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Ultrahigh density plasmonic hot spots with ultrahigh electromagnetic field for improved photocatalytic activities

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ABSTRACT

Plasmonic hot spots located among closely dispersed plasmonic nanoparticles (NPs) are intensively studied for efficient conversion of solar to chemical or electrical energy applications. Here, a successful method to synthesize high-density unaggregated plasmonic Ag or Au NPs (AgNPs or AuNPs) onto nanostructured semiconductors with 3D densely organized NPs is demonstrated. The densely dispersed plasmonic AgNPs or AuNPs are assembled chemically on the entire surface of the ZnO nanorods through bifunctional thioctic acid bridging linkers. The fabricated NPs possessing small interparticle gaps generate numerous plasmonic hot spots which boost catalytic activities of the photocatalysts. As depicted by exact 3D finite-difference time domain simulations, the electromagnetic fields are magnified exponentially among interparticle gaps, hot spots, due to the plasmonic coupling effects of the neighboring AgNPs. The electromagnetic fields are strengthened by decreasing the interparticle spacing of coupled AgNPs. It is consistent with the result that the photocatalytic reaction rate increases non-linearly with the Ag content under full-spectrum light irradiation. Using the spectral characterizations and electromagnetic field simulations, we unambiguously confirm the enhancement of photoactivity due to coupling of plasmonic hot spot effect to nanostructured semiconductors. Moreover, diverse heterostructures based on the plasmonic NPs on various ZnO nanostructures (films, nanorod arrays, branched nanowires, and mesoporous structures) or functional materials ($CuInGaSe_2$ absorber films, multiferroic $BiFeO_3$ films, visible-light photoactive Cu_2S and CdS nanorods) are successfully fabricated using the present synthesis methodology.

1. Introduction

Recently, surface plasmon resonance (SPR) is intensively studied for application in solar energy harvesting, conversion, and storage as well as environmental pollutant purification [1–8]. Plasmonic nanostructures especially for the Ag or Au nanoparticles (AgNPs or AuNPs) support the formation of SPRs in response to a visible light flux and localize the electromagnetic energy to their surfaces [9]. For visible-light-driven photocatalytic applications, the interaction of the plasmonic AgNPs or AuNPs with their neighboring semiconductor allows for an enhanced generation of electron–hole pairs in the near-surface region of the semiconductor [10]. These charge carriers are readily separated and easily migrate to the surface (short exciton diffusion length), where they can perform photocatalytic transformations. The SPR-induced enhancement in the generation rate of electron–hole pairs through the near-field mechanism is dependent on the intensity of local electromagnetic fields [11–13]. Both experimental and theoretical works have demonstrated that a high local electromagnetic field leads to increased light absorption and effective generation of electron–hole pairs at the surface of the Ag-TiO_2 [14], Ag-Cu_2O [15], Ag-AgCl [16], Ag-ZnO [17], Au-TiO_2 [18–21], Au-Fe_2O_3 [22–25], Au-Si [26], Au-SiO_2 [27], Au-GaP [28], or Au-ZnO [29] heterostructures for plasmonic enhancement of photocatalytic reactions.

Interaction of light with nanostructures gives rise to a variety of interesting optical phenomena in nanoscale. SPR concentrates the light flux (the energy of incoming photons) in small volumes surrounding the nanostructure. Duan and coworkers [30] reported that the calculated electromagnetic field enhancement ($E^2/E_0{}^2$) of more than 1 order of magnitude can be achieved around the plasmonic AgNPs or AuNPs near the surface of the Si photodiodes. The enhancement quickly decays to a much smaller enhancement

