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Plasmon resonance-enhanced photoelectrodes and photocatalysts

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ABSTRACT

Growing interest in composite plasmonic-metal/semiconductor photocatalysts is motivated by the ability of plasmonic nanostructures to capture light, most particularly at their resonance frequencies at which they exhibit high absorption and scattering cross-sections. In the cases when plasmon resonance frequency overlaps absorption spectrum of the semiconductor, large electric field enhancement near the surface of the metal nanostructure leads to increased charge carrier generation in the nearby semiconductor (plasmonic near-field effect). Another, largely evoked, kind of interaction is the spectral sensitization of a semiconductor to longer wavelengths absorbed only by the plasmonic nanostructure. In such a process, hot electrons generated in the metal nanostructure via the decay of optically excited plasmons are transferred over the Schottky barrier to the nearby semiconductor resulting in extra band-gap photoactivity. Several examples pertaining to each of these interactions will be discussed. While interest in composite plasmonic-metal/semiconductor photocatalysts is relatively recent, there has been substantial earlier work on plasmon-mediated photoelectrochemistry on a typical plasmonic metal-silver. It is shown that roughening of the silver electrode surface leads, for example, to largely enhanced cathodic CO₂ reduction photocurrents observed under illumination with UV-visible wavelengths that coincide with plasmon resonance frequencies in silver.

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1. Introduction

The plasmon-enhanced photoelectrochemical and photocatalytic systems use a combination of metal nanostructures and semiconductors. In the former case, such hybrid photoelectrodes consist most frequently of semiconductor thin films decorated with

plasmonic metal nanoparticles in contact with an electrolyte and exposed to light that drives the interfacial charge transfer process. If the photoelectrode includes an n-type semiconductor it can operate as a photoanode where an oxidation process takes place. Such reactions are performed in an electrochemical cell where the photoanode is combined either with a p-type semiconductor photocathode or with a metallic cathode. This kind of configuration, illustrated schematically in Fig. 1, was used in the photoelectrolysis cell, which first demonstrated the feasibility of photoelectrochemical water splitting where an oxygen-evolving titanium dioxide, TiO₂, photoanode was associated with a hydrogen-evolving platinum cathode [1].

Further studies focusing on the search of photoelectrodes able to operate under visible light illumination involved examination of a large number of n-type and p-type inorganic compound semiconductors [2–7]. However, the choice of a suitable system is severely restricted by the fact that the only semiconductors that do not undergo photocorrosion in aqueous media are metal oxides [5–7].

Abbreviations: E_g, band-gap energy; CB, conduction band; VB, valence band; NS, nanostructure; SHE, standard hydrogen electrode; SERS, surface-enhanced Raman scattering; SEM, scanning electron microscopy; QY, quantum yield; e_{aq}⁻, hydrated electron; e_M⁻, electron in the metal; SPR, surface plasmon resonance; NP, nanoparticle; CS, cross section (absorption, scattering); PV, photovoltaic; DSSC, dye-sensitized solar cell; IPCE, incident photon-to-current conversion efficiency; ITO, indium-doped tin oxide; OEC, oxygen evolution catalyst; AM 1.5, air mass 1.5 sunlight; DOS, density of states; FTO, fluorine-doped tin oxide; TEM, transmission electron microscopy; POM, polyoxometalate; RHE, reversible hydrogen electrode; MSE, mercurous sulphate electrode.

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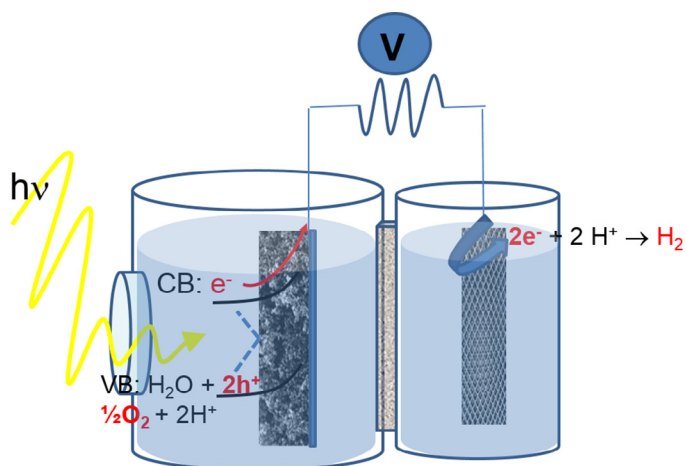


Fig. 1. Schematic representation of a typical water photoelectrolysis cell.

In reality, there are only few stable metal oxide n-type semiconductors able to absorb significant portion of solar light, including tungsten trioxide, WO_3 , band-gap energy, $E_g = 2.5$ eV [8,9], bismuth vanadate, BiVO_4 , $E_g = 2.4$ eV [10,11] and ferric oxide-hematite $\alpha\text{-Fe}_2\text{O}_3$, $E_g = 2.2$ eV [12].

