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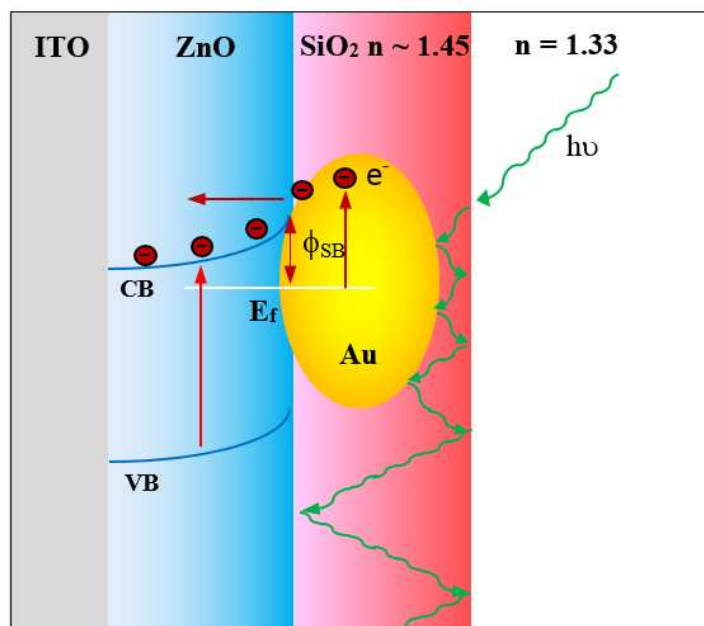
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Enhanced photoelectric response of plasmon-active ZnO nanorods by spatial modulation of dielectric environment

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ABSTRACT: One-dimensional zinc oxide (ZnO) nanorods have excellent electron mobility and exhibit great potential for photoelectric or photochemical applications. However, poor visible light absorption and rapid surface charge recombination are bottleneck for promoting its applications. In this work, plasmonic gold nanoparticles (Au NPs) and dielectric silicon oxide (SiO₂) are deposited on the surface of ZnO nanorods to tune their photoelectric performance. The localized surface plasmon resonance of Au NPs extends the absorption spectrum to visible region. The surface passivation with dielectric SiO₂ layer suppresses the photoexcited electron-hole recombination. By rational integration of the configuration, it is found that dielectric spacer (ZnO-SiO₂-Au) shows obvious photocurrent improvement. While dielectric shell-coating (ZnO-Au-SiO₂) dramatically leads to an outstanding photocurrent enhancement, which is ~ 4 - 28 times higher than that of the other counterparts. The enhanced performance is ascribed to its effectiveness for spatially separating electron-hole pairs and optimizing photo-absorption properties of the metal-semiconductor system. This strategy provides new insights into fabrication of high performance light harvesting antenna, and stands for a basis to design solar-active systems.

Keywords: ZnO nanorods, Surface plasmon resonant, Dielectric layer, Photoresponse

1. Introduction

Metal oxides such as titanium dioxide, zinc oxide and hematite oxide have shown great potential as photoelectrodes in photoelectric or photoelectrochemical cells [1-3]. Among them, ZnO presents a unique crystalline structure, a direct wide band gap (3.37 eV), a large exciton binding energy, excellent electron mobility and environmental compatibility [4-6]. One-dimensional ZnO nanorods attract more attention owing to their high aspect ratio, large specific surface area, high photon-induced charges generation and transfer rate [4, 7-11]. However, the large bandgap restricting its utilization in visible light range of solar spectrum and the high recombination rate of photogenerated electrons and holes leading to a low quantum yield and poor photoelectric properties. Various methods have been proposed for improving the photoelectric conversion efficiency across the entire ultraviolet-visible spectrum, such as doping or introducing defects, crystal growth control, surface modification, and the creation of heterostructures, etc [12, 13].

The decoration of semiconductor with metal nanoparticles (NPs) is one promising ways to improve the photoelectric conversion efficiency. This is because metal NPs have the unique ability to concentrate light through plasmonic enhancement of the local field and thereby enhance the light-matter interactions in adjacent materials [2, 14, 15]. The remarkable features of plasmon-induced photophysics is surface plasmon resonance (SPR), which arises from the collective oscillation of free electrons at the metallic interface or in small metallic nanostructures. The plasmon metal-semiconductor structures confer several distinct advantages [16, 17]. First, plasmonic metal nanoparticles act as photosensitizers in metal-semiconductor junctions and strongly absorb at specific wavelengths in the visible region. Second, the metallic nanoparticles effectively act as antenna, which are useful in semiconductors with a short minority carrier diffusion length. Therefore, under visible light irradiation, the continuously injected hot-electrons from metal nanostructure into conduction band of semiconductor as well as formation of Schottky barrier facilitates electron-hole separation and promotes the photoelectrical performance [18].

