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# Predictive model for optimizing the near-field electromagnetic energy transfer in plasmonic nanostructure-involved photocatalysts

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ABSTRACT

Förster resonant energy transfer (FRET) is critical hindrance for improving the solar-energy-conversion efficiency via the near-field electromagnetic energy transfer (NEET) mechanism in the plasmonic nanostructure-involved photocatalysts. Herein, a plasmonic nanoparticle/graphene/semiconductor ternary model system is fabricated successfully. In this fabrication, the thin graphene (RGO) layer covers completely the semiconductor with different facets exposed, and the plasmonic nanoparticles are separated from the semiconductor in a proper distance. This unique architecture raises a new opportunity to optimize surface plasmon resonance (SPR) effect in plasmonic nanostructure-involved photocatalysts by the dual modulation of interfacial layer's thickness and fluorescent frequency, resulting a tremendous improvement in the rates of photocatalytic reactions. Furthermore, this predictive model provides a new idea for the design of high-efficient photocatalysts and may upper limits of SPR-mediated enhancement of photocatalytic performance for plasmonic nanostructure-involved photocatalysts.

## 1. Introduction

Recent years have seen that SPR offers a promising scheme for improving solar-energy-conversion efficiency in the field of photocatalysis. That is due to the unprecedented abilities of plasmonic nanostructures to trap light, convert the energy of photons into hot-electron, concentrate electromagnetic fields and scatter electromagnetic radiation [1–4]. Numerous studies have demonstrated that plasmonic-metal/semiconductor composites possess significantly higher rate in various photocatalytic reactions compared with nearby single semiconductors [5–20]. Though the NEET mechanism have been proposed, the deep study to take full advantage of NEET to enhance photocatalytic performance is scarce [4,21–26]. Indeed, rationally strengthening the NEET is an effective but rough approach to further improve photoactivity of the plasmonic metal/semiconductor composite.

As known, photo-excited plasmonic nanostructure is characterized by the existence of strong electric field nearby the metallic nanostructure whose intensity is greatly higher than the field of photons used to photo-excite the nanostructure. This SPR-induced electromagnetic field is spatially non-homogenous, with the highest intensity at the surface of the nanostructure and decreasing exponentially with distance from the surface within ~20–30 nm. Namely, the near-field electromagnetic mechanism is based on the interaction of the semiconductor with the strong SPR-induced electric field [2]. That energy transfer from a plasmon to the nearby semiconductor through the SPR-induced electric field is plasmon resonance energy transfer (PRET) [1,2]. PRET acts as an antenna to confine the optical energy to the near-surface region of a semiconductor near the plasmonic metal. It means that PRET could effectively change the locations of full-charge carriers in the semiconductor and increase the concentration of photogenerated carriers, which can facilitate the photocatalytic process [1,2,27]. Paradoxically, while a metal surface close the semiconductor to promote PRET, more energy will be quenched via FRET [2,28]. FRET is depicted as energy transfer from the semiconductor (a fluorescent donor, donated as D) to plasmonic nanostructure (an absorbing acceptor, donated as A), occurring over similar length scales to those of PRET [29]. Usually, PRET may be considered as a forward reaction for exciting more electron–hole pairs in the semiconductor. FRET, in contrast, can be considered as a back reaction, through which the excited state in the semiconductor quenches without involving charge transfer [30,31]. Generally, FRET and PRET coexist in metal/semiconductor composite, which has been becoming

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a tremendous obstacle to exploring the full range of advantages of NEET. Thus, the minimization of the FRET effect and optimization of PRET effect are of great urgency and challenge.

Reportedly, the Förster energy transfer rate ($k_{\mathrm{et}}$) is inverse proportion to the fourth power of the spacing ($d^4$) for dipole-donor infinite surface-acceptor, and increases exponentially with the Förster radius ($R_0$) [32]. $R_0$ can be calculated from the following expression:

$$R_0^6 \sim \frac{9000 \ln 10 \kappa^2 \eta_{\mathrm{s}}^0}{128 \pi^6 n^4 N \nu^4} \int_0^{\infty} f_{\mathrm{s}}(\nu) \alpha(\nu) \mathrm{d}\nu \quad (1)$$

where $\kappa$ is an orientation factor ($\kappa^2 = 2/3$ for random orientation); $\eta_{\mathrm{s}}^0$ is the photoluminescence quantum efficiency of D; $n$ is the refractive index of the embedding medium; $N$ is Avogadro's constant; $\nu$ is the wavenumber; $f_{\mathrm{s}}$ is the emission spectrum of D and $\alpha$ is the absorption spectrum of A. Clearly, the less overlap between $f_{\mathrm{s}}$ and $\alpha$ is, the slower $k_{\mathrm{et}}$ is. There is also a strong correlation between wavelength and $k_{\mathrm{et}}$. The longer the wavelength is, the higher $k_{\mathrm{et}}$ is [1]. Therefore, regulating the fluorescent frequency of D for decreasing the overlap between $f_{\mathrm{s}}$ and $\alpha$, would be a potential strategy to minimize FRET without reduction of PRET.

