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Radiative properties of hedgehog-like ZnO-Au composite particles with applications to photocatalysis

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ABSTRACT

The recently proposed **hedgehog-like** ZnO **particles** (HPs) exhibit unusual dispersion behavior in fluids, which after being deposited with Au nanoparticles show great potential in the application of photocatalysis in both the ultraviolet and visible spectral range. Nevertheless, the radiative properties of hedgehog-like particles that largely determine the photocatalysis activity are not well understood. In this paper, models of **hedgehog-like** ZnO-**Au** composite **particles** (HP-Au) were built, and the discrete dipole approximation was applied to investigate their radiative properties in the spectral range from 0.3 to 0.8 µm. It is found that the absorption cross section of HPs increases notably with increasing number of ZnO nanorods in the spectral range from 0.3 to 0.4 µm, which can be five times that of the coated sphere for HPs having 300 nanorods. The absorption cross section of HP-Au increases with increasing amount of Au nanoparticles in the visible spectral range, but maintains at about 5 μm^2 at the resonant wavelength of Au particles for Au to Zn mass concentration ratio larger than 14%. In addition, for Au to Zn mass concentration ratio below 9%, the peak absorption cross section of the deposited Au nanoparticles is larger than that of the independent one with the largest enhancement ratio being larger than 1.5. However, the light absorption by ZnO nanorods is not enhanced by the deposited Au nanoparticles. Having the same amount of the deposited Au nanoparticles, the absorption cross section of HP-Au increases with increasing particle size. In terms of light absorption, HP-Au with a larger number of lanky ZnO nanorods that are sparsely deposited with Au nanoparticles for an Au to Zn mass concentration ratio of about 9% are preferred for the application of photocatlysis.

1. Introduction

Metal and semiconductor nanoparticles have been widely used in applications of photocatalysis, photo-thermal conversion and photoelectricity [1–4] due to their excellent optical and catalytic performance. However, nanoparticles frequently join together to form aggregate clusters in nanofluids, which significantly restricts the absorption ability of nanofluids [5–7]. Recently, Bahng et al. [8] synthesized the **hedgehog-like** ZnO **particles** (HPs), which demonstrate unusual dispersion behavior in both hydrophilic and hydrophobic media. As a wide gap semiconductor, ZnO can only absorb light in the ultraviolet (UV) range, which means that ZnO can only utilize an amount of energy that accounts for 5% of the total solar spectrum. Metal/semiconductor composite particles have been designed to realize light absorption in a broad spectral range [9] and enhance the efficiency of photocatalysis [10–13]. Using the unusual dispersion property of HPs, Wang et al. [14] synthesized the **hedgehog-like** ZnO-**Au** composite hierarchical **particles** (HP-Au) for the application of photo-thermal conversion and photocatalysis. As shown by the SEM images of the HPs in Fig. 1 [14,15], HP-Au possess spike-like surface structure and are composed of three component including the polystyrene core, the ZnO nanorods and the Au nanoparticles.

The light absorption process of photocatalyst is the precondition for the photocatalysis reaction. In the ultraviolet spectral range, the photon absorption generates the electron-hole pairs in semiconductor. The electron-hole pairs are then used for the oxidation–reduction reaction [13]. In the visible spectral range, HP-Au can act as a composite plasmonic metal/semiconductor photocatalyst, which achieve significantly stronger photocatalytic activity compared with their pure semiconductor counterparts [16–19]. The photocatalytic activity of metallized semiconductor is induced by the surface plasmon resonance of the metal nanoparticle. Specially, the role of Au nanoparticles is to create hot charge carriers through the absorption process in the mechanism of plasmon induced photocatalysis. The excited electrons with enough energy

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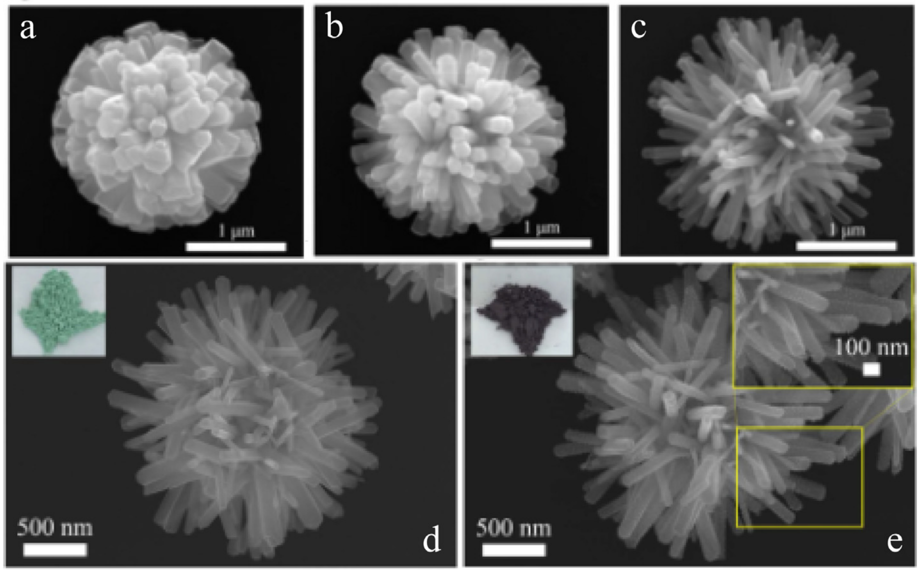