In what is usually considered as a photocatalytic system (where the semiconductor is not connected to the external electric circuit), shown schematically in Fig. 2a, illuminated semiconductor particles are suspended in water containing, for example, low amounts of organic compounds. In such applications of particulate photocatalysts, pertaining to the treatment of emerging pollutants in aerated water, oxygen acts as scavenger of electrons photogenerated in the semiconductor [13–16]. Alternatively, films of supported semiconductor particles can be exposed to ambient air where they can induce, most generally, the photooxidation of therein present impurities. The simplest view of a particulate photocatalytic system, illustrated in Fig. 2b, is that of a short-circuited photoelectrochemical cell in which the photooxidation reactions involving, e.g., organic compounds occur at the same semiconductor particle together with oxygen reduction process.

The main motivation for using plasmonic metal nanostructures in photoelectrochemical and photocatalytic systems is to enhance light absorption and the photogeneration of charge carriers in the semiconductor. The most important optical and electronic effects that can arise when a semiconductor is decorated with plasmonic metal nanostructures (NS) will be addressed in the subsequent sections and illustrated with selected examples of recent work. However, correct understanding of the interactions that can occur at the interface between semiconductors and plasmonic metal NS requires

first recalling of the earlier experiments that demonstrated how decay of optically induced plasmons leads to photoemission phenomena from metal surfaces.

2. Effect of surface plasmon excitation on photoemission processes from metals

The first demonstration that allowed a connection to be established between optically excited surface plasma oscillations and vacuum photoemission from a nearly free-electron metal is by Endriz and Spicer [17,18]. Their photoemission studies conducted on aluminium films of varied surface roughness showed, in fact, a direct correlation of the measured maxima of the photo-yield with the surface plasma frequency – consistent with the optical reflectance of the surfaces. The key result of those studies was a dramatic increase of the photoemission yield for the rough aluminium films, much larger than the corresponding changes in the optical reflectance. The reported photoemission effects had been explained in terms of the decay of optically excited surface plasmons into excitation of single electrons [18]. While observations regarding aluminium metal are restricted to deep ultraviolet, *ca* 10 eV, frequencies, another “free-electron” metal – silver has much lower surface plasmon energy of 3.5 eV easily accessible to standard optical measurements. However, since the latter value is considerably smaller than the work function of the metal (4.3 eV), vacuum photoemission could only be observed when silver surface was coated, for example, with a layer of caesium or of polar organic molecules allowing to decrease the effective work function [19–21]. Importantly, another way to reduce the effective work function was demonstrated by Sass et al. [22] by placing silver in an electrochemical cell where, in addition to the modified dielectric constant of the medium (aqueous solution), the work function of the metal electrode can be monitored by changing the imposed potential. Both these effects contribute to fulfil the condition under which surface plasma oscillations will occur

$$\varepsilon_{\text{metal}}(w_s) + \varepsilon_{\text{medium}}(w_s) = 0$$

where $\varepsilon_{\text{metal}}$ and $\varepsilon_{\text{medium}}$ are the complex dielectric constants of silver and of the electrolyte and w_s is the surface plasma frequency. The experiments performed with illuminated silver electrodes immersed in 0.5 M sulphuric acid solution, where hydrogen ions served as scavengers of photoemitted electrons, revealed a sharp peak of the photocurrent that occurred at incident photon energies around 3.5 eV close to surface plasmon energy of silver. The photocurrents measured under intermittent illumination and phase-sensitive current detection, reported with respect to the number of absorbed photons, peaked out at an apparent quantum yield of 6×10^{-4} at 3.5 eV and were reached at a imposed potential of -0.2 V versus standard hydrogen electrode (SHE). However, a smaller

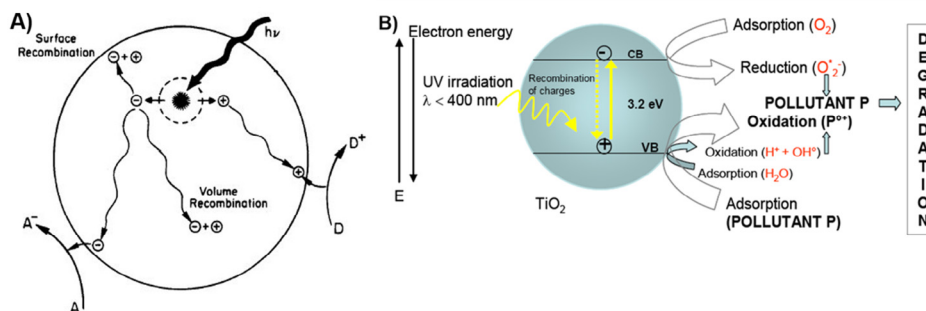


Fig. 2. (a) Processes occurring within irradiated photocatalyst particle suspended in a reaction medium; (b) Typical conduction band and valence band reactions involved in the degradation of an organic pollutant. Reprinted with permission from Ref. 13. Copyright 2005 Springer.

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