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Short review

Enhancement of photocatalytic properties of transitional metal oxides using conducting polymers: A mini review

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ABSTRACT

Transition metal oxide based semiconductors hold great promise for photocatalytic applications. But critical factors such as the high rate of charge-carrier recombination and limited light absorption have restricted their commercial application. Lately, improvements have been made in their photocatalytic activity by sensitizing them with organically conducting polymers. The present review highlights the work done in enhancing the photocatalytic activity of some transition metal oxides using conducting polymers. The mechanism behind the interaction of these inorganic semiconductors with different conducting polymers upon illumination with light is discussed in detail which can help in designing these fascinating materials with superior photocatalytic response toward UV and visible light.

1. Introduction

Heterogeneous photocatalysis has undergone rapid expansion during the last four decades, especially with reference to energy and the environmental remediation. The most highly investigated fields in photocatalysis have been solar water splitting, purification of air and water containing variable concentrations of pollutants. Inorganic semiconductors such as ZnO, TiO_2, CdO, CdSe etc. exhibit remarkable electronic and physicochemical properties and have found applications in the areas of photovoltaics, [20,97,34,12,57,18], photoluminescence, [93,45] and photochromism [51,54,29]. Generally, semiconductors act as good photosensitizers in photocatalytic reactions due to their filled valence band (VB) and empty conduction band (CB) in the ground state. Photocatalysis occurs when these semiconductors are excited by energy greater then their band gap leading to the formation of excitons, i.e. electrons at the CB and holes at the VB, respectively. However, the photocatalytic efficiency is always dominated by 2 factors (i) the low quantum yield due to faster recombination of electron–hole (e^-–h^+) pairs; (ii) the wide band gaps of semiconductors which limit absorption only within the UV region [24,90], Fig. 1. Various efforts have therefore been made to improve upon the efficiency of photocatalysis of these materials. One of the effective techniques has been coupling these semiconductors with noble metals to improve their catalytic activity under UV and visible radiation [3,11]. The photocatalytic activity of these metal oxides is usually associated with non-selective free radical reaction processes. Hence, they are widely used for the photodegradation of organic pollutants in water, i.e. mediating the total destruction of these pollutants to CO_2 and H_2O with O_2 under UV irradiation.

Although, TiO_2 is the most widely studied semiconductor photocatalyst, ZnO has also attracted much attention due to its high catalytic efficiency, low cost and ease of synthesis. ZnO is a direct band gap semiconductor with a wide band gap of 3.3 eV and is reported to be one of the most widely used photocatalysts for the degradation of dyes [43,89,84]. Researches have shown that ZnO has low photo energy conversion efficiency due to relatively low charge separation efficiency and faster recombination of charge carriers [52,33,88]. In some studies, ZnO has been reported to be more effective than TiO_2 when used for photo-oxidation of phenol and photocatalysed oxidation of 2-phenyl phenol [16,46,36,37]. Nanostructured ZnO has been extensively investigated and exhibits numerous novel characteristics, such as high surface area to volume ratio, high electron conductivity, as well as transmission capability [28,102,112,47,22,94]. The biggest advantage of ZnO as compared with TiO_2 is its ability to absorb a comparatively larger

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Abbreviations: APS, ammonium persulfate; CB, conduction band; CP, conducting polymer; CPNCs, conducting polymer-based nanocomposites; CSA, camphorsulfonic acid; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; MeO, methyl orange; MB, methylene blue; NPs, nanoparticles; PAc, poly(acetylene); PANI, polyaniline; PNA, poly(1-naphthylamine); P3HT, poly(3-hexylthiopene); PMPD, poly(*m*-phenylenediamine); PPy, polypyrrole; PTh, polythiophene; QY, quinoline yellow; RhB, rhodamine B; SDS, sodium dodecylsulphate; TEM, transmission electron microscopy; THF, tetrahydrofuran; VLA, visible-light-active; VB, valence band.

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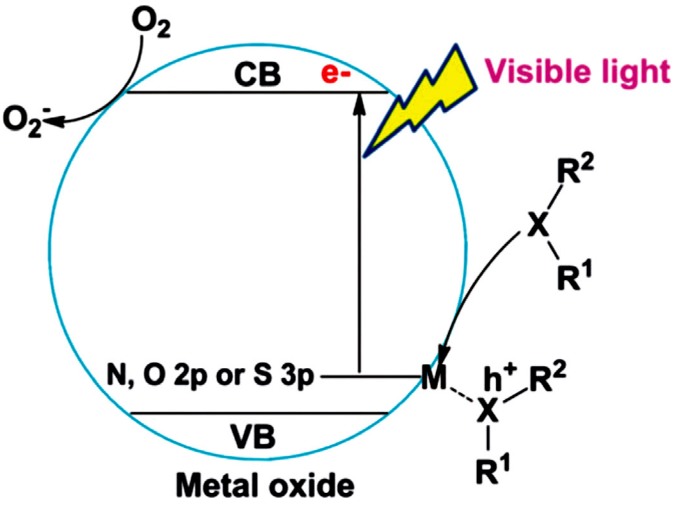

Fig. 1. Surface complexation heteroatoms (X = O, N or S) on metal (Ti, Nb or Zn) oxide for visible-light-induced reactions.
(Reprinted with permission from RSC, Chen et al. Chem. Soc. Rev., 2014, 43, 473–486).

fraction of the UV spectrum. Numerous reports have shown that modified ZnOs with other elements reveal enhanced photocatalytic properties.

