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Photocatalytic applications of conducting polymers (CPs)

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Abstract
Photocatalysts provide a sustainable method of treating organic pollutants in wastewater and converting greenhouse gases. Composite photocatalysts based on conducting polymers and metal oxides have emerged as novel and promising photoactive materials. It has been demonstrated that conducting polymers can substantially improve the photocatalytic efficiency of metal oxides owing to their superior photocatalytic activities, high conductivities, and unique electrochemical and optical properties. Consequently, conducting polymer/metal oxide composites exhibit a high photoresponse and possess a higher surface area allowing for visible light absorption, low recombination of charge carriers, and high photocatalytic performance.

Keywords: Conducting polymer, Metal oxides, Photocatalyst, Polyaniline, HOMO

Introduction

Photocatalysis plays a critical role in the development of emerging technologies for environmental applications, such as wastewater treatment and CO_2 reduction [1, 3]. Currently, advanced photocatalytic materials consist mainly of metal oxides, such as TiO_2, SnO_2, ZnO, and spinel ferrites [4, 5]. Many strategies have been investigated for tailoring and modulating the light adsorption ability, as well as enhancing the charge separation, in metal oxide semiconductors, including (i) band-gap engineering approaches [6]; (ii) developing co-photocatalysts [7]; (iii) doping with metal nanoparticles (i.e., Au, Pt, Cu) [8]; and (iv) design of different composite photocatalysts [9]. Among them, the development of composite photocatalysts has been regarded as one of the most promising approaches due to several advantages. First, the surface properties of metal oxide-based composite structures can be tuned to achieve mid-band-gap electronic states and produce a high absorption in the visible light spectrum [10]. Metal oxide composites can also enhance photocatalyst stability and enable the fabrication of advanced photocatalysts with novel structures, such as microporous, hollow shells, or hierarchical structures.

Among photocatalysts, TiO_2 is preferred because of its novel bandgap, easy synthesis, cheapness, high photo-activity, resistance to photocorrosion and high oxidizing power. Generally, TiO_2 exhibits three different phases: anatase, rutile, and brookite. Among the three phases, anatase has good photochemical behavior due to its high bandgap of 3.2 eV. Titanium dioxide can be easily prepared hydrothermally or by a sol-gel approach. Polyaniline with organic semiconductors is a great research prospect because it has good electron-hole charge separation, a good absorption coefficient of visible spectra, a high mobility of charge carriers, and low-cost and easy synthesis. The process behind dye degradation includes incidence of light on the photocatalyst, photo-induced holes, the accumulation of electrons on the semiconductor surface, initiation of a redox reaction, and degradation of the reaction product. Reddy and his coworkers synthesized a TiO_2/polyaniline hybrid system by an *in situ* polymerization technique. They studied the photocatalytic activity of the composite for the degradation of rhodamine, acetic acid, and methylene blue. Under continuous 3 h UV irradiation, RhB was degraded by 80%, and methylene blue and phenol were degraded by 67% and 51%, respectively, in 200 min of irradiation time. The photocatalyst still gives good activity after 3 cycles of irradiation. It is clear that the catalyst has a reusable property. In the photocatalytic mechanism of TiO_2/PANI studied by ESR spin trapping experiments, under UV irradiation, the main oxidative species are superoxide anion radicals, $O_2^{\cdot-}$, hydroxyl radicals,

($^{\cdot}OH$) and holes (h^+). When polyaniline is exposed to UV irradiation, a π–π* transition happens. This means that photogenerated electrons become excited to the π* orbital of polyaniline. Which has the same energy as the conduction band of titania, resulting in chemical bonding. This helps in the transfer of a photogenerated electron from polyaniline to TiO_2. These absorbed electrons migrate to the surface of the photocatalyst and react with water and oxygen to produce hydroxyl and superoxide anion radicals, which cause oxidation of the contaminants. Similarly, photogenerated holes migrate from the valance band of TiO_2 to the high energy state of polyaniline, because the VB of TiO_2 and the CB of polyaniline have the same energy level. And these photogenerated holes migrate to the surface of the photocatalyst, and oxidation of contaminants occurs [11, 12].

Polyphenylene is widely used as a photocatalyst due to its high chemical and thermal stability. Gu and his team reported catalytic behavior in a Pd/polyphenylene composite synthesized by a palladium catalyzed Suzuki reaction. They observed that polyphenylene has a high light harvesting property along with energy transfer through its conjugated backbone. The reduced size effect of palladium causes a better catalytic reaction. From the UV-vis absorption data it is clear that the catalyst has better light absorption and the composite has higher conversion efficiency in the transition of *p*-NPh to *p*-APh. The Pd/polyphenylene catalyst shows better reusability after a series of reaction cycles. The light energy harvesting of polyphenylene causes the migration of electrons towards the palladium surface, resulting in a high electron density over the palladium surface. It also causes better hydrogen activation and thereby better photocatalytic activity.

