particles can be explained using a sphere-cavity model.<sup>2</sup> This demonstrates that the optical resonances and the near electromagnetic field response can be tuned by changing the dimension of the core and shell components. Because of these advantages, the dielectric core - metallic nanoshell particles have a great potential for optoelectronic and biomedical applications. We design the structure of the core-shell particles to arouse the coupling of the surface plasmons with visible light. This coupling is found to increase the absorption and scattering of the light in the photoelectrodes, which contributes to enhancing the energy conversion efficiency of the DSSCs. In newly designed DSSCs, the role of localized surface plasmons on the light absorption, scattering, and energy conversion efficiency is systematically investigated.

## Experimental

**Synthesis of SiO<sub>2</sub> core - Ag shell composites.** Uniform SiO<sub>2</sub> spheres were prepared via Stöber method.<sup>3</sup> Ammonium hydroxide (J. K. Baker, 28%) and tetra ethoxy silane (TEOS, Sigma-Aldrich, 98%) were used as raw materials. The average diameter of silica particles was controlled to be 400 nm.

The SiO<sub>2</sub> core - Ag shell composites were synthesized by a seed mediated two-step method. Ag nanoparticles were first formed on the surface of SiO<sub>2</sub> particles, which was followed by the subsequent deposition of the Ag thin layer. Ag nanoshell seeds were synthesized by modifying the sonochemical reaction. Silica particles were added into deionized water. Then, silver nitrate (Sigma-Aldrich, 99.8%) was dissolved in ammonium hydroxide solution that was subsequently poured into the aqueous slurry of the SiO<sub>2</sub> particles. After Ag source and SiO<sub>2</sub> particles were mixed, the slurry was sonicated for 3 hrs by using the high-intensity ultrasound radiation.

**Preparation of TiO<sub>2</sub> nanoparticle - composite mixture films.** Anatase TiO<sub>2</sub> nanoparticles were prepared using a hydrothermal reaction. A mixture of titanium (IV) isopropoxide and 2-propanol was slowly dripped into a mixture of acetic acid and deionized water at 0 °C. Then, the solution was preheated at 80 °C for 8 hrs and was reacted at 220 °C for 6 hrs in a microwave accelerated reaction system (MARS, CEM Co.). The phase of TiO<sub>2</sub> nanoparticles is

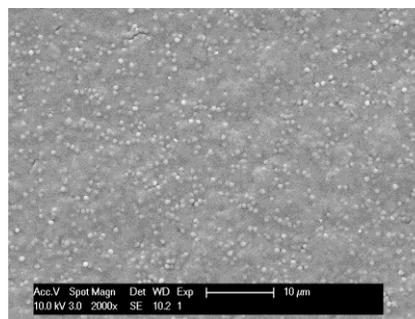
anatase. A mixture of TiO<sub>2</sub> slurry and core-shell composite slurry were added with a small amount of ammonium hydroxide to increase the viscosity of the mixed slurry. As a reference sample, a viscous paste of TiO<sub>2</sub> nanoparticle -uncoated SiO<sub>2</sub> particle mixture was also prepared using a same method. The paste was spreaded on a transparent conducting glass substrate (FTO) by the doctor-blade technique and annealed at 400 °C for 2 hrs.

**Fabrication of DSCs and Characterization of Their Photovoltaic Properties.** The TiO<sub>2</sub> mixture films were sensitized in the solution of N719 dye [ruthenium (2,2'-bipyridyl-4, 4'-dicarboxylate)<sub>2</sub>(NCS)<sub>2</sub>, Solaronix SA, dissolved in ethanol] at room temperature for 24 hrs, and then sandwiched with thermally platinized FTO counter electrode. Two substrates were separated by 25 μm thick hot melt sealing tape (SX-1170-25, Solaronix SA) and the internal space of the cell was filled with liquid electrolyte (Iodolyte AN-50, Solaronix SA). A part of sensitized thick films were immersed in NaOH solution to desorb the dyes. The amounts of dyes desorbed from different photoelectrodes were examined by measuring UV/Vis absorption spectra. The photovoltaic properties of the DSCs were tested under AM 1.5 G simulated sunlight (PV Measurements, Inc) with the aid of the electrochemical workstation.

## Results and Discussion

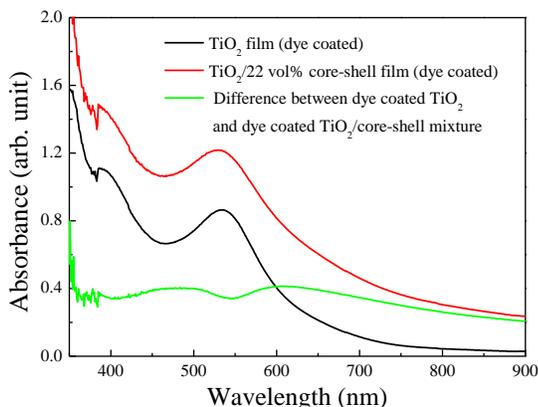
Structural and optical analyses of the core-shell particles show that the 1 hr deposition reaction provides a uniform, smooth, and high-crystalline Ag layer that can absorb an enough amount of light to excite the surface plasmons. Therefore, 1 hr reaction was selected as a coating time of Ag shells onto SiO<sub>2</sub> cores in examining the effect of the surface plasmons on the light absorption and photon-electron conversion of DSSCs. The 1-hr reacted core-shell particles were mixed with TiO<sub>2</sub> nanoparticles and chemically agglomerated to be several μm thick mixture films. **Figure 1** shows SEM micrographs of the mixture films in both plan-view and cross-section modes. Large particles in SEM micrographs are core-shell particles that are uniformly dispersed within the mixture films. A distance between core-shell particles decreases as the amount of core-shell particles increases. In a 22 vol% core-shell particles added mixture film, a normal distance between the surfaces of the core-shell particles is about 300 nm, which is quantitatively consistent with the results of the calculation assuming that the core-shell particles are uniformly distributed in the mixture films.

