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A review on plasmonic metal–TiO_2 composite for generation, trapping, storing and dynamic vectorial transfer of photogenerated electrons across the Schottky junction in a photocatalytic system

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ABSTRACT

The titania based nanomaterials are an attractive candidates for energy and environmental applications. TiO_2 is one of the most important photocatalyst for its special multiple characteristics like high reactivity, low toxicity, low cost, high flexibility, long term stability especially in aqueous medium, shows relatively high energy conversion efficiency, easy to prepare several modifications with various morphologies, with good recycle ability, favorable band edge positions and superior physicochemical and optoelectronic properties. However, large band gap of titania and massive charge carrier recombination impairs its wide photocatalytic applications. As an alternative to various strategies reported extensively in literature, noble metal deposition on the titania surface seems to be effective and reliable method for increasing the life time of excitonic pairs and to extend the band gap absorption to visible range of the solar spectrum. In this focused review, we discuss the fundamental and critical issues in the photocatalytic activity of metal deposited titania taking into consideration the influence of various parameters like preparation methods, metal dispersion on titania, formation of heterojunctions and optimum metal loadings on the interfacial charge carrier dynamics. The metal deposition onto the varied hierarchical morphology, crystal structure, defective surface of titania along with extended modification like simultaneous doping and heterostructure coupling with other semiconductors is also highlighted. It was revealed that deposited metal is involved in multiple crucial roles like; (i) it serves as passive electron sink with high capacity to store electrons to suppress photogenerated charge carrier recombination; (ii) it facilitates rapid dioxygen reduction to generate reactive free radicals; (iii) visible light response for titania can be achieved through surface plasmon resonance effect; (iv) direct excitation of metal nanoparticles especially under visible light and vectorial electron transfer to the TiO_2 CB. This review attempts to provide a comprehensive update of design and fabrication of metallization on the surface of TiO_2 semiconductor particles highlighting some of the advancements made in the energy and environment applications.

