UNDERSTANDING PLASMON ENHANCEMENT FOR NEXT-GENERATION SOLAR CELLS FOR AEROSPACE TECHNOLOGY

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ABSTRACT

Photovoltaic cells that harness solar energy and convert it to electricity are essential to NASA’s work in outer space, as wired electricity does not exist. However, current solar cells are inefficient and inflexible. Dye-sensitized solar cells (DSSCs), a type of organic-based solar cell, show promise as a potential solution to this problem. DSSCs are novel technologies though, and their inefficiency makes them currently economically infeasible. Research on the molecular mechanisms of DSSCs could lead to improvements on their efficiency and a possible marketable commercial product. This paper discusses research involving the introduction of silver nanoparticles into DSSCs to enhance their efficiency through plasmon enhancement, the improved absorbance of a dye molecule due to the enhanced electromagnetic field surrounding a photoexcited metal particle. The plasmonic effect is distance dependent, so it will be studied using silica-encapsulated silver nanoparticles with dyes attached at varying lengths. The structures will be studied using single molecule fluorescence, a technique that will allow the study of single particles rather than the average of a group. This research will hopefully lead to a more efficient model for the DSSC.

INTRODUCTION

NASA uses satellites and other aerospace technologies to study both the Earth and outer space. However, because they are not within the reaches of wired electricity, these technologies require some other source of power. In order to combat this problem, NASA has instituted initiatives aimed at the development of efficient photovoltaic cells. Photovoltaic cells (commonly known as solar panels) are devices that harness the energy of the sun and convert it to electricity. Currently, a majority of photovoltaic cells are silicon-based. However, next-generation technologies are relatively low-cost, do not sacrifice energy conversion efficiency, and are made of more flexible and durable materials. In particular, organic-based photovoltaic cells have shown promise as successors to silicon-based cells. Organic-based cells using dye sensitizers, quantum dots, or conductive polymers have shown the greatest potential. This research paper will discuss recent research on dye-sensitized solar cells (DSSCs), organic-based cells that could eventually serve as a less costly alternative to the silicon-based solar cell. In particular, the original DSSC efficiency was reported at 7% in 1991, but since then it has plateaued at ~11%. An understanding of the fundamental mechanisms of DSSCs and identification of the hindrances to their improved efficiency could lead to a better molecular model for DSSCs and, hopefully, a marketable commercial product.

DSSCs are composed of arrays of semiconductor nanoparticles, usually titanium dioxide (TiO$_2$), that have been outfitted with dye molecules that act as sensitizers to absorb radiation from the sun (see Figure 1). When a photon of light hits the dye molecule, an electron within the molecule is excited. The excited electron is then transferred to the...
neighboring semiconductors through a nonradiative process (meaning no photon of light is released) called forward electron transfer (FET). The electron can then move on to an electrode which produces a current, leading to the generation of electricity. Sometimes, however, the electron returns to the dye, returning it to its ground state, in a process termed back electron transfer (BET). BET is an undesirable process in this situation and a major hindrance to the efficiency of DSSCs.

The dye can also return to its ground state through a reducing interaction with an electrolyte solution, meaning the electrolyte solution donates an electron to the dye molecule. The electrolyte is subsequently restored by another reduction that occurs at the counterelectrode.

It has been previously reported that the kinetics of the aforementioned electron transfer processes are related to device performance and efficiency. However, the process of electron transfer is not fully understood. It is believed that ET kinetics are dependent on the dye sensitizer, the surface of the semiconductor, and the geometry of the device. Because of the complexity of the interactions among these variables, a model for the ET kinetics within this type of DSSC has not yet been developed.

Although the complexities of the ET kinetics are not fully understood, it is believed that the efficiency of DSSCs can be improved by simply improving the absorption of the dye sensitizer, leading to a larger overall amount of FET and therefore production of a greater amount of electricity. This argument is based on the fact that more dye excitation will lead to the flow of more electrons. Although BET will still exist, the chances of more electrons reaching the electrode will be greater because more electrons are excited.

One proposed method to increase the absorption of the dye sensitizer is through the introduction of metallic nanoparticles into the system (see Figure 2). More specifically, metallic nanoparticles that exhibit a plasmon resonance are thought to be able to significantly enhance absorption. Plasmon resonance increases dye’s absorption through the enhanced electromagnetic field generated around a metal nanoparticle that has been excited by radiation.

It has been postulated that plasmon-enhanced DSSCs will exhibit enhanced

![Figure 1. A molecular model of a DSSC showing the processes of photoexcitation of the dye, forward electron transfer to the semiconductor (TiO₂), and back electron transfer to the dye. Adapted from source 8.](#)

![Figure 2. A model of a DSSC with plasmonic structures incorporated to enhance efficiency of the dye's absorption.](#)
efficiency for several reasons. One theory posits that excited electrons can be transferred directly from the metal nanoparticle to TiO$_2$ and then move to the electrode.$^{11}$ Another theory postulates that the electromagnetic field produced by the metal couples with the electronic resonance of the dye resulting in enhanced absorption of radiation by the dye.

The introduction of plasmonic materials into DSSCs shows promise as a method to increase their efficiency. However, the plasmonic effect is not greatly understood, and because it is distance dependent, simply adding metal nanoparticles to a DSSC may not increase its efficiency. The nanoparticles may need to be in a specific orientation or at a fixed distance from the dye sensitizers. The research outlined in this paper will review recent work performed at The College of William and Mary to study the effects of plasmon resonance on the efficiency of plasmon-enhanced DSSCs.

