Applied Catalysis A: General 462–463 (2013) 178–195

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Review

Polymer-supported titanium dioxide photocatalysts for environmental remediation: A review

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ARTICLE INFO

Article history:
Received 19 March 2013
Received in revised form 23 April 2013
Accepted 25 April 2013
Available online xxx

Keywords:
TiO_2 photocatalyst
Polymer substrate
Buoyant photocatalyst
Immobilization
Photocatalytic activity
Dye decolorization
Biodegradable polymer

ABSTRACT

Since the past two decades, immobilization of titanium dioxide (TiO_2), a popular photocatalyst, on different substrates has been drawing a lot of attention because it eliminates the need of costly post-treatment separation processes. Considering the various substrates that have been tried for supporting TiO_2 photocatalysts, polymer substrate seems to be very promising due to its several advantages such as flexible nature, low-cost, chemical resistance, mechanical stability, low density, high durability and ease of availability. This review covers over a hundred published papers in the field of polymer-based photocatalysts and presents a comprehensive study on the preparation, photocatalytic activity and reuse of TiO_2/polymer photocatalysts. Polymer-supported buoyant TiO_2 photocatalysts and biodegradable polymer-supported TiO_2 photocatalysts are also discussed. Finally, the scope for future work and challenges for commercialization of polymer-supported TiO_2 photocatalysts in visible and/or solar light have been highlighted.

Contents

Abbreviations: VLA, visible-light-active; UV, ultraviolet; PE, polythene/polyethene; PS, polystyrene; EPS, expanded polystyrene; PET, polyethylene terephthalate; PP, polypropylene; PPF, polypropylene fabric; PVC, polyvinyl chloride; PVA, polyvinyl alcohol; PANI, polyaniline; PC, polycarbonate; PMMA, poly(methyl methacrylate); PVAc, polyvinyl acetate; ABS, acrylonitrile–butadiene–styrene; PU, polyurethane; PTFE, poly(tetrafluoroethylene); PDMS, poly(dimethylsiloxane); PHB, polyhydroxybutyrate; PFT, poly(fluorene-co-thiopene); P3HT, poly(3-hexylthiopene); HDPE, high-density polyethylene; PSP4VP, poly(styrene)-co-poly(4-vinylpyridine); LDPE, low-density polyethylene; CNP, carbon nitride polymer; PCL, polycaprolactone; ITO, indium tin oxide; KOX, potassium oxalate; TEA, triethylamine; CVD, chemical vapor deposition; APCVD, atmospheric pressure chemical vapor deposition; PECVD, plasma-enhanced chemical vapor deposition; MOCVD, metal–organic chemical vapor deposition; HPCVD, hybrid physical chemical vapor deposition; GC, gas chromatography; ESR, electron spin resonance; XRD, X-ray diffraction; TEM, transmission electron microscopy; CAM, contact angle measurements; FTIR-ATR, Fourier Transform Infrared-Attenuated Total Reflectance; IR, infrared; PCA, photocatalytic activity; COD, chemical oxygen demand; TOC, total organic carbon; MB, methylene blue; MO, methyl orange; IC, indigo carmine; TB, trypan blue; DR, drimaren red; R6G, rhodamine 6 G; 2-CP, 2-chlorophenol; 4-CP, 4-chlorophenol; 2,4-DCP, 2,4-dichlorophenol; acac, acetylacetone; AcOH, acetic acid; THF, tetrahydofuran; CP, conductive polymer; VB, valence band; CB, conduction band; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

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0926-860X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.04.039