Although tuning SPR by size, shape and distribution of noble metal has been widely explored, the surrounding environments are key parameter from physics point of view [18-21]. It was found that the plasmon resonant frequency and intensity intimately related to the dielectric

properties of surrounding environment [14, 22-24]. Besides, the semiconductor suffers electrolyte corrosion during the photoelectrochemical process, the presence of gold metal nanoparticles and dielectric oxide layer such as silicon dioxide could improve the photochemical stability [2, 3, 25]. Moreover, SiO₂ coating as dielectric circumstance enables higher refractive index resulting in a red shift and stronger localization of electromagnetic field [23, 26, 27]. Therefore, rational integration of functional components in composite nanostructures is important for solar energy harvesting since that is advantageous to extend the light absorption, reduces the charge carrier recombination and resists the electrolyte corrosion simultaneously.

In this work, we investigate the light harvesting and photoelectrochemical performance of ternary heterojunctions by introducing Au NPs and SiO₂ overlayer on ZnO nanorods. The ZnO nanorods is synthesized on ITO glass by a two-step fabrication process. Au NPs and SiO₂ film are sputtered on the nanorods with diverse spatial configurations. The optimal size of Au particle and the thickness of SiO₂ overlayer are acquired through precise controlling the duration of sputtering. The results show that the dielectric shell-coating nanorods ZnO-Au-SiO₂ deliver the best photocurrent density response compared to the other references. Such enhancement is ascribed to the synergistic effect of SPR induced by Au NPs and surface passivation resulted from the dielectric SiO₂ overlayer.

2. Experimental

2.1. Material preparation

The raw material zinc nitrate [Zn(NO₃)₃], absolute ethanol, zinc acetate [Zn(CH₃CO₂)₂], hexamethylenetetramine and indium tin oxide (ITO) coated glasses were purchased from Sigma-Aldrich. All chemicals were used as received without further treatment. Nanorods ZnO were synthesized on ITO glass via a two-step process. To prepare the seeding solution, 10 ml of zinc acetate 0.08 M in absolute ethanol with addition of 0.25 ml water were stirred for 2 hours. The ITO substrate was dipped into zinc acetate solution for 20 s with a fixed withdrawing speed and then dried in oven at 75 °C for 35 min. This process was repeated four times. The seeded substrate was then annealed in air at 220 °C for 1 hour and immersed up side down in the solution of 0.025 M zinc nitrate and hexamethylenetetramine. The hydrothermal treatment was conducted at 90 °C in 4 hours. Finally, the ITO glass was rinsed several times with water and ethanol, dried at room temperature and calcined at 450 °C in 30 min.

During the sputtering process, Au and SiO₂ films were prepared by radio frequency magnetron sputtering. A cleaned FTO substrate and the sample were placed parallel to the target at room temperature. For the reference, a thin layer of film were deposited onto the FTO substrate and annealed under the same annealing conditions for estimating the deposition thickness [28]. The Au sputter coater (VG Microtech SC500) was operated at 10 mA for 110 s with the vacuum pressure of Argon process level at 10⁻² mbar to produce approximately 5 nm of the film. By controlling the sputtering duration and the annealing process, the film thickness could be flexible tuned in the range of 5-20 nm. The tools SEM and TEM have been used to characterize the film thickness and particle size. For the thin film SiO₂ sputtering process (5 nm, AJA sputter), the Ar flow at 5 sccm, the power applied to the SiO₂ target is 130 W and the pressure is 3.3 mTorr. By the sputtering process with various loading orders. Five spatial configurations including ZnO, ZnO-SiO₂, ZnO-Au, ZnO-SiO₂-Au, ZnO-Au-SiO₂ were fabricated by using magnetron sputtering on ZnO nanorod arrays (Fig. 1).

2.2. Characterization

Surface morphology and detailed microscopic structure of the samples were analyzed using scanning electron microscope (SEM, Hitachi 1081) at 30 kV accelerating voltage and transmission electron microscope (TEM, JEOL JEM2100F). The high angle annular dark field (HAADF) and energy-dispersive X-ray spectroscopy (EDS) were acquired on a FEI TalosF200X. The light absorption spectra were recorded on a spectrophotometer (SHIMADZU, UV-2600 with ISR-2600 integrating sphere attachment) in range of 220-850 nm with fine BaSO₄ powder as reference. The electrochemical characterization was conducted using three electrode methods with a standard electrochemical workstation (Zahner elektrik IM6). The ITO glass with difference loadings on nanorods ZnO (effective layer 1 cm²) was used as the working electrode following by Ag/AgCl and Pt electrode as the reference and counter electrode, respectively. The solution 0.5 M Na₂SO₄ (pH=6.8) was the supporting electrolyte for all measurement. A light source (halogen lamp 15V/150W) is utilized to record the photocurrent in visible region with bias of +0.3, +0.5 and +0.7 V.

