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Broadband Enhancement in the Spectral Response of Photovoltaic Modules with Flower-like Silver Particles

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Abstract: Recent research has indicated that metal nanoparticles, known for their unique optical properties, can enhance the spectral response of photovoltaic modules. Since most nanoparticles demonstrate enhancement effects within a specific wavelength range, broadening the spectral response of photoelectric devices is critical for their application in imaging, energy harvesting, and optical communication. In this study, we applied flower-like silver particles to achieve this broadband enhancement. The optical absorption of photovoltaic modules, featuring an amorphous Si p-i-n structure, was improved across a broad wavelength range of 400–2000 nm by integrating these flower-like silver particles, resulting in an approximately tenfold increase in peak spectral responsivity. The theoretical investigation further elaborates that the enhancement originates from the near-field effects of silver particles due to the interaction of different parts of the flower-like silver particles. Through these studies, we demonstrate that utilizing the flower-like silver particles with roughness surface can achieve the spectral response of the photoelectric device enhanced in broadband range, which can improve the utilization efficiency of optical energy for the applications of sensing, imaging, optical communication, and energy harvesting.

Keywords: broadband enhancement; photovoltaic; flower-like silver particles

1. Introduction

Due to their low cost and ease of fabrication, semiconductor photovoltaic modules have found widespread applications in both military and civilian industries [1–3]. A photodetector possessing a broadband spectral response holds significant implications for sensing, imaging, optical communication, and energy harvesting [4–8]. Therefore, developing a photodetector with a broadband spectral response has become a primary research area. Significant efforts have been directed towards improving the spectral response by modifying the material and structure of photovoltaic modules [9–11]. Over the past decade, with the advancement of plasmonics, enhancing the performance of photodetectors through the exploitation of metal nanostructures has been considered viable [12–15]. For instance, Naomi J. Halas and colleagues achieved enhanced spectral response in a photodiode within the range of 1250–1650 nm by using a gold (Au) antenna [16]. A substantial increase in the photoconductivity of amorphous silicon was also reported through the use of silica-coated gold nanorods [17]. Notably, metal nanoparticles with sizes up to 100 nm exhibit the most pronounced surface-localized field distribution. As we all know, the surface plasmon resonance of a single metal particle is primarily determined by factors such as particle composition, size, geometric shape, and environmental dielectric function. Particularly, metal particles with sizes within 100 nm exhibit the strongest surface localized field distribution. Recent studies have indicated that textured or defective surfaces on metal nanoparticles induce changes in the far-field
and near-field optical properties of the nanoparticles [18]. Furthermore, when there’s a coarse texture on the macroscopic metal surface or thin film, boundary conditions can be disrupted, enabling direct excitation of surface plasma waves. Our previous work systematically explored the fabrication and optical properties of flower-like silver nanoparticles. In our findings, we observed that these nanoparticles, characterized by their rough morphological features, exhibited broadband plasmon resonance peaks spanning across the visible and near-infrared regions of the spectra. Moreover, due to these specific characteristics of the flower-like silver nanoparticles, we achieved enhanced Surface-Enhanced Raman Scattering (SERS) intensity [19]. These results inspired us to design a nanoparticle-coupled semiconductor with the objective of achieving enhanced response over a broad spectral range. By providing this brief yet comprehensive summary of our previous work, we aim to give reviewers a clearer understanding of the basis and the objectives of our current study.

In this paper, we successfully fabricated an amorphous silicon (a-Si) photovoltaic module embedded with flower-like silver particles. We measured the transmittance, reflectance, and absorption characteristics of the spectra, with a particular focus on the spectral responses of the photovoltaic modules both with and without silver particles. Our findings show that, compared to modules without silver particles, the ones with silver particles demonstrate enhanced absorption and response across a broadband spectral range, extending from the visible to the near-infrared region. Furthermore, we examined the near-field optical properties of the flower-like silver particles with an average diameter of 500 nm. The results revealed that the interaction induced by the rough surface of the different components of the silver particles provides the flower-like silver particle with a unique field enhancement capability in the broadband range. This feature plays a pivotal role in the broadband enhancement of spectral response for the photovoltaic structure.

2. Materials and Methods

2.1. Preparation of Flower-like Silver Particles

Flower-like silver particles were synthesized using the standard chemical reduction method of silver nitrate, as reported in the existing literature [20,21]. All starting materials were of reagent grade and were used as received unless specified otherwise.

