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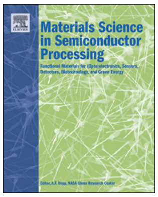

Copper-incorporated titania nanotubes for effective lead ion removal

Srimala Sreekantan [a,*], Syazwani Mohd. Zaki [a], Chin Wei Lai [b], Teoh Wah Tzu [c]

[a] *School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia Engineering Campus, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia*

[b] *Nanotechnology & Catalysis Research Centre (NANOCAT), Institute of Postgraduate Studies (IPS), University of Malaya, 3rd Floor, Block A, 50603 Kuala Lumpur, Malaysia*

[c] *Department of Civil and Environmental Engineering, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2118, Japan*

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ABSTRACT

Small copper (Cu^{2+}) dopant levels were successfully diffused into titanium dioxide (titania or TiO_2) nanotube lattice via an incipient wet impregnation technique. This study investigated the optimum Cu^{2+} dopant content to be incorporated into the TiO_2 nanotubes to achieve an effective lead ion (Pb(II)) removal system. The exciton states of the PL intensities varied in the following order: pure $TiO_2 > 0.6$ M Cu–$TiO_2 > 0.1$ M Cu–$TiO_2 > 0.06$ M Cu–$TiO_2 > 0.01$ M Cu–TiO_2. The significant quenching of the PL intensity indicates that incorporation of the appropriate amount of Cu^{2+} dopants into the TiO_2 lattice markedly enhanced the charge-carrier separation and transport. The photocatalytic ability of the samples was evaluated by the removal of the Pb(II) ions under UV illumination. The results show that the Cu dopants in the TiO_2 lattice at the optimum concentration (0.8 at%) acted as photoinduced electron mediators and thus increased the Pb(II) ion removal efficiency. The maximum Pb(II) ion removal rates for the 0.01 M Cu–TiO_2 nanotubes and after five hours of UV illumination were approximately 56.3% and 79.5% at pH 5 and pH 11, respectively. The generation of strong oxidizing agents (•OH radicals) effectively reduces the toxic Pb(II) ions into PbO/PbOH.

1. Introduction

The rapid growth of electronic waste (e-waste) volumes in the Association of Southeast Asian Nations (ASEAN) region has increasingly gained international attention. Economies face huge demands for electrical and electronic products, whereas governments are confronted with difficulties in dealing with the increasing volumes of e-waste [1]. In addition, economic growth and higher living standards has led to a rapidly increasing demand for electrical and electronic equipment (EEE) [1]. As a consequence, large volumes of waste and pollution are discharged into streams, rivers, or seas. In a scientific report, Goosey [2] showed that the volumes of e-waste are growing three times faster than that of average solid waste. In addition, at least 50 million tons of e-waste are produced each year [3]. The U.S. Environmental Protection Agency (U.S. EPA) estimates that only 15–20% of e-waste is recycled; the rest of these electronics go directly into landfills and incinerators [4]. Thus, initiatives and strategic measures must be immediately implemented to remove toxic heavy metal ions from e-waste.

Among various types of semiconductor photocatalysts, titanium dioxide (TiO_2) has the most promising photocatalysts

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[*] Corresponding author. Tel.: +60 45995255; fax: +60 45941011.
E-mail addresses: srimala@usm.my (S. Sreekantan), cwlai@um.edu.my (C.W. Lai).

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in environmental purification because of its strong oxidizing power, photoinduced hydrophilicity, non-toxicity, and long-term photostability [5–8]. Titanium dioxide (titania or TiO_2) is generally considered as a noble photocatalyst because of its many intrinsic properties, such as chemical inertness, photostability, low cost, nontoxicity, and high oxidative power. Therefore, improving the photocatalytic ability and efficiency of TiO_2 is critical in increasing the availability of this photocatalyst and lowering its production cost without disrupting the global ecological balance [8–10]. To achieve high efficiency, TiO_2 photocatalyst must have a suitable architecture that minimizes electron loss at nanostructural connections while maximizing photon absorption [11]. TiO_2 has been widely used in various types of nanoscale architectures, including nanoparticles, exfoliated nanosheets, nanofibers, nanorods, and nanotubes, to enhance the active surface area for photocatalytic reactions [12–15]. However, these nanodimensional TiO_2 remain unsuitable in environmental purification. The inherent limitations of TiO_2 include rapid recombination losses of electron–hole pairs, fast backward reaction, inefficient visible-light utilization, and wide band gap energy [8–11,16–18]. The TiO_2 photocatalyst also exhibits low degradation rates for many pollutants because of the extremely low surface coverage of the photocatalyst particles; it also has poor response to visible-light irradiation as a result of its wide band gap (~3.2 eV) and exhibits poor absorption of the solar spectrum (4–5%). Moreover, the short charge-separation distances within the particle as well as the rapid charge-recombination speed lead to a low quantum yield [8–11,19,20].