3. Results and discussion

3.1. Morphology and structure

Fig. 2a shows a photograph of the samples including ZnO, ZnO-SiO₂, ZnO-Au, ZnO-SiO₂-Au, ZnO-Au-SiO₂ nanorod arrays. It can be seen that first two samples of ZnO, ZnO-SiO₂ exhibit semi-transparent color, while the color of other samples change to dark grey after introducing gold nanoparticles, suggesting that they absorb a considerable portion of visible light. Fig. 2b and 2c show a series of scanning electron microscopy (SEM) images of the nanorod composites ZnO-Au-SiO₂, which has uniform size and ordered shape with a diameter about 300-350 nm and length of 1-2 micrometers. The high-resolution image (Fig. 2c) indicates that small nanoparticles distributed on the surface of nanorods.

The transmission electron microscopy images (Fig. 3a and b) provide a more distinct comparison and confirmation for the nanorod ZnO-Au-SiO₂. It is clearly seen that the sample is an assembly of uniform three dimensionally ordered core-shell nanoparticles on the nanorod. The high-resolution image (Fig. 3a) shows the lattice fringes of crystalline component. The back scattered electron image in Fig. 3b shows the nanoparticles are evenly distributed on the nanorod surface and the average size of particle is around 8 nm (~10% errors). Compared with small Au NPs, the Au-SiO₂ core-shell NPs are not easier to aggregate as the surface energy is relatively lower. The selected SAED pattern (Fig. 3c) reveals the crystalline nature of nanorods as the spotted rings and dots can be detected.

The element distribution maps of the nanorod are shown in Fig. 3d. HAADF and elemental maps confirm the co-existence of Au, Si and O, that they are homogeneously dispersed on the surface of ZnO nanorod. The mapping image of Si shows Au NPs are capped with SiO₂, which further confirms the formation of core-shell structure (Fig. 3a). The interface between the ZnO and Au core is expected to be important for the hot-electron injection from Au to the conductive band (CB) of ZnO upon localized surface plasmon resonant (LSPR) excitation. A single nanorod is further analyzed using EDS spectrum to detect distribution of individual elements (Fig. 3e). The Au, Si, Zn and O peaks along with Cu and C peaks can be clearly observed in the spectrum, demonstrating their co-existence in the composite. The ratio between Zn and O is roughly unity presenting for ZnO with small amount of gold (8.46 % at) that uniformly dispersed on the surface of nanorod. Due to the nature and thin layer of silicon oxide (< 5nm), it is hard to be detected in the EDS spectrum.

3.2. Light absorption and photoelectric properties

Fig. 4a shows the UV-vis absorption spectra of ZnO nanorods, ZnO-SiO₂ and ZnO-Au nanorods (two components), ZnO-SiO₂-Au and ZnO-Au-SiO₂ nanorods (three components), respectively. All the samples are of the same size and thickness. For ZnO nanorods, the strong absorption at wavelength range below 400 nm matches the intrinsic interband transition absorption of ZnO, exhibiting its UV absorption properties. The nanorods with thin film SiO₂ on ZnO performs stronger light absorption than pristine ZnO, which could be explained by the higher refractive index properties of SiO₂. In this manner, the charge-carrier generation, separation and collection of ZnO can be improved by means of resonant light trapping in ultrathin SiO₂ films designed as optical cavities. Interference between forward- and backward-propagating waves enhances the light absorption in quarter-wave, amplifying the intensity close to the surface wherein photogenerated minority charge carriers can reach the surface [29, 30]. While the gold decorated nanorods show a broad peak at 600 nm, corresponding to SPR absorption of Au nanoparticles, which could be tuned by varying their size, shape and surrounding environment [14, 20]. After the deposition of SiO₂ on Au nanoparticles, the SPR absorption peak red-shifts to 620 nm because of the strong electromagnetic coupling of Au and SiO₂. This implies that the SiO₂ with higher dielectric constant directly contacting with Au NPs would lead to red shift of the SPR band [14].

The SPR exists in two distinct forms: surface plasmon polaritons (SPP) and LSPR [31]. SPP or propagating surface plasmons are travelling charge oscillations resonantly excited on the surface of thin metal films, whereas LSPR is the stationary, non-propagating collective oscillation of the surface electrons in metal nanostructures. SPP and LSPR in plasmonic nanostructures improve the solar energy conversion efficiency of semiconductors via two pathways: photonic enhancement and plasmonic energy-transfer enhancement. In present work, the nanorods act as miniature fiber optics to create the confined modes, which traps the incident light to enhance the light absorption [32, 33]. The intense local field enhancement of the LSPR overlapped with the absorption band edge of ZnO, enhancing solar energy harvesting at the energies below the band edge through the resonance energy transfer mechanism [34]. As a result, the photonic (~ 425 nm) and the plasmonic energy-transfer enhancement (~ 650 nm) are observed in the absorption spectrum (Fig. 4b).