In our previous work, we found that the unique model system of thin RGO layer completely coating semiconductor with different facets exposed (RGO/semiconductor) could subdivide the intrinsic fluorescence of semiconductor into two fluorescent emissions with different frequency, via the facet-driven dual-selectivity-channel carrier separation mechanism [33]. It means that this unique structure make it possible to modulate fluorescent frequency of D. Inspired by this fact, we come up with an ideal model for enhancing PRET while limiting the FRET, which is integration of this unique structure with plasmonic nanostructure. Concrete model is listed as follows: Firstly, there must be some overlap between the bandgap absorption of semiconductor and SPR absorption of plasmonic nanostructure to ensure the NEET occurring. Secondly, the interfacial RGO layer should possess an optimal thickness (generally a few nanometers) for compromising the PRET and FRET process [2,4,22]. Thirdly, the selected plasmonic nanostructure could not induce hot-electron so the hot-electron injection effect could be eliminated. Lastly, but most essentially, at least one fluorescent emission does not overlap with the SPR absorption of plasmonic nanostructure, to minimize the overlap between $f_{\mathrm{s}}$ and $\alpha$. This designed model structure would optimize NEET by lowering the FRET effect.

For the implementation of this concept, we engineer the unique architecture as follows: $BiVO_4$ with different facets exposed and Au nanospheres (NSs) are respectively chosen as photocatalyst and plasmonic nanostructure due to the overlap between the band gap absorption of $BiVO_4$ and SPR absorption of Au NSs and the little overlap between one kind of fluorescent emission (~440 nm) for RGO/$BiVO_4$ and the SPR absorption of Au NSs. In addition, for significant hot electron generation or injection is only found in smaller plasmonic metal nanoparticles (<30 nm) [2,3,34]. Only Au NSs with 50–100 nm in a diameter are utilized in this construction, excluding the enhancements of photoactivity on account of the hot-electron injection. Typically, we synthesize the RGO/$BiVO_4$ by our previous method [33]. Then Au NSs (50–100 nm) are deposited on RGO surfaces (to construct Au/RGO/$BiVO_4$) by the photo-deposition method.

## 2. Experimental

### 2.1. Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$, >99.0%) ammonium vanadate ($NH_4VO_3$, >99.9%), ammonia water ($NH_3{\cdot}H_2O$, 26–28 wt%), nitric acid ($HNO_3$, 26–28 wt%), chloroauric acid tetrahydrate ($AuCl_3{\cdot}HCl{\cdot}H_2O$, AR), ethanal absolute ($CH_3CH_2OH$) and methanal absolute ($CH_3OH$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). GO was purchased from Nanjing XFNANO, Inc. All materials were analytical grade and used without any purification process. Deionized (DI) water used in the synthesis came from local sources.

### 2.2. Synthesis of $BiVO_4$

$BiVO_4$ with {1 1 0} and {0 1 0} facets exposed was synthesized by a hydrothermal procedure. Typically, 36 mmol $Bi(NO_3)_3{\cdot}5H_2O$ and equal amount of $NH_4VO_3$ were dissolved into 300 mL $HNO_3$ solution (2 M) and the pH value of the solution was then adjusted to 2.0 with ammonia solution under stirring until formation of an orange precipitate. After about 2 h aging, the orange precipitate at the bottom of the beaker was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 24 h and then allowed it cool down. A vivid yellow powder was separated by filtration, washed with DI water for several times. Then the products were dried at 60 °C overnight in vacuum oven.

### 2.3. Synthesis of GO/$BiVO_4$

GO/$BiVO_4$ was synthesized through a evaporation-induced self-assembly process. Briefly, 1 g $BiVO_4$ powders and 20 mg GO were put into 100 mL ethanol and 50 mL DI water respectively, and ultrasound treated for 1 h to disperse the samples evenly. Then the obtained 50 mL GO solution was dropped into the $BiVO_4$ solution under vigorous stirring and the obtained mixtures were kept stirring for 12 h without sealing in a fuming hood. Then, the residual solution was dried in a 60 °C water bath with stirring. Lastly, the obtained sample was further kept overnight to let the GO combine tightly with $BiVO_4$ polyhedrons.

### 2.4. Synthesis of RGO/$BiVO_4$

The RGO/$BiVO_4$ composites have been fabricated by a mild photoreduction process. In detail, 100 mg GO/$BiVO_4$ was dispersed into a breaker containing 80 mL DI water and 20 mL methanol. Then, the solution was irradiated with full-wave band light for 2 h with stirring. Collected the precipitate and washed it with DI water. The final product was dried in a vacuum oven.

### 2.5. Synthesis of Au/$BiVO_4$

The Au/$BiVO_4$ composites have been fabricated by a mild photodeposition process. In detail, 100 mg $BiVO_4$ and a calculated amount of $AuCl_3{\cdot}HCl{\cdot}H_2O$ (3 wt%) was dispersed into a breaker containing 90 mL DI water and 10 mL methanol, respectively. And the suspension was ultasounded for 5 min. Then, the solution was irradiated with full-wave band light for 1.5 h under stirring. Collected the precipitate and washed it with DI water. The final product was dried in a vacuum oven.

### 2.6. Synthesis of Au/RGO/$BiVO_4$

The Au/RGO/$BiVO_4$ composites have been fabricated by a mild photodeposition process. Normally, 100 mg RGO/$BiVO_4$ was dispersed into a breaker containing 90 mL DI water and 10 mL methanol. Subsequently, a calculated amount of $AuCl_3{\cdot}HCl{\cdot}H_2O$ (3 wt%) was dropwise added into the above suspension under vigorous stirring. Then, the solution was ultrasounded for 5 min and irradiated with full-wave band light under stirring for 1.5 h. Collected the precipitate and washed it with DI water. The final product was dried in a vacuum oven.