The photocatalytic behavior of the g-C_3N_4/TiO_2@PANI composite was investigated. The composite has better photocatalytic activity against Congo red toxic dye due to the better electron–hole pair separation and reduced band gap of the composite. This was observed from UV-Vis analysis, PL and band gap analysis. The composite shows almost 100% photocatalytic activity towards Congo red molecules at some particular concentrations. The composite does not show active photocatalytic behavior beyond a particular concertation of Congo red due to the lack of optical density and a deficiency of active radicals to activate photocatalysis [13].—The photocatalytic activity of polypyrrole with TiO_2 nanoparticles for the degradation of organic dyes has also been studied. The energy level between the VB and the CB is denoted as the bandgap E_g. Materials get excited only when the energy of an incident photon is equal to or higher than the E_g. The electrons absorb energy from the photons, and they are excited to the CB from the VB. But in the case of TiO_2, it has a wide energy gap. Due to this, the excitation in sunlight is limited and excitation shows best under UV irradiation. When making a composite with conjugative polymers, the bandgap is reduced compared to pristine TiO_2. This is why a polymer TiO_2 composite absorbs more photons, and the degradation of dyes is enhanced. The photocatalytic mechanism is almost the same here as in the case of polyaniline. Under sunlight irradiation the electrons in Ppy/TiO_2 are excited from the highest energy state of polypyrrole into the lowest energy level. Then they will migrate into the CB of TiO_2. The holes in the polypyrrole are left as such in the HOMO. The electrons in the VB of TiO_2 move to the HOMO of polypyrrole and holes are left in the VB of TiO_2, so the recombination of electrons–holes occurs. This means a huge amount of electron–hole generation takes place in the surface of the TiO_2. These photogenerated holes and electron react in the presence of oxygen and water to form photoinduced anions like O^{2-} and OH^-. These two photoanions are responsible for dye degradation. Here in this study Wang and co-workers investigated the performance of the polypyrrole/TiO_2 in a (1:100) molar ratio. The first-order rate equation was used to determine the rate of degradation. From the data, it is clear that polypyrrole/TiO_2 (1:100) has a higher κ value [14].

The electronic property of a conducting polymer is easily tunable when a composite is made with metallic semiconductors. Pristine conducting polymers have problems with the high rate of electron–hole pair recombination, so it is mandatory to modulate this property to enhance photocatalytic activity. g-C_3N_4 has a moderate band gap energy, so it is easily excited under sunlight. Polyaniline has an outstanding electron-donating tendency and is an excellent hole acceptor. A hybrid of polyaniline and g-C_3N_4 has a decreased rate of electron–hole recombination and a unique production of photocatalysts so that the above composite is extensively using in the photocatalytic degradation of organic dyes. The above composite has been investigated for the degradation of methylene blue. 92.8% degradation and a high cycle life of the catalyst have been observed. Alenizi *et al.* have synthesized a novel ternary g-C_3N_4/TiO_2@polyaniline composite and investigated the degradation of Congo red dye under sunlight. The deterioration of Congo red was studied previously by using WO_3–TiO_2/activated carbon, alginate/Fe_2O_3/CdS and TiO_2-SWNT-P-21 composites, but the efficiency of degradation was not more than 85%. But here in this study, Congo red dye was decolorized by 100% in 3 h of reaction under sunlight. The composite has a higher rate of reusability after the fourth cycle with an efficiency of 90.1%. The mechanism behind this composite was the same as before. When it was exposed to sunlight, electrons were separated from the composite, migrated from the CB of TiO_2 to the valence band of g-C_3N_4, and recombination with holes occurred. Generated holes migrate towards the surface of the polyaniline and the electrons left in the conduction band of g-C_3N_4 react in the presence of oxygen, H_2O and OH^- to form photoanions. These photo-induced products drive the photocatalytic reaction. The exciting factor behind this composite is its higher efficiency compared to its pristine form or a binary composite of the above materials [3].

Conclusion

The development of highly active composite photocatalysts for use in environmental applications is considered to be a sustainable way of eliminating organic pollutants and heavy metals. Among them, composite photocatalysts based on inorganic semiconductors, especially metal oxides, and CPs emerges as novel promising photoactive materials. It was demonstrated that these composite photocatalysts have several outstanding characteristics, such as light absorption in the visible range of the spectrum, high photocatalytic activity and stability, good reusability, low cost, convenience, and scalability of production. Both binary and ternary conducting polymer/metal oxide composites show promising photocatalytic activity for the degradation, reduction, and adsorption of organic pollutants, CO_2 gas, and heavy metals. However, ternary composites were confirmed as superior to binary ones due to the synergistic effects of three components in promoting photocatalytic activity and improving photocatalyst stability. Therefore, conducting polymer/metal oxide composites are currently one of the most promising candidates for photocatalysts in environmental applications.

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