We added 0.6 mL of 1 M AgNO$_3$ and 6 mL of 100 mM polyvinylpyrrolidone aqueous solutions to 30 mL of pure water. The mixture was stirred continuously at room temperature, after which 0.6 mL of 1 M ascorbic acid was rapidly introduced. The stirring continued until no further color change was observed. After about eight minutes, the mixed solution turns dark gray in color and the reaction is complete. Following a centrifugation at 4000 rpm for 15 min, the flower-like silver particles were obtained. Additionally, since the silver particles obtained from the reaction inevitably retain some solvent residues, we introduce five times or more pure water into the silver particles. After centrifugation, we remove the supernatant using a pipette. Repeating this process three times to yield almost pure silver particles.

2.2. Preparation of a-Si p-i-n Photovoltaic Structure

The a-Si p-i-n photovoltaic structure was fabricated using plasma-enhanced chemical vapor deposition (RF-PECVD) technology. Firstly, ITO glass with a transparent conductive film was used as the substrate material and was cleaned using a high-temperature heating method. The ITO conductive glass was placed into the RF-PECVD device, the temperature was set to 160–180 °C, and it was maintained at a constant temperature for 2 h.

Then, the substrate was placed in three different reaction chambers and N, I, and P thin films were deposited in sequence. The reaction gas in the N chamber was silane, phosphane, and hydrogen gas, with a reaction power of 28 W and a film thickness of about 50 nm. The reaction gas in the I chamber was silane, germanane, and hydrogen gas, with
a reaction power of 8 W and a film thickness of about 400 nm. The reaction gas in the P
chamber was silane, borane, methane, and hydrogen gas, with a reaction power of 30 W
and a film thickness of about 50 nm.
Finally, after the deposition of the three layers of thin film has been completed, the
temperature drops to room temperature, and the substrate was removed from the RF-
PECVD system, placed in the coating machine, and coated with metal electrodes.

2.3. Deposition of Flower-like Silver Particles

By using the self-assembly method, flower-like silver particles were deposited onto
the photovoltaic structure. Firstly, the substrate (photovoltaic structure) was processed
and ultrasonically cleaned in detergent for about 10 min. Then, it was ultrasonically
cleaned in five times or more pure water for 10 min, and this step was repeated three times.
Afterward, the substrate was cleaned in an ethanol solution, ultrasonically, for 10 min,
followed by ultrasonic cleaning in a large amount of pure water for 10 min, this being
repeated three times. After these steps, remove the substrate and dry it with nitrogen gas.

Next, attach a polymer layer. The polymer used here is 3-Aminopropyl
trimethoxysilane. Mix it with pure water to obtain a polymer solution with a volume
fraction of 1%. Soak the processed substrate in the solution for a period of time, remove it,
and clean it with a methanol solution. Then, clean it with a large amount of ultrapure
water and dry it with nitrogen gas.

Finally, proceed to the sedimentation process. Mix the prepared silver nanoparticles
with five times or more pure water and stir thoroughly. Place the substrate in a sealed
glove box filled with nitrogen gas and immerse it in the prepared flower-like silver particle
solution for at least 2 h. Then we used a pipette to draw off the water on the surface.
Afterward, take it out and gently blow-dry it with nitrogen gas.

2.4. Optical Modeling

Building upon our previous work, the flower-like silver particles consist of two
components. One is the core particle, approximately 400 nm in size, and the other consists
of surface protrusions, each around 100 nm in size. This design ensures that the total size
of the particle is 500 nm [19], as illustrated in Figure 1.

Figure 1. Schematic diagrams of flower-like silver particles.

The surface local fields of the silver particles were calculated using the three-
dimensional finite difference time domain (FDTD) method. The dielectric data for silver
was adopted from Palik [19,22]. A perfectly matched layer (PML) was employed as the
boundary condition. The excitation light was set to be incident in the positive z-direction
and polarized along the x-axis.

2.5. Instrumentation

The photovoltaic structure was prepared using a PlasmaPro 800Plus RF-PECVD
device from Oxford Instruments. Scanning electron microscopy (SEM) images of the
specimens were acquired with a JEOL JSM-6700f scanning electron microscope at 3.0 kV.
The transmittance and reflectance spectra were recorded using a Cary500 UV-visible-
infrared absorption spectrometer. The photocurrent was assessed with a Keithley 6430 digital source meter.

3. Results and Discussion

The flower-like silver particles were deposited onto the surface of an a-Si p-i-n structure, which was immobilized on ITO glass, and then left to dry naturally in a nitrogen environment. As shown in Figure 2a, the thickness of the a-Si p-i-n structure is measured to be 500 nm. From the SEM image shown in Figure 2b, it can be observed that the silver particles, with an average diameter of ~500 nm, are distributed randomly on the surface of the a-Si p-i-n structure.

