Investigation of plasmonic gold–silica core–shell nanoparticle stability in dye-sensitized solar cell applications

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ABSTRACT

Plasmonic core–shell $Au@SiO_2$ nanoparticles have previously been shown to enhance the performance of dye-sensitized solar cells (DSSCs). A thin silica coating can provide a better stability during thermal processing and chemical stability to survive the corrosive electrolyte used in DSSCs. However, the thickness and completeness of the silica shell has proven crucial for the performance of the plasmonic particles and is largely controlled by the linking chemistry between the gold core and silica shell. We have evaluated four different silica coating procedures of ∼15 nm gold nanoparticles for usage in DSSCs. The chemical stability of these core–shell nanoparticles was assessed by dispersing the particles in iodide/triiodide electrolyte solution and the thermal stability by heating the particles up to 500 °C. In order to maintain stable gold cores a complete silica coating was required, which was best obtained by using a mercaptosilane as a linker. In situ TEM characterization indicated that the heating process only had minor effects on the core–shell particles. The final step was to evaluate how the stable $Au@SiO_2$ nanoparticles were influencing a real DSSC device when mixed into the TiO_2 photoanode. The plasmon-incorporated DSSCs showed a ∼10% increase in efficiency compared to devices without core–shell nanoparticles.

1. Introduction

Noble metal nanoparticles show interesting catalytic and physical properties in comparison with their bulk counterparts [1,2]. One particularly important optical phenomenon appearing for such particles is the localized surface plasmon resonance, which can be utilized in a variety of applications [3–5], including surface-enhanced Raman scattering (SERS) [6] and biosensing [7,8]. These plasmons give rise to extremely high optical cross sections for light absorption and light scattering, which have recently been predicted to enhance light absorption in thin film photovoltaic devices [9–11]. In order to reach high efficiencies in thin film solar cells, the photon-harvesting layer typically needs to be relatively thick to generate a large enough photocurrent, while then again a too thick film would result in poor efficiencies due to extensive charge recombination and/or increased materials cost. As a result of the substantially thinner semiconductor layer compared to

conventional silicon-based solar cells, the overall efficiencies of thin film solar cells remain low. However, by utilizing plasmonic particles in thin film solar cells, the efficiency can be improved due to the increased optical path length of the device [12,13], meaning that the thickness of the device and the materials cost to produce the cell can substantially be reduced [14]. This enhancement in light absorption can be attributed to the near-field or far-field effects of the nanoparticles, depending on the particle size [15]. Plasmonic particles have already been demonstrated to enhance the performance in a variety of thin film solar cell technologies, including thin film silicon cells [16,17] and organic bulk heterojunction solar cells [18].

One of the most widely studied third generation solar cell technology suitable for large-scale manufacturing is the so called dye-sensitized solar cell (DSSC) [19]. In a conventional DSSC, a porous TiO_2 semiconductor layer is sensitized by a light absorbing dye, giving rise to a large light absorption in the visible wavelength range. Up to now, there have been a few reports where plasmonic particles (both Ag and Au NPs) have been incorporated into DSSCs [12,20–26]. For instance Brown et al. [20] demonstrated that silica-coated gold nanoparticles ($Au@SiO_2$ core–shell nanoparticles)

could be mixed into the TiO$_2$ photoanode resulting in a higher overall efficiency for both liquid electrolyte and solid state DSSCs. The use of a thin silica shell surrounding the gold cores serves four essential purposes: (1) It acts as an insulator to avoid charge recombination within the metal, (2) it adjusts the plasmon-dye separation distance to minimize quenching, (3) it protects the metal core from corrosion when the particles are subjected to electrolyte solution, and (4) it gives a better thermal stability that prevents sintering of the gold cores. However, since dye molecules cannot inject charges directly into the silica layer (only to the nearby TiO$_2$ particles), the potential enhancement remains fairly low for these devices. Instead Au@TiO$_2$ nanoparticles have been used to circumvent this issue, but only with minor success due to increased charging effects in the metal core that occurs instead [21]. Sheehan et al. have demonstrated that a combination of both a thin silica coating and an additional subsequent thin TiO$_2$ layer can be beneficial to fulfill all the criteria mentioned above [12]. Neither the chemical and thermal stability have been extensively studied for core–shell-type particles to be used in DSSCs. By making Ag@TiO$_2$ core–shell particles by atomic layer deposition, Standridge et al. were able to determine the minimum TiO$_2$ shell thickness required to protect the Ag nanoparticles from dissolving in I$^-$/I$_3^-$ electrolyte [27]. Zhang et al. studied the deformation of Au@SiO$_2$ nanoparticles using EXAFS and SAXS measurements as a function of calcination temperature [28]. Furthermore, Brown et al. encountered both of these stability issues, but no systematic study of these problems was reported [20]. Thus, we have here focused on studying the chemical and thermal stability effects on silica-coated gold nanoparticles to be used in liquid electrolyte DSSCs.