Fig. 5a displays linear sweep voltammogram curves of the samples versus Ag/AgCl applied potential from 0.0 to 0.8 V under visible-light illumination. For the ZnO and ZnO-SiO₂ nanorods,

their photocurrents are relatively low. The ZnO-Au-SiO₂ nanorods present the highest photocurrent, while ZnO-SiO₂-Au exhibits a lower value as compared to gold decorated ZnO. Fig. 5b shows photoresponse of the samples at 0.5 V vs. Ag/AgCl under light illumination. It can be seen that the bare ZnO or ZnO-SiO₂ nanorod array almost does not produce photocurrent. Most of the responses present in a pulse shape corresponding to light excitation. The ZnO-Au-SiO₂ nanorods show the fastest photoresponse once the light is turned on, and exhibit a maximum current density of 0.86 $\mu\text{A}/\text{cm}^2$, which is about 4.3, 9.6, 17.2 and 28.7 times compared with the values of ZnO-Au (0.20 $\mu\text{A}/\text{cm}^2$), ZnO-SiO₂-Au (0.09 $\mu\text{A}/\text{cm}^2$), ZnO (0.05 $\mu\text{A}/\text{cm}^2$) and ZnO-SiO₂ (0.03 $\mu\text{A}/\text{cm}^2$). Fig. 5c shows the transient photoresponse of ZnO-Au-SiO₂ nanorods, which exhibits a good reproducible photocurrent density over the times at different bias. This clearly confirms that the nanorod arrays have superior visible-light photoelectrochemical properties.

3.3. Light harvesting mechanism and photoelectrical physics

Due to chemical inertness and light transparency, SiO₂ has been utilized as a stabilizer, protecting, passive or dielectric layer in a series of photoelectric and photochemical applications. As a protecting layer, SiO₂ retards the interaction with oxygen and results in electron-hole recombination [3, 25]. This recombination significantly reduces the photocurrent (Fig. 5b). While gold nanoparticles loaded ZnO nanorods is a well-known plasmonic structure under visible light irradiation [5, 35]. Therefore, gold nanoparticles loaded ZnO nanorods shows strong visible light absorption due to the plasmonic effect. Besides, the incorporating gold with ZnO results in the Schottky barrier at the contact interface causing the band bending. The hot electrons with enough energetic potential jump through the Schottky barrier into the CB of ZnO (Fig. 6). In ZnO-SiO₂-Au configuration, the dielectric SiO₂ layer acts as insulator between gold nanoparticles and ZnO nanorods. This dielectric layer weakens the electromagnetic field intensity, which depresses the electron-hole separation. On the other hand, under visible light irradiation, the energetic electron can tunnel through the thin film SiO₂ to inject into the nanorods ZnO [36]. Therefore, the photocurrent of ZnO-SiO₂-Au is lower than the gold decorated ZnO nanorods but still higher than that of the pristine ZnO nanorods.

Interestingly, ZnO-Au-SiO₂ nanorods exhibit an outstanding photoresponse. There are several reasons contributing for this high photocurrent density. Firstly, gold plasmonic structures

have the possibility to interact with the electrolyte components that decreases the amount of energetic electrons injected into the ZnO nanorods. The thin layer SiO₂ inhibits the electron in conduction state interacting with the electrolyte, which not only increases the electron injection efficiency from photoexcited Au nanoparticles, but also suppresses the possibility of charge recombination [37]. Secondly, the structure exhibits more intensive electromagnetic field at the semiconductor-plasmonic metal interface as well as deeper penetration into the semiconductor than the other counterparts. This greatly increases the light absorption cross-section of plasmonic nanoparticle [38-40]. In addition, as compared to electrolyte, the higher refractive index of dielectric layer and multi-scattering effect induced by nanorods establish light-trapping structures, which extends the pathway of incident light [30, 41-43]. Therefore, the light-trapping structures enhance the light absorption of the sample, reflecting in an enhanced photocurrent.