![Figure 2](image_url)

Figure 2. (a) Schematic of the a-Si p-i-n photovoltaic structure with silver particles on the surface. (b) The SEM image of the flower-like silver particles on the surface (the scale bar = 1µm).

The transmittance (Figure 3a) and reflectance (Figure 3b) of the a-Si p-i-n photovoltaic structure, both with and without silver particles, were respectively measured using the diffuse reflection method. Absorptance, defined as \( \text{Abs} \% = 1 - R \% - T \% \), is depicted in Figure 3c. For the sample adorned with silver particles, a decrease in transmittance is noted across the wavelength range of 450–2000 nm, particularly between 450 nm and 1600 nm. As for reflectance, it decreased across the full wavelength range of 200–2000 nm when silver particles were present on the photovoltaic structure. Hence, absorptance was enhanced across the entire wavelength spectrum, from 200 nm to 2000 nm. A comparison of the spectral curves of the a-Si p-i-n structure with and without silver particles reveals no change in the shape of absorption. This phenomenon is attributed to the flower-like silver particles possessing broadband plasmon resonance peaks in the visible and near-infrared regions of the spectra, thereby enhancing absorption across the entire wavelength range for the photovoltaic module. A comparison of the spectra of the semiconductor with and without flower-like silver particles demonstrates that the spectral response of the a-Si p-i-n structure can be enhanced through the incorporation of flower-like silver particles.
Figure 3. The spectra measured for (a) the transmittance, (b) the reflectance, and (c) the absorptance, respectively.

Then, the photocurrent in the wavelength range of 400–800 nm of the a-Si p-i-n photovoltaic structure with and without silver particles was further measured, respectively. The responsivity was calculated by $R = I_L/P_{inc}$, where $R$ is defined as the responsivity, $I_L$ is the photocurrent, and $P_{inc}$ is the power of the incident light. We plotted the responsivity $R$ as a function of wavelength, as shown in Figure 4. The results show that the structure without silver particles has a spectral response at the wavelength range of 400 nm to 800 nm, which is consistent with the results in the previous report [23]. Compared to the structure without silver particles, the spectral response of the composite structure has been obviously enhanced. Especially, at the wavelength of 650 nm, i.e., at the peak of the responsivity, the responsivity was enhanced by about 10 times. At the same time, the spectral response shape was consistent with that of the structure without silver particles.
Figure 4. The responsivity of the a-Si p-i-n structure with and without silver particles, respectively.

For a semiconductor, the responsivity $R_{\lambda I}$ is proportional to the intensity of the radiation field and can be expressed as

$$R_{\lambda I} \propto C|E|^2$$

(1)

where the parameter $C$ represents a constant. Consequently, an increase in the intensity of the radiation field leads to an enhancement of the spectral response. In our photovoltaic structure with silver particles, the incident light initially interacts with the flower-like silver particles deposited on the surface of the a-Si p-i-n structure, stimulating the localized surface plasmon resonance of the silver particles and enhancing the field around them. This interaction consequently amplifies the intensity of the radiation field of the semiconductor.

The results shown in Figure 3 demonstrate that the flower-like silver particles, with an average diameter of 500 nm, can enhance the spectral response across the full wavelength range of 400–800 nm. This suggests that the flower-like silver particles possess a distinctive field enhancement capability within the 400–800 nm wavelength range. Therefore, it is believed that the surface roughness structure of the flower-like silver particle plays a pivotal role in contributing to field enhancement.

We have previously published papers on enhancing the fluorescence signal of polycyclic aromatic hydrocarbons in diesel using silver nanoparticles [24]. The experimental results and theoretical analysis indicate that due to the presence of silver nanoparticles, the absorption of excited light by polycyclic aromatic hydrocarbons is enhanced, thereby increasing the fluorescence signal by 4.6 times. Combining the experimental results in Figures 3 and 4, it can be concluded that silver nanoparticles enhance the absorption of photovoltaic devices.

To further investigate the influence of the surface protrusions, the flower-like silver particle was considered to comprise of two components: a large core particle of ~400 nm in size, and smaller surface particles of ~100 nm, as shown in Figure 1. The plasmon resonance mode for the surface particles maintains the form of a dipole consistently across the 400 nm to 800 nm wavelength range. However, for the core particle, the plasmon resonance mode starts as a multipole at short wavelengths, transitioning to a dipole at longer wavelengths [25].

