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Nanoparticle loading effects on the broadband absorption for plasmonic-metal@semiconductor-microsphere photocatalyst

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ABSTRACT

Encapsulating a single plasmonic-nanoparticle inside a large semiconductor-microsphere could substantially enhance its broadband absorption [Sun et al., ACS Catal. 4 (2014) 4269–4276]. However, the multi-nanoparticle loading effect is unclear and hinders the practical catalyst design. Herein, we study the nanoparticle loading effect of plasmonic-metal@semiconductor-microsphere photocatalyst on its broadband absorption in the visible light spectrum. Finite-element-study suggests that the broadband absorption holds a universal logarithmic relation with the number of nanoparticles at moderate loading range. Higher loading brings the nanoparticles in proximity, inducing plasmonic-coupling effect which causes red-shift on the absorption spectrum and rendering the logarithmic increment no longer valid. Based on the universal scaling of plasmonic-coupling, an analytical expression to estimate the loading rate at coupling-onset (below which no plasmonic-coupling presents) is derived for arbitrary plasmonic-metal@semiconductor-microsphere (for instance, the loading rate is 10.92 wt% for 30 nm-Au@0.6 μm-TiO_2 microsphere with 399 broadband absorption enhancement at coupling-onset). Further considering the diminishing increment nature of the logarithmic relation, the actual loading is recommended to be lower than that at coupling-onset to achieve better cost-efficiency (with loading 30% lower than that at coupling-onset, the broadband absorption reduces only 10%). These findings could provide the experimentalists useful guidelines in the development of the plasmonic-metal@semiconductor-microsphere photocatalyst.

1. Introduction

Nobel metal nanoparticles (NPs) such as Au and Ag particles, owing to surface plasmon resonance (SPR) [1–4], have been demonstrated with the capability to extend light harvesting to the visible light region that is difficult be accessed with conventional metal-oxide semiconductor photocatalysts (e.g. TiO_2, Cu_2O etc.) [5–8]. Compared to other photosensitizers such as organic dyes or quantum dots [9–11], the plasmonic metal NPs do not require a favorable band alignment to enable free carrier transport [12–14]. In the meantime, the plasmonic metal NPs possess incomparable advantages in term of the chemical/thermal stability [15,16], flexibility [17–19] and selectivity [15,20]. These features make the plasmonic metal NPs promising for a wide range of photocatalytic applications including methyl degradation [21], *p*-nitrophenol reduction [22], hydrogen production [23], hydrolysis of ammonia borane [24], and so forth.

Generally, the SPR could enhance the catalytic efficiency on the basis of two mechanisms. (1) The SPR induced local electromagnetic field enhancement (LEMF) can increase the interband transition rate of the semiconductor to generate free electron–hole pairs [3,16,17,25,26]. For LEMF, only photons with energy beyond the semiconductor bandgap can be utilized [19,21]. With a typical metal-oxide semiconductor such as TiO_2, this absorption is limited in the ultraviolet (UV) region (around 5% of the total solar radiation power) [4,6]. (2) Direct electron transfer mechanism (DET), under the excitation of the incident light, the conductive electrons at the metal surface will gain energy above its Fermi energy level, which is high enough to cross the Schottky barrier at the metal-semiconductor interface [19,21,27]. As a result, these electrons can move into the conduction band of the semiconductor to facilitate the chemical reaction [28]. It is later shown that the photo-excited electrons can be directly injected into the semiconductor's conduction band via quantum tunneling process even with energy lower than the Schottky barrier [25,29,30]. Unlike LEMF, DET allows free

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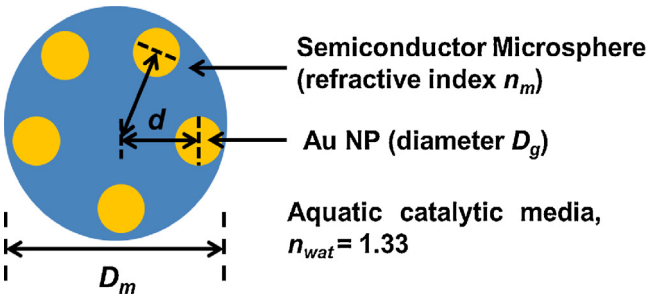

Fig. 1. Cross-section schematic of the plasmonic-metal@semiconductor microsphere. Multiple NPs are embedded inside the microsphere with equal eccentricity *d*.

carrier generation with sub-bandgap photon absorption, hence it is the dominant mechanism in the visible light region (42–43% of the total solar radiation power with the highest irradiance intensity [31]). Experiments have clearly demonstrated that the enhanced photocatalytic rate possesses the same spectral dependence as the broadband absorption in the visible light region [14,21,29,32]. Therein, improving the broadband absorption is consistently pursued in designing the plasmonic photocatalysts.