4. Conclusions

In this work, Au NPs and SiO₂ overlayer are synergistically integrated on ZnO nanorods for solar energy harvesting. Photoelectric behavior of the gold and silicon oxide decorated ZnO nanorods are explored under solar irradiation. As a result, the increased absorption in visible region due to the SPR effect and the enhanced photogenerated electron-hole separation originated from the surface passivation lead to a significantly improved photoelectric performance. The ZnO-Au-SiO₂ nanorods exhibit superior photoresponse that is ~4 times higher than that of the ZnO-Au nanorods. This is ascribed to 1) the dielectric SiO₂ intensifies SPR-mediated hot electron injection, 2) the effective electron transfer channel through the ZnO backbone, 3) the light trapping structures due to its higher dielectric index and multi-scattering effect induced by photonic nanorod arrays. While the presence of thin dielectric layer between gold and ZnO nanorods weakens the response to visible light owing to the electromagnetic inhibition induced by passivation effect. The rational design of plasmonic-dielectric-semiconductor system paves a new avenue to develop highly efficient photoactive materials for solar energy harvesting.

Notes

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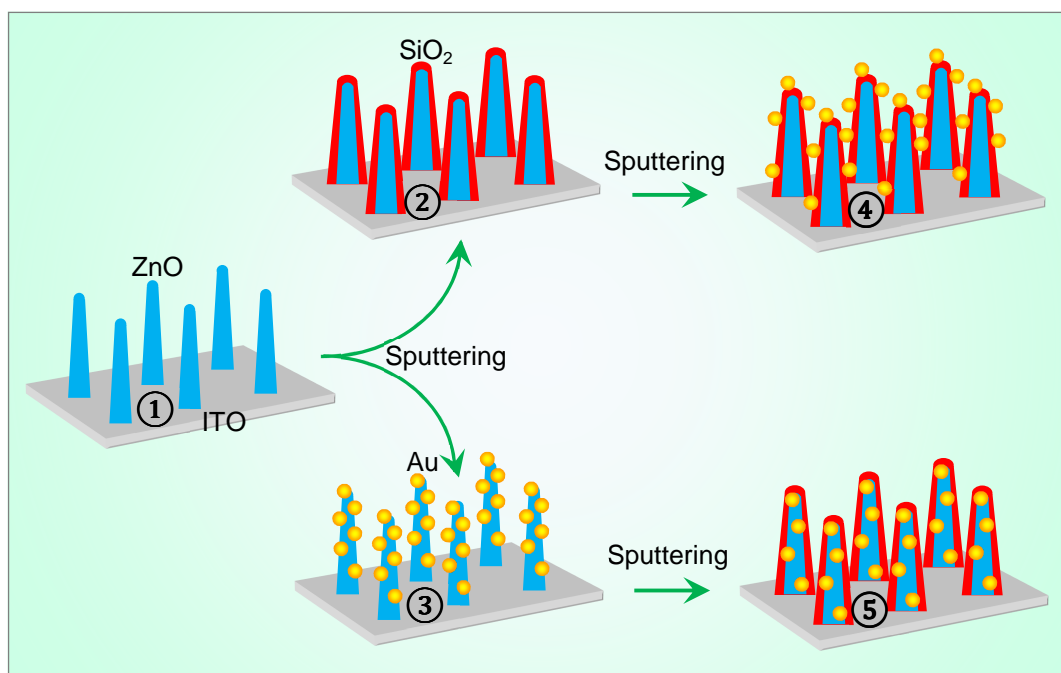