The FDTD method was subsequently utilized to simulate the changes in local field intensity and distribution of flower-like silver particles and the central large sphere at wavelengths of long wave (650 nm) and short wave (410 nm), as depicted in Figure 5. Under the excitation of light at a wavelength of 410 nm, a localized field distribution of multipole plasma resonance appears on the surface of the central sphere, as illustrated in
Figure 5a. This observation aligns with the Mie theory calculation results. As the excitation wavelength shifts to 650 nm, the excitation wavelength falls within the range of dipole plasmon resonance scattering peaks of silver particles. Consequently, the surface local field exhibits a dipole plasmon resonance distribution, as presented in Figure 5b. According to the foundational theory of metal surface plasmon resonance, when the size of metal nanoparticles exceeds 100 nm, an increase in particle size will diminish their surface enhancement effect. Thus, for a central sphere with a diameter of 400 nm, the local surface field is significantly reduced due to particle size limitations. For flower-like silver particles measuring 500 nm in size, the local field distribution is showcased in Figure 5c,d.

In contrast to the central sphere, the local field intensity of the flower-like silver particles has markedly improved. At excitation wavelengths of 410 nm and 650 nm, the maximum local field enhancements are 35 times and 6.3 times, respectively. Concurrently, the local field distribution on the surface of flower-like silver particles exhibits notable changes compared to the distribution on the central sphere. With an excitation wavelength of 410 nm, the local field of flower-like silver particles is primarily distributed between the grooves of the surface structure. At 650 nm, the most pronounced localized field emerges in the peripheral region of the flower-like silver particles, oriented parallel to the polarization direction of the incident light. The local field distribution of silver particles is predominantly dictated by their plasmon resonance mode. Comparing the local field distribution of flower-like silver particles to that of the central sphere reveals that while the distribution patterns of the two particle types are similar, the presence of edge balls substantially amplifies the local field strength surrounding the flower-like silver particles.

![Figure 5. The electric field distribution of different silver nanoparticle models (a,b) corresponds to the 400 nm spherical silver nanoparticles model excited at 410 nm and 650 nm, respectively; (c,d) correspond to the flower-like silver nanoparticles model excited at 410 nm and 650 nm, respectively.](image)

In summary, the plasma resonance mode of submicron silver particles is similar to that of the central sphere, with multipole resonance in the short wave and dipole resonance in the long wave. The vibration of the internal electrons is also mainly determined by the central large sphere. Therefore, we investigated the local field...
distribution of the edge sphere under the action of the central sphere at excitation wavelengths of 410 nm and 650 nm, respectively. Figure 6 depicts the local field of three neighboring surface particles stimulated by the local field of the core particle. Under the 410 nm radiation, the strongest field for the surface particles occurs in the gap of the surface roughness structure, as depicted in Figure 6a. Under 650 nm wavelength radiation, the electric field of surface particles is concentrated on the outer area of the surface, as presented in Figure 6b. These simulation results disclose that the effects of the core particle on the surface particles differ in the short and long wavelength ranges, and the “hot spot” of the surface particles also varies accordingly. Furthermore, the interaction between surface particles was also examined. It is found that the electron distribution of the surface particles is determined by the core particle, considered as a whole.

![Figure 6](image_url)

**Figure 6.** The distribution of the electric field around three neighboring surface particles excited by the local field of the core particle. (a) at the wavelength of 410 nm, and (b) at the wavelength of 650 nm.

For a single surface particle, the resonance model is solely a dipole in the wavelength range of 400–800 nm and can therefore be considered as a dipole. Under the radiation at a wavelength of 410 nm, the resonance model of the core particle is multipole. The internal electron oscillations are not just parallel but also perpendicular to the polarization of the incident light. As a result, for neighboring particles in the “Shoulder to Shoulder” pattern (the axis of which is parallel to the polarization of the incident light) of the surface particles, the interaction between electrons can occur [26,27], as illustrated in Figure 7a. The strongest electric field occurs in the gap between the two particles which are in the “Shoulder to Shoulder” pattern.

Under radiation at a wavelength of 650 nm, the resonance model of the core particle is a dipole, and collective electron oscillations are parallel to the direction of the incident light. The internal electrons concentrate on both sides of the core particle. Therefore, the interaction of surface particles in the “Shoulder to Shoulder” pattern is suppressed. Conversely, for neighboring particles in the “Head-to-Head” pattern (the axis of which is perpendicular to the polarization of the incident light) among the surface particles, the local field is enhanced under the action of the core particle, as depicted in Figure 7b. In this case, the electric field is concentrated in the outer area.
Figure 7. A sketch of the electric field distribution of two neighboring surface particles. (a) “Shoulder to Shoulder” pattern, under the action of the core particle at 410 nm. (b) “Head-to-Head” pattern, under the action of the core particle at 650 nm wavelength.