2. Role of conducting polymers in enhancing photocatalysis

Conducting polymers have been widely investigated for their electronic and optoelectronic properties [5–8,64–72,75]. Studies on the improvement of their processibility have also been extensively reported (Riaz et al., 2008e, [73,74,76–80,83]. Due to their remarkable electroactive properties, they have lately proven to act as stable photo-sensitizers for semiconductors such as TiO_2 and ZnO owing to their high electron-hole carrying efficiency [104,10]. Polymers such as (PANI), poly (acetylene) (PAc), polypyrrole (Ppy), polythiophene (PTh) show remarkable charge-transporting properties, along with high thermal and photochemical stability [72,76,81,53,38,41,106]. The upcoming section describes the photocatalytic performance of ZnO based conducting polymer nanocomposites.

3. Synthesis and photocatalytic properties of conducting polymer/ZnO catalysts

Conducting polymers blended with wide band gap inorganic semiconductors are gaining immense attention for photocatalytic and photoelectric conversion applications [61,26,63,19]. They are reported to act as p-n junctions that can be tailored by combining a p-type conducting polymer with an n-type semiconductor to overcome the disadvantages of semiconductor oxides such as poor response to visible light, high rate of electron-hole recombination, leaching and thermal decomposition.

3.1. PANI/ZnO catalysts

Polyaniline PANI is one of the most investigated conducting polymers among all conducting polymers due to its high conductivity, facile synthesis procedure, and good environmental stability [78,85]. It has shown to possess a large variety of applications in electro-chromic devices, light emitting diodes, corrosion protective coatings and electrostatic discharge protection [105,39,77]. Eskizeybek et al. [15] prepared PANI homopolymer and PANI/ZnO nanocomposite via chemical oxidative polymerization of aniline to investigate its photcatalytic behaviour against methylene blue (MB) and malachite green (MG) dyes in aqueous medium under natural sunlight and also upon UV light irradiation. Results revealed that upon addition of ZnO nanoparticles in the PANI homopolymer, the photocatalytic efficiency was largely enhanced under natural sunlight irradiation. PANI/ZnO nanocomposite photocatalyst (0.4 g/L) degraded both dye solutions of MB and MG after 5 h of irradiation under natural sunlight showing 99% efficiency. Kinetics of photocatalytic degradation of organic pollutants was described by first order reaction. The decolorization efficiency of the PANI was lower than the PANI/ZnO nanocomposite under similar conditions. The mechanism of photocatalysis was discussed and it was explained that when ZnO nanoparticles were irradiated with UV light, electron–hole pairs were generated, which reacted with water to yield hydroxyl and super-oxide radicals [42,44,86]. These radicals oxidized and mineralized the organic and inorganic molecules. PANI revealed a with a band gap of 2.81 eV, (narrower than 3.3 eV of ZnO) and was therefore able to sensitize ZnO leading to efficient photocatalytic activity. Olad and Nosrati [56] also prepared PANI/ZnO nanocomposites via in-situ polymerization method for studying the photodegradation of MB dye. PANI core–shell nanocomposites were synthesized that showed higher photocatalytic activity than pristine ZnO nanoparticles and PANI under visible light irradiation. According to their studies, the % removal of MB after 1 h irradiation was 28% under UV irradiation and 82% under visible light irradiation. It was argued that the coating of ZnO nanoparticles with PANI shell rendered the nanocomposite photoactive under visible light irradiation because of the efficient charge separation of electron and hole pairs in the excited states that prevented the of recombination of charge pairs for a longer time, under visible light irradiation. Kant et al. [27] developed composites of $Fe_{0.01}Ni_{0.01}Zn_{0.98}O$ nanoparticles (FNZPs) with PANI via in-situ free radical polymerization method. The average particle size of FNZPs was reported to be 15–30 nm while that of the composite was shown to be 30–50 nm. The photocatalytic efficiency against MB showed that after 5 h of irradiation, FNZP/PANI degraded 99.47% of MB, while 79% degradation was achieved in case of FNZP. The FNZP/PANI nanocomposite degraded MB dye to 98.55% within 2 hrs after which degradation rate was almost constant. According to their proposed mechanism, electrons and holes were generated upon absorption of sunlight that interacted with water and oxygen to form $HO^{\bullet}$ radicals. These radicals disrupted the conjugation in organic dye and rapidly mineralized it, (Fig. 2) [98,99]. Pandiselvi et al. [58] synthesized chitosan–polyaniline (CPA) and chitosan–polyaniline/ZnO hybrids using aniline with different content of ZnO for removal of reactive orange 16 (RO16), Figs. 3 and 4. It was noted that the removal rate of the RO16 varied with dark and light exposure times. The decolorization efficiency rate was less than 5% after 1 h irradiation, but when the experiments were done under dark condition, the decolorization efficiencies were 37% and 64% for CPA and CPA–ZC2.5 composites, respectively. The authors explained that CPA–ZC/ZO composites showed enhanced the photocatalytic activities as compared to CPA from 47% to 73–99%, while the highest degradation efficiency was achieved with composites containing 2.5 wt% $ZnCl_2$. Pei et al. [59] developed monolayer PANI hybrid containing oxygen vacancy (*V*o) and interstitial zinc (Zni) via chemisorption method and the CPT technique, Fig. 5. The fabricated composite displayed remarkably enhanced photocatalytic activity towards MeO degradation, due to the synergic effect between defects and PANI Fig. 5. It was shown that the Z-D-P sample (Z-P stands for PANI coated ZnO, and Z-D stands for CPT treated defective ZnO) exhibited remarkably improved performance with its photodegradation rate being 2.5 times higher than that of pure ZnO. The % degradation values obtained for MeO were 32%, 74%, and 150%, respectively for Z-P, Z-