Fig. 1. Schematic illustration of fabrication process of the nanorod arrays

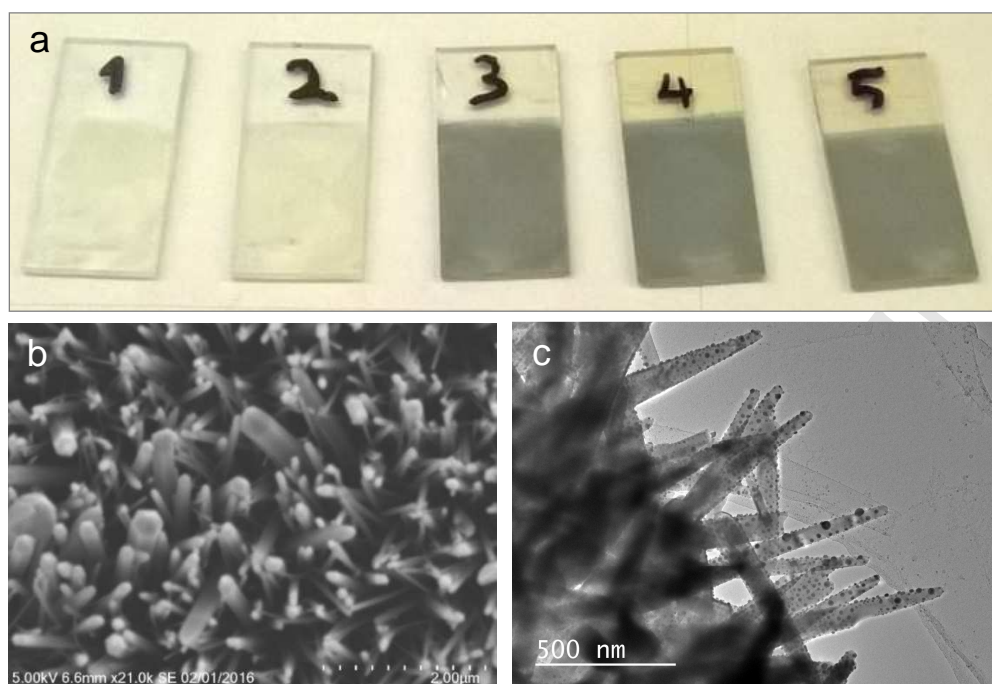


Fig. 2. a) A photograph of the resulting samples of ZnO, ZnO-SiO₂, ZnO-Au, ZnO-SiO₂-Au, ZnO-Au-SiO₂, corresponding to the samples in Figure 1, b) and c) SEM images of ZnO nanorods with Au and SiO₂ deposition.

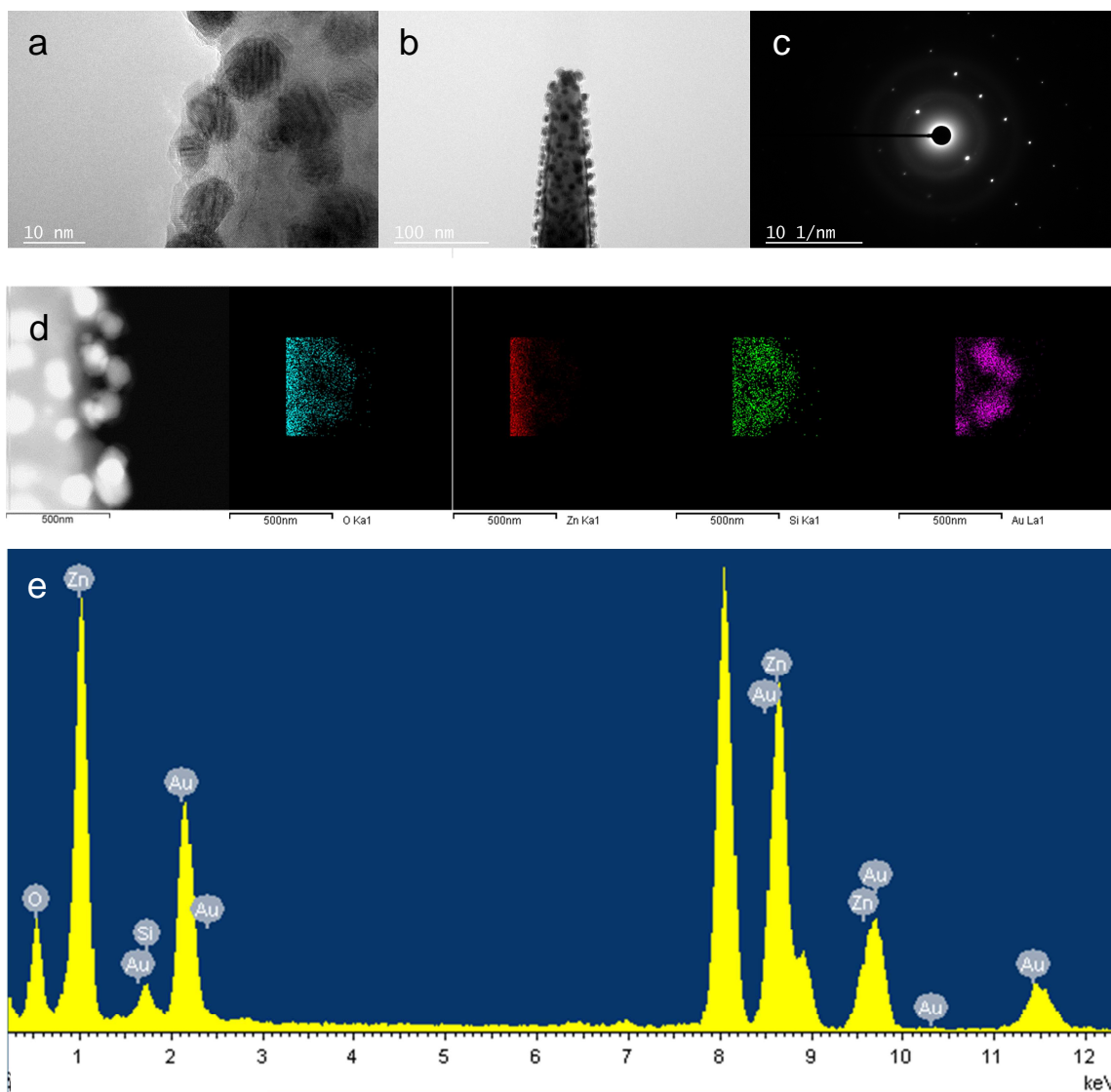


Fig. 3. a) and b) TEM images of a ZnO nanorod with Au and SiO₂ deposition. c) Selected Area Electron Diffraction (SAED) images of the sample. d) The high angle annular dark field (HAADF) and Energy-dispersive X-ray spectroscopy (EDS) elemental mapping image of the sample. e) EDS spectrum.