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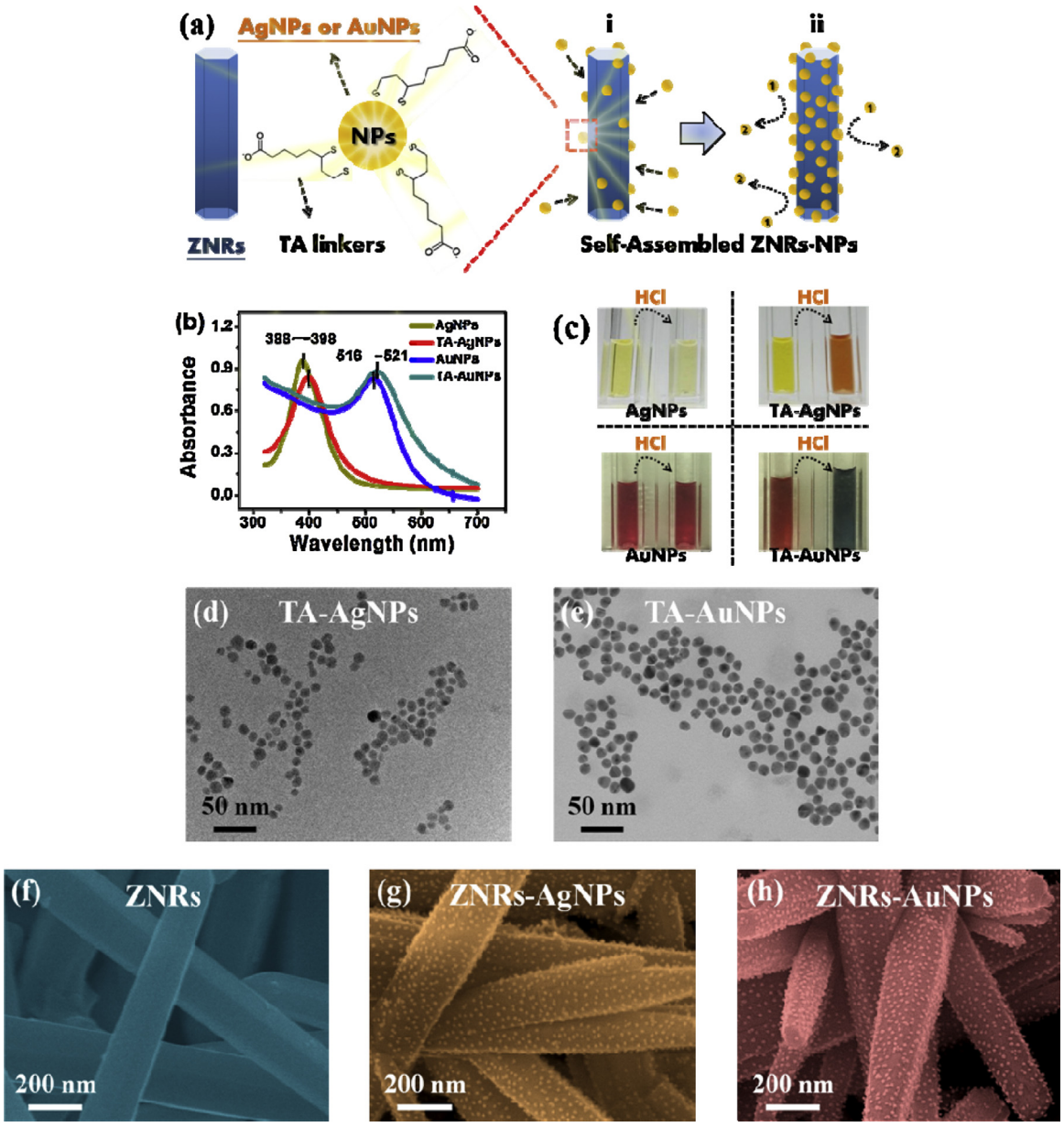

Fig. 1. (a) Schematic of the synthesis methodology for ZNRs-NPs heterostructures using TA linkers. (b) Optical absorption spectra of AgNPs and AuNPs before and after modification with TA. (c) Photographs of AgNPs, AuNPs, TA-functionalized AgNPs, and TA-functionalized AuNPs before and after adding HCl solution. TEM images of (d) TA-functionalized AgNPs and (e) TA-functionalized AuNPs. SEM images of (f) ZNRs, (g) ZNRs-AgNPs (30 wt.%), and (h) ZNRs-AuNPs (30 wt.%) heterostructures. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

factor of 1.5–5 at a distance of 15 nm from the plasmonic NPs. The wavelength and the intensity of the SPR of metal particles are highly sensitive to the metal species, size, shape, interparticle spacing, and the dielectric environment [31,32]. Most importantly, numerous experimental and theoretical efforts have confirmed that the local "hot spot", which locates in the gap region between closely dispersed plasmonic particles in 2D-patterned plasmonic particle arrays, can enhance the local electromagnetic field by several orders of magnitude higher than that by isolated particles [3,21,33–37]. Very recently, Mangelson et al. [38] developed a procedure for synthesizing Au nanorod dimers embedded within TiO_2 sheets as case study for the incorporation of plasmonically active materials into generic semiconductor films. They showed that this composite amplifies the electric field of incident light within the gap between nanorod segments. These studies stimulated keen interests in fabricating 3D heterostructures composed of closely dispersed plasmonic NPs decorating on the surface of semiconductor nanostructures, aiming for high number density plasmonic hot spots with high electromagnetic field to overcome the limited efficiency of photocatalysts and photovoltaic devices.

With the pertinent motivation, we firstly develop a controlled synthesis of remarkable 3D photocatalysts composed of high-density unaggregated plasmonic AgNPs or AuNPs chemically bound to one dimensional ZnO nanorods (ZNRs) through thioctic acid (TA) as a bifunctional molecular linker, as shown in Fig. 1a. The hence successfully fabricated new materials of plasmonic metal-semiconductor 3D heterostructures have high number density of plasmonic hot spots with ultrahigh electromagnetic field. As depicted by 3D finite-difference time domain (FDTD) simulations, significant incoming photon confinement and enhancement around the metal-semiconductor interfacial plasmon hot spots contribute to efficient conversion of light energy to electron–hole