Although there are several approaches to produce thin silica shells described in the literature, it is not necessarily trivial to reproduce these coating protocols due to the highly sensitive synthesis parameters, such as pH, temperature, and chemical purity [29]. For many decades, growth of SiO$_2$ nanoparticles and coating of other types of particles with SiO$_2$ shells have followed the method first presented by Stöber et al. [30]. Using this approach, silica can be nucleated and grown on top of gold cores to produce silica coatings ranging from a few nanometers up to micrometers via a sol–gel route using poly(vinylpyrrolidone) (PVP) as a coupling agent [31]. PVP is needed to facilitate the transfer to the ethanolic base solution used in the Stöber process and to improve the chemical affinity between gold and silica to avoid homogeneous nucleation that generates silica particles without gold cores. The major drawback with this approach is the difficulty to obtain very thin silica shells in a controlled fashion.

In addition to the Stöber approach, there are several other methods presented in the literature regarding the growth of thin SiO$_2$ shells on Au nanoparticles, but most methods generally follow the route presented by Liz-Marzan et al. [32]. In this method, the first step is to replace any capping ligands (e.g. citrate) on the surface of the gold nanoparticles with a monolayer of functional silane linker molecules (typically aminosilanes or mercaptosilanes) that can facilitate the affinity of silicate species on the gold surface. Aminosilanes can typically be used in aqueous environments, i.e. directly after the synthesis of the gold cores, while the mercaptosilane modification is usually done under less reactive EtOH conditions (i.e. a PVP coupling agent is needed). Since the semi-covalent thiol-gold interaction is substantially stronger than the electrostatic amino-gold interaction (which is also pH sensitive), one can expect a more homogeneous silane monolayer when using a mercaptosilane linker [33]. The siloxane groups of the monolayer provide excellent reaction sites for subsequent silica growth using sodium silicate as the silica source. By careful control of the added sodium silicate amount, pH and reaction time, the silica shell thickness can be grown to the desirable size (2–4 nm). If needed,

the silica shell thickness can be further increased by a subsequent Stöber reaction step. The most crucial step in forming a thin but complete silica shell is the precise tailoring of the silica-gold interface, which requires careful control of the linking silanes to the particle surface. An overview of various silica coating methods can be found in the review by Liu and Han [34].

In the present work, we have evaluated four different methods for preparing thin silica coatings on gold nanoparticles, based on either aminosilane [32] or mercaptosilane [35] linking chemistries, and/or the Stöber sol–gel process [36]. These approaches give rise to thin silica coatings ranging from 1 to 20 nm in thickness. We demonstrate the importance of the thickness and more importantly the completeness of the silica coating when subjecting the core–shell particles to iodide/triiodide electrolyte solution. Furthermore, we have also investigated the influence of temperature treatments on the stability of the particles, as cracking of the shell could have a detrimental effect on the final solar cell. Finally, the core–shell particles synthesized with the most promising method were incorporated into DSSCs and the photovoltaic properties were measured. An enhancement of the light absorption and thus the overall efficiency could be seen in the cells with added plasmonic particles.

2. Experimental

2.1. Chemicals used

Gold(III) chloride hydrate (HAuCl$_4$, 99.999% trace metals basis), sodium citrate tribasic dihydrate (99%), polyvinylpyrrolidone (PVP, MW 10.000 g/mol), α-terpineol (anhydrous), and sodium silicate solution (purum, ⩾10% NaOH basis, ⩾27% SiO$_2$ basis) were purchased from Sigma–Aldrich. (3-aminopropyl)trimethoxysilane (APTMS, 97%), (3-mercaptopropyl)trimethoxysilane (MPTMS, purum 97%), tetraethylortosilicate (TEOS, purum 98%) and ethyl cellulose were purchased from Fluka. Millipore water was used for the preparation of all aqueous solutions.

2.2. Gold nanoparticle synthesis

The Au nanoparticles used were prepared according to the well-established method presented by Turkevich et al. [37]. Briefly, an aqueous solution of gold(III) chloride hydrate (HAuCl$_4$) (500 mL, 0.5 mM) is brought to boil. To this solution, sodium citrate (2.5 mL, 1 mM) is added and left to boil for 30 min. The solution will turn from light yellow to ruby-red, indicating the formation of gold nanoparticles. In the conventional Au nanoparticle synthesis, sodium citrate acts as both the reducing agent and as the capping agent. For further modification, the capping agent usually needs to be exchanged to improve stability in non-aqueous solutions (needed in the MPTMS and Direct Stöber coating methods described below) [31]. The capping agent commonly used is polyvinylpyrrolidone (PVP). The citrate capping agent was exchanged to PVP by adding 3.20 mL of a fresh aqueous solution (12.8 mg/mL) of PVP to the Au nanoparticles under vigorous stirring. The solution was stirred for 24 h, centrifuged and washed with water.

2.3. Coating methods

We have used the linking silanes (3-aminopropyl)trimethoxysilane (APTMS[1]) and (3-mercaptopropyl)trimethoxysilane (MPTMS)

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[1] (3-Aminopropyl)trimethoxysilane is normally abbreviated "APS", but we have chosen to use the denotation "APTMS" to highlight the molecular similarity to the (3-mercaptopropyl)trimethoxysilane (MPTMS) compound used in this study.