Contents

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1. Introduction

Nano metal deposits on semiconductor surface provide a simple and convenient way to tailor the physicochemical-optical properties of the photocatalysts. A great deal of research on photocatalyst engineering has been carried out to customize the electronic band structure of various semiconducting materials for a specific chemical reaction with unique opto-electronic property [1,2]. TiO_2 is one of the most widely used semiconductor photocatalyst for the oxidative destruction and mineralization of vast number of organic substrates [3–8]. The main aim is to explore novel photocatalyst materials with suitable band structure which allows efficient photogeneration of electron–hole pairs to participate in oxidative/reductive processes preferably in the visible region [9–11]. The high charge-carrier recombination rate is the consequence of deeper penetration depth of photons (beyond the space charge region) and the short mean free paths of charge carriers, which stipulates the charge carriers to recombine before they could reach the semiconductor surface to participate in photochemical reactions [12]. Attempts to address this problem were mainly centered on fabricating the photocatalyst structure in order to maximize the photon absorption and minimize the charge carrier recombination. Apart from introducing various bulk imperfections via doping to provide shallow trap states for electrons, another effective method for increasing the life time of electron–hole pairs and to extend the band gap absorption of titania to the visible region is to deposit the noble metal on the titania surface [11–15]. Noble metals in bulk are photoactive only to a small extent but when deposited on the surface of semiconductors like TiO_2, possess electron storage properties leading to improved charge separation or charge rectification. The noble metal nanoparticles when deposited on the surface of the semiconductor have distinct optical and catalytic properties which are not usually observed in the case of bulk metal. Gerisher has highlighted the importance of dioxygen reduction by conduction band (CB) electrons which prevent the recombination of photogenerated charge carriers and he further inferred that the superoxide radical formation may be the slowest step in the reaction sequence occurring in the millisecond time regime leading to the oxidation of substrates [16]. A nano noble metal deposit on TiO_2 surface can enhance the photocatalytic efficiencies due to the faster rate of interfacial electron transfer from semiconductor to metal deposits and vice versa compared to the surface trapping states induced by the bulk modification [16]. The metal nano particles deposited on the TiO_2 surface change the original charge carrier concentration equilibrium by withdrawing the electrons out of TiO_2 bulk structure which in turn accelerate the dioxygen reduction. In any photocatalytic process involving metal/TiO_2 composite, deposited noble metal has the mediating role in trapping and transfer of photogenerated electrons from the TiO_2 to an acceptor. These activities greatly reduce the possibility of electron–hole recombination resulting in efficient separation and enhancing the rate of photocatalytic reactions [17]. In general, metallization decreases the probability of charge carrier recombination and increases the fraction of photogenerated holes undergoing the interfacial charge transfer reaction resulting in faster degradation of organic intermediates. Metal deposition on TiO_2 surface does not significantly alter the structure and microstructure of TiO_2, although marginal changes in surface area and pore diameter can be observed in most of the cases which are not large enough to influence the photoactivity in a drastic way [18]. Hence, it can be tentatively proposed that the deposited metals exert a more significant effect in the separation of photogenerated charge carriers and also on the catalysis process. The absorption properties of metallized TiO_2 depend on the optical properties of the deposited metal, the matrix and the volume fraction of the metal in the composite mixture. Metal deposited TiO_2 shows an absorption band in the visible region due to surface plasmon resonance (SPR) effect [19]. SPR is a characteristic feature of any metal nanoparticle deposited on semiconductor and this effect arises as a result of collective modes of oscillation of the free CB electrons induced by its interaction with electromagnetic field [20]. At the semiconductor/metal interface a significant redistribution of charge occurs due to the overlap of the wave functions from the two sides, depending on the work function of metal and semiconductor. The formation of a depletion zone causes the bending of valence band (VB) and CB of semiconductor for example in an n-type semiconductor the bands are shifted downwards and p-type semiconductors the bands are bent upwards in relation to the Fermi level [20]. The transfer of the photoexcited electrons from the CB edge of the semiconductor to the metal deposit is facilitated when the band edge positions of both match with each other, but the opposite scenario is prevented to certain extent by the formation of Schottky barrier [21]. The interaction of the CB electrons with the electromagnetic field of specific wavelengths in the nano metal deposits causes coherent electron cloud oscillations leading to the increase in the energy density at the surface. Thus, noble metal nanoparticles immobilized on the semiconductor surface can enhance the local field energy under visible light excitation through the SPR effect and then these electrons participate in the photocatalytic redox reactions or in the energy conversion process [22]. The plasmon absorption band of metal deposited TiO_2 will be generally observed at higher wavelengths compared to the unmodified TiO_2. Interfacial and interparticle interactions dictate the shift and broadening of plasmon band of metal nanoparticles deposited on the TiO_2 surface [23]. The choice of noble metal for the surface deposition to enhance the photocatalytic activity of TiO_2 depends on its work functions, size and shape which in turn influences the optical properties of TiO_2 [24,25]. Highly dispersed metal nanoparticle on the semiconductor surface will have low degree of aggregation due to the stabilization provided by the surface charges and further it prevents the scattering effects and allows the efficient absorption of photons by the metal/TiO_2 composite system. The chemical transformations of the substrate molecules at the metal/TiO_2 interface may be detrimental to the long-term stability of the metal/TiO_2 heterojunction, since the transformations may alter the valency of the metal species during the photocatalytic reactions [26]. Since the experimental conditions like reaction medium, redox species at the interface and the intensity of excitation directly influence such chemical transformations, it is necessary to consider these issues while designing a composite photocatalyst for long term irradiation experiments. Photometallization process carried out for longer duration (under UV irradiation) results in a decrease in the efficiency of photoelectrochemical and photocatalytic activity. The possibilities of oxidation of deposited metal by the photogenerated hole and/or surface hydroxyl radicals was proposed as the reason for the observed deterioration of the catalytic performance of the nanocomposite [27]. In this regard researchers have used several noble metals like Pt, Au, Pd and Ag for deposition on TiO_2 surface. The advantages and limitations of each metal deposited on TiO_2 surface is discussed elaborately in further sections.

2. Photocatalytic activity of platinum deposited titania (Pt/TiO_2)

It is well known that Pt is one of the best noble metal catalyst used in the conventional thermal oxidation processes. Deposition of Pt on TiO_2 surface is thought to enhance charge carrier separation and increase the extent of surface adsorption of various organic compounds. Pt serves as an electron trap forming a charge-transfer complex between Pt and TiO_2 [27–31].

Sakata et al. discussed the photocatalytic properties of Pt loaded TiO_2 particles in terms of photochemical diode [27].