**EXPERIMENTAL**

**Synthesis of Silver Colloid Solution**
All glassware was cleaned with aqua regia and rinsed thoroughly with ultrapurified water with a resistance of 18.4 MΩ. To 500 mL ultrapurified water, 90 mg AgNO$_3$ was added while heating and stirring the solution. Once boiling, 10 mL of 1% sodium citrate solution was added to the silver nitrate solution. The solution was allowed to boil, and a color change to a muddy greenish brown was observed within the first 5 minutes. After boiling for a total of 30 minutes, the silver colloidal solution was removed from the heat and allowed to cool.

**Synthesis of Silica-Coated Silver Colloids**
Silver colloid solution was sonicated for 30 minutes transferred to 1.5 mL centrifuge tubes. An ethanol-based solution of 16-mercaptophexadeconic acid (MHA) was added to each tube to a final concentration of 20 µM. The solutions were allowed to sit overnight to react, then centrifuged at low speed to concentrate the nanoparticles. The resulting MHA-treated colloids were then resuspended in ethanol and sonicated for 30 min. Next, an ethanol-based solution of tetraethoxysilane (TEOS) was added to the colloid solution to a final TEOS concentration of 0.25 mM. An aliquot of aqueous Dimethylamine (DMA) was then rapidly injected into the colloid solution (for a final DMA concentration of 0.6 M), and the solution was allowed to react for ~2.5 hours. The resulting solution was sonicated and centrifuged at low speed. The final solution of silica-coated colloids was redispersed in ultrapure water.

**Transmission Electron Microscope (TEM) Characterization**
Samples for TEM were prepared by dropping a sonicated solution onto Formvar TEM grids. Grids were allowed to air dry overnight. All solutions were viewed using a Zeiss EM109 transmission electron microscope operating at 80,000 V.

**RESULTS AND DISCUSSION**
In order to study the plasmonic effect in plasmon-enhanced DSSCs, silica-encapsulated silver nanoparticles have been synthesized.$^{12}$ First, colloidal silver nanoparticles were synthesized through a citrate reduction. The solution contained particles of varying sizes and shapes, including triangular prisms, rectangular prisms, rods, spheres, and amorphous shapes (see Figure 3). The resulting particles were stabilized with an electrostatically-attached citrate capping ligand.

The colloidal silver nanoparticles were then encapsulated in a coat of silica. The advantages of silica shells are threefold: (1) they stabilize the silver nanoparticles, (2) they prevent the silver nanoparticles from
Figure 3. A TEM image of silver nanoparticles of varying shapes and sizes covered in silica shells.

photodegrading, and (3) they serve as a linkage point for dye molecule attachment.

The silica-coating procedure was adapted from previous syntheses. In order to coat the colloids in silica, the citrate cap needed to be replaced with a silane coupling agent to initiate silica shell growth. In this case, the coupling agent 16-mercaptohexadecanoic acid (MHA) was used. The thiol moiety of MHA formed a strong covalent bond to the silver nanoparticle. Because this bond was so much stronger than the electrostatic interaction between the citrate and the silver surface, the stabilizing citrate molecules surrounding the nanoparticle were displaced. The MHA molecules formed bonds around the surface of the silver nanoparticles that act as a binding site for silica attachment. At the other end of the MHA molecule, the carboxyl group formed a bond with tetraethoxysilane (TEOS). The formation of this bond was facilitated through the use of a catalyst, dimethylamine (DMA). Once the initial bond was formed with the MHA molecules, subsequent TEOS molecules polymerized onto the established silica layer and lead to a thickening of the shell over time.

It was found that by varying the concentration of TEOS added to the MHA-treated nanoparticle solutions, the thickness of the silica shell layer could be controlled (see Figure 4). Since the plasmon enhancement is distance-dependent, shells with a thickness of \( \sim 10 \) nm are needed in order to observe absorption enhancement of attached dyes.

The structural and optical properties of silica-coated silver nanoparticles are characterized using transmission electron microscopy (TEM) and localized surface plasmon resonance (LSPR) measurements. The LSPR is sensitive to changes in dielectric constant (i.e., local environment), so optical properties of the uncoated and coated nanoparticles are expected to significantly differ.

Future work is aimed at developing an attachment procedure for dye molecules to silica-coated particles. The dyes will be attached using an aminosilane linker that covalently attaches to the silica shell as well as the dye molecule. More LSPR measurements will be obtained when this synthesis is completed, and all the particles will eventually be studied using fluorescence spectroscopy.

Fluorescence spectroscopy is a process enabling the characterization of an entire group of molecules through the use of lasers to measure their emission. Single-molecule fluorescence (SMF) microscopy is a technique that will enable the study of individual dye-nanoparticle complexes as it measures property distributions rather than the average properties of a collection of molecules. Therefore, SMF will be used to measure the distance dependence of plasmonic...
enhancement at the single molecule level. SMF will be used to study the properties of the dye molecules attached to silica-coated nanoparticles at differing distances so that the optimal distance for plasmonic enhancement of the dye’s absorbance can be determined. Improved understanding of plasmon enhancement in these model systems will hopefully lead to a better and more efficient model for plasmon-enhanced DSSCs.

In conclusion, a study of the distance dependence of the plasmonic effect on dye molecules within a DSSC has been initiated. The results of this investigation will hopefully lead to a more efficient model for the DSSC and a product that can be used on NASA’s outer space technologies and in the homes of consumers worldwide.

ACKNOWLEDGEMENTS

The author would like to thank Dr. Kristin Wustholz who advises this project. I would also like to thank all faculty and staff at The College of William and Mary who make this research possible. Furthermore, I would like to thank Lindsay Oakley, Stephen Dinehart, Matthew Blum, Hannah Mayhew, and David Fabian for synthesizing silver colloids. I would like to thank Matthew McCarron who worked with me on this project and who is currently working on the dye attachment procedure. Finally, I would like to thank the Virginia Space Grant Consortium and NASA for sponsoring this research.

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