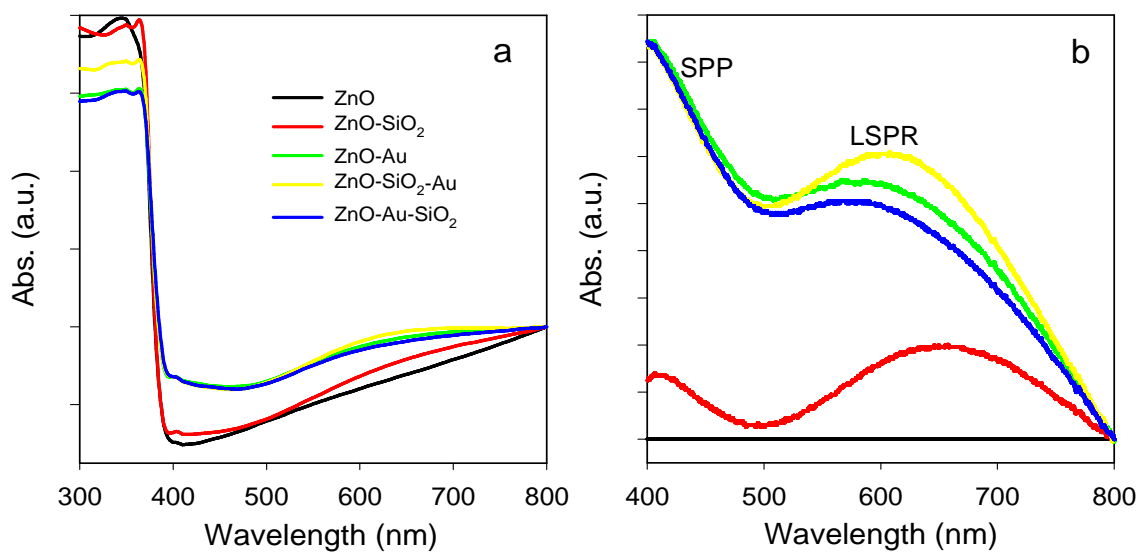


Fig. 4. a) UV-vis absorption spectra of the nanorods with and without coating, b) the absorption spectra by subtracting the spectra of ZnO.