The local field of the surface particles reciprocally impacts the local field of the core particle. The electric field distribution of the core particle, under the influence of the local field of the surface particles, is calculated using the FDTD method, and the results are presented in Figure 8. Figure 8a displays the electric field distribution of the core particle when the surface particles are in the “Shoulder to Shoulder” configuration, with an excitation wavelength of 410 nm. Influenced by the surface particles, the local field of the core particle is enhanced, especially in the gap between the particles. Figure 8b demonstrates the electric field distribution of the core particle when the surface particles are in a “Head-to-Head” arrangement, with an excitation wavelength of 650 nm. The most intense field of the core particle is primarily located in the outer area of the particle, due to the presence of the surface particles.

In comparison to the local field distribution of smooth spheres in the incident light, the local field of the flower-like silver particle is repositioned due to the surface particles and is significantly amplified in both the short and long wavelength ranges. This result aligns with our previous findings on flower-like silver particles [19,25].

Figure 8. The electric field distribution of core particles under the effect of the local field of surface particles. (a) at the wavelength of 410 nm, (b) at the wavelength of 650 nm.

The interaction between the surface particles and the core particles allows the flower-like silver particles to achieve a near-field enhancement across a broad spectrum. The field enhancement is defined as $|E|/|E_0|$ and is plotted as a function of wavelength in Figure 8. Here, $|E_0|$ is the incident field and $|E|$ is the maximum local field of the flower-like silver particle.

Figure 9 reveals that the field enhancement of the flower-like particle persists across a broad wavelength range of 400–800 nm, with the field enhancement being more significant in the shorter wavelength range. However, as the local field distribution is
concentrated in the gap of the surface particles in the short wavelength range, the enhancement ratio of the spectral responsivity is conversely lower than in the long wavelength range.

![Figure 9](image-url)

Figure 9. The local field enhancement $|E|/|E_0|$ of the flower-like silver particles to the wavelength.

After the incident light acts on the silver particles, due to the LSPR effect of the silver particles, the radiation field acting on the semiconductor is enhanced. After the semiconductor absorbs the photons, the internal electronic transition process can be explained by the perturbation theory in quantum mechanics [28,29]. According to Fermi’s Golden Rule, the transition probability $w_{if}$ of the semiconductor can be expressed as:

$$w_{if} = C|\mathbf{E}|^2|M_{if}|^2$$

(2)

where $C$ is a constant, $M_{if}$ represents the transition matrix element, $\mathbf{E}$ is the radiation field acting on the semiconductor. The relationship between the semiconductor’s absorption coefficient $\alpha$ and the transition probability $w_{if}$ can be expressed as:

$$\alpha \propto \sum w_{if} n_i n_f$$

(3)

where $n_i$ and $n_f$ represent the density of states of the semiconductor in the initial and final state, respectively. According to Equations (2) and (3), for amorphous silicon photovoltaic modules containing silver particles, the action of the silver particles enhances the radiation field acting on the semiconductor, thereby increasing the probability of internal electronic transitions in the semiconductor and raising the absorption coefficient. Generally speaking, for the same semiconductor, its absorption coefficient is a fixed value, but the introduction of silver particles can be expressed as an increase in its absorption coefficient. Thus, when the light of the same intensity acts on amorphous silicon photovoltaic modules with and without silver particles, the photovoltaic modules containing silver particles have a larger absorption coefficient, therefore their light absorption is stronger, resulting in a larger photocurrent.

4. Conclusions

In summary, an a-Si p-i-n photovoltaic structure with flower-like silver particles deposited on the surface was fabricated. The transmittance, reflectance, and absorptance spectra measurements revealed that the absorption of this photovoltaic structure was enhanced in a broad wavelength range from 200 nm to 2000 nm by adding flower-like silver particles on the surface. Furthermore, the spectral response of the a-Si p-i-n structure with and without silver particles, respectively, was measured at the wavelength range of 400–800 nm, which revealed that the maximum enhancement ratio of the responsivity can
reach about 10, and the spectral response shape of the composite structure was consistent with the structure without silver particles. The FDTD method was employed to investigate the mechanism. In our analysis, the sample was divided into two parts including the core particle and surface particles. We found that the interaction between the core particle and surface particles leads to the unique optical characteristics of the flower-like particles, which improved the performance of the a-Si p-i-n photovoltaic structure in a broadband range. Through these studies, we demonstrate that utilizing the subwavelength silver particles with roughness surface can achieve the spectral response of the photodetector device enhanced in broadband range, which can improve the utilization efficiency of optical energy for the applications of sensing, imaging, optical communication, and energy harvesting. The theoretical analysis provides improved insight into the coupling of physical properties in photovoltaic modules incorporating metal particles.

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