Among various plasmonic photocatalysts [3,21,33,34], metal NPs embedded inside semiconductor microspheres (metal@semiconductor microsphere) have outperformed other configurations because of their superior catalytic efficiencies, good reusabilities, and easy storages [35–38]. Our recent study further revealed that encapsulating a plasmonic NP inside a large semiconductor microsphere can lead to a substantial interference-induced broadband absorption enhancement (from 3.22 to over 100 times depending on the locations) over the entire visible spectrum as compared to a pure NP dispersed in the catalytic medium [39]. In our previous study, the focus was on a single NP to prove the concept. In reality, multiple NPs are used, and how many NPs need to be loaded become a practical and critical issue. However, the multi-NP loading effect on the broadband absorption remains elusive and hinders the design of metal@semiconductor microsphere photocatalyst.

In this contribution, we carry out a fundamental study to understand the multi-NP loading effect by performing a numerical "experiment" using finite-element-method (FEM). First, we investigate the change in the broadband absorption over the visible light region with respect to the number of the NPs loaded, and reveal a universal logarithmic increment of the broadband absorption at moderate loading range. Following that, we explore the validity of such logarithmic relation by considering the higher loading scenario where the adjacent NPs are brought in proximity and significant plasmonic-coupling effect presents [40,41]. Consequently, the logarithmic increment breaks as the plasmonic resonance or peak absorption shifts to longer wavelength. An analytical expression to estimate the loading rate at coupling-onset (below which no plasmonic-coupling presents and the logarithmic increment remain valid) is then developed for arbitrary NP size and eccentricity. In the end, we make recommendation to the experimentalist to achieve a cost-effective design of metal@semiconductor microsphere photocatalyst based on the nature of the logarithmic relation.

2. Simulation method

Finite-element-method (FEM), which is widely adopted to analyze the light-matter interaction in many research fields such as sensing [42], solar cell [43] and photocatalysis [39] among others, is employed to compute the absorption spectrum of metal@semiconductor microsphere using the commercial software COMSOL Multiphysics. The 3D Maxwell equation is solved to obtain the broadband absorption spectra in the visible light region. The center of the metal@semiconductor microsphere is located at origin, and is surrounded by the homogenous catalytic medium. The thickness of the catalytic medium is set to be one wavelength λ. Outside the catalytic medium is the perfect matching layer (PML) to prevent any unphysical reflection at the boundary. The thickness of PML is set to be λ/2. The maximum mesh size of metal NP is set to be smaller than the skin depth in the visible light region.

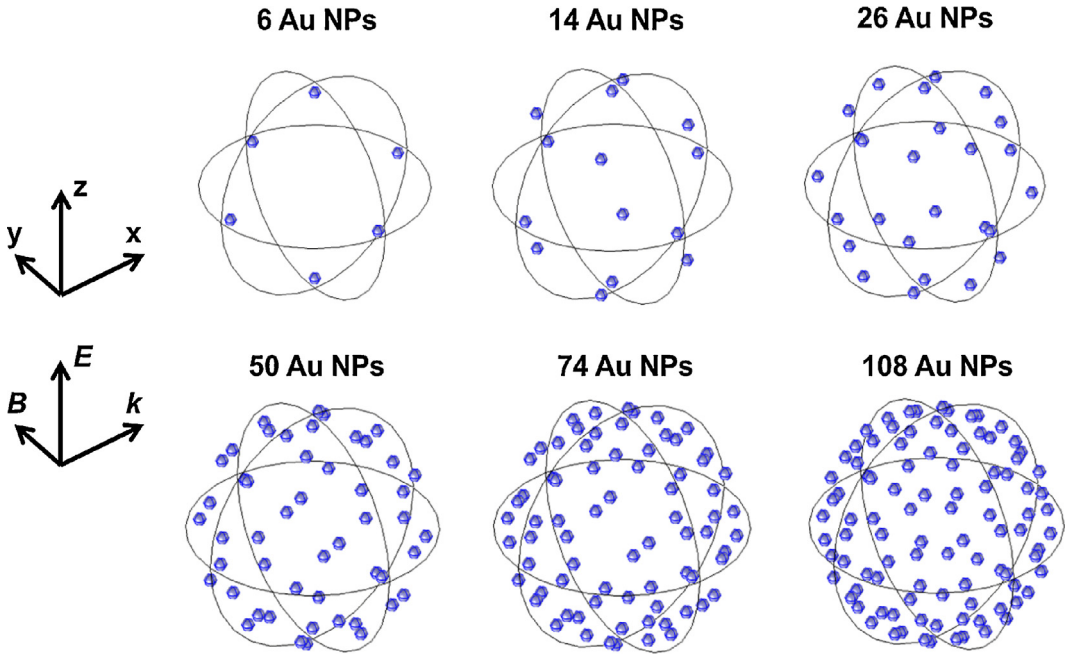

Fig. 2. The schematics of the Au NP distributions at different Au NP loadings. The Au NPs are pattern uniformly inside the microsphere with equal eccentricity. The *x*–*y*–*z* represents the geometrical orientation while the *E*–*k*–*B* represents the plane wave excitation.

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