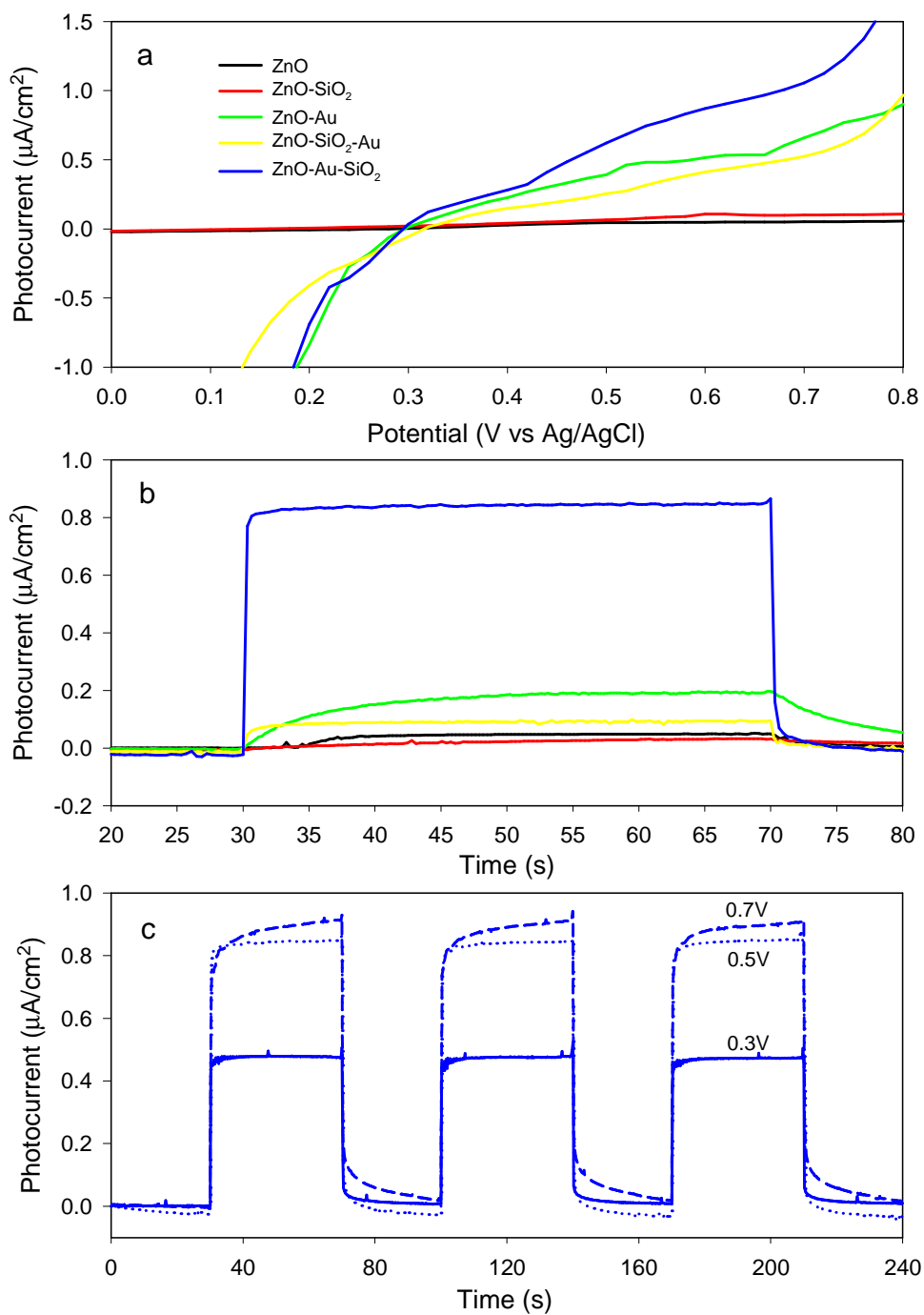


Fig. 5. a) I-V curves of the nanorods ZnO, Zn-SiO₂, Zn-Au, ZnO-SiO₂-Au, ZnO-Au-SiO₂ under white light illumination b) Photoresponses of the nanorods at 0.5 V bias under white light illumination c) Transient photoresponse of the nanorods ZnO-Au-SiO₂ at 0.3, 0.5, 0.7 V bias.

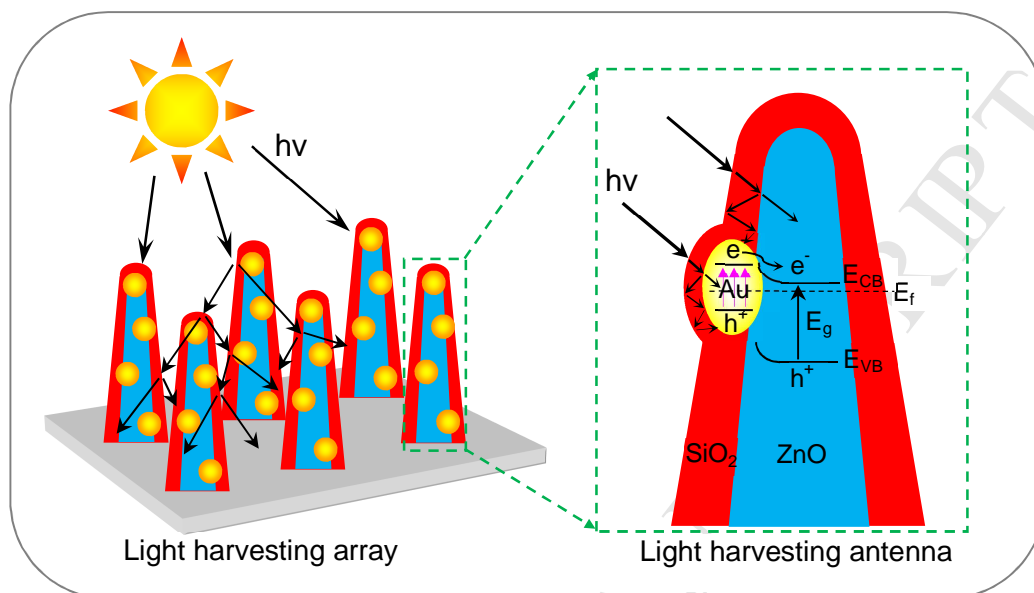


Fig. 6. Light harvesting mechanisms and photoelectrical physics.

Highlights

- Nanorods ZnO-Au-SiO₂ are synthesized to understand the dielectric effect on their photoelectric behavior
- The photoelectric performance strongly depends on the spatial configuration of nanorods
- The nanorods ZnO-Au-SiO₂ show the fast and strong photoresponse
- This enhancement comes from the synergistic effect of SPR and surface passivation