Various techniques, such as the addition of electron donors (hole scavengers), incorporation of carbonate salts, noble-metal loading, metal-ion doping, anion doping, dye sensitization, use of composite semiconductors, and metal-ion implantation, are used to improve the photoefficiency of TiO_2 photocatalysts [8,11,12,21–24]. Of these techniques, doping with transition metal ions, such as cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), vanadium (V), and tungsten (W), has shown promising results in improving the photocatalytic performance of TiO_2 in environmental purification applications [28]. In addition, the incorporation of appropriate concentrations of metal ions reportedly enhanced the photoreactivity of TiO_2 under both ultraviolet (UV) and visible-light irradiation [19–23,25–28]. Majority of studies on incorporation of metal ions into TiO_2 photocatalyst used coprecipitation, incipient wet impregnation method, and the sol–gel method [23–26,28–31]. However, the most frequently used modification method for metal-ion incorporation into the TiO_2 lattice is the incipient wet impregnation because of its simplicity and cost-effectiveness [32–34]. Choi and coworkers [35] reported that metal ion-doped TiO_2 exhibits enhanced photocatalytic activity. As the metal ions are loaded into the TiO_2 lattice, an impurity energy level is formed between the semiconductor band gap energies [36]. Modification of the electronic structure of the energy level system then ensues. In this case, the modification of TiO_2 creates an interfacial potential gradient with a corresponding energetic position within the heterostructure system; this potential gradient facilitates the transport and separation of charge carriers [37,38]. Furthermore, the photocatalytic efficiency of metal-ion dopants depends on whether these dopants serve as mediators of the interfacial charge transfer or as recombination centers. In addition, the ability of a dopant to function as an effective trap is related to its concentration, its energy level with the TiO_2 lattice, its distribution within the particles, and the electron donor concentration [8,30,39]. The improved photocatalytic activity is clearly related to the efficiencies of the doping centers in trapping charge carriers and interceding in the interfacial transfer. Trapping either an electron or a hole alone is insufficient for photodegradation because the immobilized charged species rapidly recombines with its mobile counterpart. Thus, metal ions can also serve as charge-trapping sites and reduce the electron–hole recombination rate [40,41].

Generally, metal ion dopants can be dispersed via three possible dispersion modes: substitutional sites, interstitial positions, or separated surface oxides. The local structures of the dopants can be deduced based on the ionic radii. From previous reports, a number of metal-ion dopants, such as Pt^{4+}, Cr^{3+}, and V^{3+} ions, are most likely substituted into Ti^{4+} sites within TiO_2 because of the similarities between the ionic radii of the dopants (Pt^{4+}, 0.765 Å; Cr^{3+}, 0.755 Å; V^{3+}, 0.78 Å) and that of Ti^{4+} (0.745 Å). By contrast, metal-ion dopants, such as Co^{2+}, Cu^{2+}, and Pt^{2+} ions, are most likely located in the interstitial positions of the lattice rather than directly into the Ti^{4+} sites because of the large size difference between the dopant ions (Co^{2+}, 0.89 Å; Cu^{2+}, 0.87 Å; Pt^{2+}, 0.94 Å) and Ti^{4+}. However, Ag^+, Rb^+, Y^{3+}, and La^{3+} ions are too large to be incorporated into the TiO_2 lattice and thus are more likely to be found as dispersed metal oxides within the crystal matrix or on the TiO_2 surface [35,42]. Recently, extensive studies have been conducted on the use of various types of potential transition-metal ions to improve photocatalytic efficiency. Of these metal-ion dopants, Cu^{2+} ions are found to be the most suitable dopants for incorporation into the TiO_2 lattice because of their high photocatalytic activity against volatile organic compounds. This high activity promotes the removal of heavy metals, particularly of Pb(II) ions, and can lead to the formation of more hydroxyl radicals during photocatalytic reactions. The higher rate of Pb^{2+} oxidation can significantly reduce the Pb(II) ion concentrations in the solution. To the best of our knowledge, detailed studies on the synthesis of self-organized Cu^{2+} ion-incorporated TiO_2 nanotubes through simple anodization and wet impregnation techniques to achieve highly efficient Pb(II) ion removal remain lacking. In this study, a comprehensive experiment was conducted to optimize the content of Cu^{2+} dopants in TiO_2 nanotubes using a Cu-containing precursor solution to achieve effective photocatalytic degradation of Pb(II) ions.

2. Experimental procedure

A Ti foil (0.13 mm thick, 99.6% purity, Strem Chemicals) was used as a substrate for the formation of well-aligned TiO_2 nanotubes. Prior to the anodization process, the Ti foil was cut into 1 cm × 4 cm pieces (0.26 g). The TiO_2 nanotubes were produced via electrochemical anodization of