To examine the effect of the surface plasmons on the optical cross section of ruthenium dyes, the mixture film were coated with N719 dyes and its absorption was measured.



**Figure 1.** Plan-view scanning electron micrographs of TiO<sub>2</sub> nanoparticle - core-shell particle mixture films containing 10 vol% of the core-shell particles.

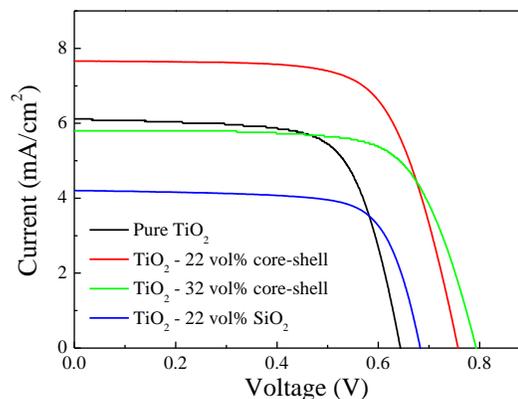
**Figure 2** shows that the light absorption of dye coated TiO<sub>2</sub> and TiO<sub>2</sub>/core-shell particle (22 vol%) films and their difference. In **Fig. 2**, the difference curve between UV/Vis absorption spectra of TiO<sub>2</sub> and TiO<sub>2</sub>/core-shell films exhibits two small humps with peaks of 480 nm and 610 nm, respectively. The appearance of two small humps in the difference curve suggests that a combined use of the core-shell particles and the dyes produces a synergy effect in absorbing light, which becomes more pronounced in the regime of blue light and red light. This can compensate well for the weakness of currently dominant polypyridyl ruthenium dyes whose optical cross-section is not uniform in the visible range. The role of the core-shell type particles is explained as follows. First, the plasmon excitation increases the optical density of incoming light near the surface of metal nanostructures. Therefore, if the dye materials are placed on the outer surface of core-shell particles, the dye materials within the near-field range are exposed to the light which is intensified by the surface plasmons. This, in turn, causes the dye materials to harvest more photons. Second, the enhanced multiple scattering of the core-shell particles in the far-visible range will prevent transmission of incoming light and increase the chances of dye materials to convert the photons to the electronic carriers. In other words, more photons are trapped in the mixture films for longer period due to the light scattering effect of the core-shell particles.



**Figure 2.** UV/Vis absorption spectra (a) and transmittance spectra (b) of N719 dye coated TiO<sub>2</sub> film and mixture films containing different amount of SiO<sub>2</sub> core – Ag shell particles (as a reference sample, a mixture of bare SiO<sub>2</sub> particles and TiO<sub>2</sub> nanoparticles was also tested); UV/vis measurements are performed using an integrating sphere.

DSSCs were fabricated using the N719 adsorbed films. **Figure 3** shows I-V curves of DSSCs employing TiO<sub>2</sub> films and mixture films containing different amount of core-shell particles. A thickness of the films is controlled to be 5 μm. The overall conversion efficiency of DSSC is improved when the core-shell particles are added. Compared with pure TiO<sub>2</sub> films, the mixture films containing 22 vol% core-shell particles increase the efficiency of DSSCs from 2.7 % to 4.0 %. It is noted that the higher energy conversion efficiency of core-shell particle embedded DSSC is due to the increase in both short circuit current ( $J_{sc}$ ) and open circuit voltage ( $V_{oc}$ ).  $J_{sc}$  of DSSCs containing 22 vol% core-shell particles is 7.8 mA cm<sup>-2</sup>, which is higher than  $J_{sc}$  of pure TiO<sub>2</sub> film based DSSCs, 5.9 mA cm<sup>-2</sup>. The addition of core-shell particles also slightly increases  $V_{oc}$  from 0.63 V to 0.76 V. Given that the amount of dyes adsorbed on TiO<sub>2</sub> films is 33% larger than the mixture film of 22 vol% core-shell particles, this difference cannot be attributed to dye content or transport kinetics of electrons in the films. The energy conversion

efficiency of DSSCs is moderately improved to 3.4 % when the concentration of added core-shell particles is 32 vol%. It is noted that DSSCs using 32 vol% of the core-shell particles possess higher open circuit voltage and slightly lower short circuit current than DSSCs using only TiO<sub>2</sub>, though there is a significance decrease in the amount of dye sensitizers.



**Figure 3.** I-V curves of DSSCs using TiO<sub>2</sub> film or mixture films containing different amount of core shell particles, as photoanodes (as a reference sample, the TiO<sub>2</sub> - SiO<sub>2</sub> mixture film was also tested),

## Conclusions

The effect of the surface plasmons on the photovoltaic performance of DSSCs has been investigated. Core-shell particles coated with the uniform Ag layer were synthesized by a two-step method. Light absorption and scattering in the visible range is significantly enhanced in the mixture film containing the core-shell particles, leading to higher optical cross section of dyes adsorbed on the mesoporous mixture films. The effect of the core-shell particles is theoretically explained from a viewpoint of local field intensity and scattering efficiency. When 22 vol% of the core-shell particles are added, the conversion rate of incident photons to electrons increases more than 20%. It is found that a balance among the near-field intensity, light scattering efficiency, and surface area in the photoanodes determines the energy conversion efficiency of DSSCs containing the core-shell particles.

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