1. Titanium dioxide photocatalysis – an introduction

Heterogeneous photocatalysis using semiconductor titanium dioxide, a popular photocatalyst has been an active area of research since 1972 when Akira Fujishima and Honda first reported photoinduced decomposition of water on TiO_2 electrodes [1,2]. TiO_2 has been reported as one of the most efficient photocatalyst because of its following properties: (i) highly stable, (ii) economical, (iii) non-toxic (to environment or humans), (iv) high turnover, (v) can be supported on various substrates, (vi) complete mineralization of organic pollutants, (vii) high catalytic activity, (viii) strong oxidizing power, (ix) stable against photo corrosion, (x) chemical resistance [3–13]. TiO_2 photocatalysis is a popular research area and finds its application in various fields like air purification, photo-induced hydrophilic coating and self-cleaning devices, self-sterilization/water disinfection, wastewater treatment, production of hydrogen fuel [3,14,15]. It must be noted that photocatalytic water splitting for generation of hydrogen is a hot and critical research topic which has been attracting a lot of recent attention. This is because it involves generation of renewable energy without emission of greenhouse gases. For further reading, few recent research papers in the area of solar fuel generation are available [16–20]. In this review article, we primarily focus on the use of polymer-supported titanium dioxide photocatalysts for wastewater treatment.

1.1. Mechanism of photocatalysis

The mechanism of TiO_2 mediated photocatalysis has been discussed in various papers [21–26]. Nevertheless, for better understanding, a commonly proposed simple mechanism for mineralization of most of the organic contaminants by TiO_2 photocatalyst has been illustrated by Eqs. (1.1)–(1.6) [14,27,28].

Step 1. Generation of photoinduced holes (h^+_{VB}) and electrons (e^-_{CB})

$$TiO_2 + h\upsilon \rightarrow h^+_{VB} + e^-_{CB} \quad (1.1)$$

Here, h stands for Plancks constant and υ is frequency of light.

Step 2. Formation of hydroxide radicals ($^\bullet OH$) by photogenerated holes

$$H_2O + h^+_{VB} \rightarrow H^+ + {}^\bullet OH \quad (1.2)$$

Step 3. Formation of Superoxide anion radical ($O_2^{\bullet-}$)

$$O_{2(ads)} + e^-_{CB} \rightarrow O_2^{\bullet-} \quad (O_{2(ads)}: \text{Adsorbed oxygen}) \quad (1.3)$$

Step 4. Oxidation of organic contaminant

$${}^\bullet OH + \text{contaminant} \rightarrow\rightarrow\rightarrow CO_2 + H_2O \quad (1.4)$$

$$O_2^{\bullet-} + \text{contaminant} \rightarrow\rightarrow\rightarrow CO_2 + H_2O \quad (1.5)$$

$$\text{Contaminant} + h^+_{VB} \rightarrow \text{contaminant}^{\bullet+} \rightarrow \text{the degradation products} \quad (1.6)$$

Furthermore, the mechanism of organic dye-sensitized TiO_2 photocatalysis in visible light irradiation has been described by Han et al. [29] and Pei et al. [30]. An interesting feature of these reactions is that organic dye can act as a sensitizer along with being a substrate to be degraded. The initial mechanism involves excitation of the dye molecule on absorption of visible light (Eq. (1.7)). The excited dye molecule (Dye^*), generally injects electrons into the conduction band (CB) of TiO_2 photocatalyst and itself is converted into its cationic radical ($Dye^{\bullet+}$) (Eq. (1.8)). Subsequently, these electrons assist in generating reactive species which leads to degradation of the dye as summarized by Eqs. (1.9)–(1.13) [29].

$$Dye + h\upsilon \rightarrow Dye^* \quad (1.7)$$

$$Dye^* + TiO_2 \rightarrow Dye^{\bullet+} + TiO_2(e^-_{CB}) \quad (1.8)$$

$$TiO_{2(e^-_{CB})} + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \quad (1.9)$$

$$O_2^{\bullet-} + TiO_{2(e^-_{CB})} + 2H^+ \rightarrow H_2O_2 + TiO_2 \quad (1.10)$$

$$2O_2^{\bullet-} + 2H^+ \rightarrow O_2 + H_2O_2 \quad (1.11)$$

$$H_2O_2 + TiO_{2(e^-_{CB})} \rightarrow {}^\bullet OH + OH^- + TiO_2 \quad (1.12)$$