Fig. 1. SEM images of HPs and HP-Au. The shapes of HPs generated by different reaction conditions are shown in (a-c) [15]; the comparison between HPs and HP-Au can be seen in (d) and (e), the insets are the photographic images of the prepared powders [14].

overcome the barrier between the Au nanoparticles and ZnO to form electron-hole pairs [10,11]. Therefore, a larger light absorption ability of HP-Au is expected to achieve a higher photocatalysis efficiency.

It is noted that the absorption property of particles depends on the size, shape and component [20,21]. By varying the morphological features, it is found that the absorption ability of the particles can be enhanced [17,22]. Yet, the absorption property of HP-Au with respect to its morphological factors has not been well understood till now. In addition, the radiative properties of particles should be specified accurately to determine the efficiency of nanofluids and to design the solar collectors with maximum light availability [23].

Therefore, the radiative properties of HP-Au should be studied with respect to its morphological factors, as an effort to find an optimized particle morphology in terms of light absorption for the application of photocatalysis. The aim of this paper is to establish models to represent the morphological details of HP-Au and to investigate their radiative properties. The discrete dipole approximation (DDA) is applied to calculate the radiative properties of HP-Au in the spectral range from 0.3 to 0.8 μm. The effects of the particle size, the spike-like surface structure and the amount of Au nanoparticles on the radiative properties of HP-Au are analyzed. Specially, we mainly focus on the absorption ability of HP-Au that significantly impacts the photocatalysis efficiency.

2. Establishment of the model

To study the radiative properties of HP-Au, a vivid particle model should be established first to describe its main features [20], as was done by numerous researches. Liu et al. [24] developed a numerical model with hexagonal grids and barbs to represent one kind of realistic pollen particles; Dong et al. [25] built a sphere with surface spines model to represent some species of microorganisms. With such particle models, their results indicate that the spikes have a significant effect on the radiative properties of the particles. As to HP-Au, a suitable model should be established to represent the features of ZnO nanorods deposited with Au nanoparticles.

The primary structural features of hedgehog-like hierarchical particles is shown in Fig. 1. As shown, the ZnO nanorods with nearly the same size tend to grow normally to the surface of the polystyrene microsphere to finally produce HPs, thus the overall morphology of the hedgehog-like hierarchical particles is nearly spherical. The ZnO nanorods in the surface structure can be thick or lanky depending on the reaction conditions [8,14] as shown in Fig. 1(a-c). The spikes can be irregularly distributed as shown in the SEM images. However, for simplicity, we suppose that all the spikes have the same size, which are uniformly and vertically distributed on the sphere surface. The cylinders are located at uniformly distributed points on the sphere surface. As shown in Fig. 2(a), the number N of the cylinders with length l and radius r were distributed on the top of a spherical core with radius R. The cylinders and the spherical core were used to represent the ZnO nanorods and the polystyrene microsphere, respectively.

By varying the N, l/R, and r/R, spike-like surface structures with various morphologies can be realized. It should be noted that the volume ratio of ZnO nanorods to the core sphere is fixed to about 3.7 in this work. The volume of ZnO nanorods can only be calculated by the number of the dipoles instead of the geometrical parameters listed in Table 1, considering that the nanorods would intersect with each other near the surface of the core sphere as shown in Fig. 1. However, the volume ratio varies within 1% among different geometrical parameters due to the volume errors in the discretization of ZnO nanorods. Different surface spike-like structures are represented by varying only the number N of ZnO nanorods in the following sections. Fig. 2(b) shows the model of HPs with different number N of ZnO nanorods. The number N of ZnO nanorods is 165, 200, 300, with l/R varied from 0.90 to 1.50 and r/R varied from 0.18 to 0.10. In addition, the radii R of the polystyrene microsphere of 0.30, 0.40 and 0.50 μm are considered while keeping N, l/R, and r/R invariable. The geometrical

Table 1
Geometrical parameters of hedgehog-like hierarchical particles considered in this work.

Varying number N of the cylinders				Varying radius R of core			
R (μm)	N	l (μm)	r (μm)	R (μm)	N	l (μm)	r (μm)
	165	0.45	0.09	0.50		0.75	0.05
0.50	200	0.60	0.07	0.40	300	0.60	0.04
	300	0.75	0.05	0.30		0.45	0.03