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Visible light induced photocatalytic removal of Cr(VI) over TiO_2-based nanosheets loaded with surface-enriched CoO_x nanoparticles and its synergism with phenol oxidation

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ABSTRACT

Visible-light-driven (VLD) CoO_x loaded TiO_2-based nanosheets (Co-TNSs) with surface-enrich CoO_x nanoparticles were successfully synthesized by using a facile one-pot hydrothermal method. The photocatalysts were characterized by SEM, AFM, HRTEM, XRD, Raman, XPS, FL and the surface photocurrent (SPC) technique, etc. The as-synthesized samples exhibit sheet-like structure with large specific surface area (260–350 cm^2/g) and small thickness (3–4 nm). The CoO_x nanoparticles (1–2 nm) are highly dispersed on the surface of TNSs. Loaded CoO_x nanoparticles not only have influenced the crystal structure, crystallinity and surface area of the TNSs, but also resulted in considerable enhancement of visible-light (VL) absorption and a red-shift of the band gap of the TNSs. XPS results reveal that cobalt mainly exists in the form of Co^{2+} and Co^{3+}, and the binding energies of Ti—O bonds are changing with the loaded amount of CoO_x nanoparticles. FL and SPC results indicate appropriate amount of CoO_x (2.5 at.%) loading can effectively inhibit the recombination of photo-generated electron-hole pairs, thus improve the separation efficiency of charge carriers.

The photocatalytic activity of the samples was evaluated by the dichromate (Cr(VI)) solution under VL irradiation. It can be found that the Co-TNSs photocatalysts showed excellent VL photocatalytic activity for the removal of Cr(VI). Initially the photocatalytic activity increased with the content of CoO_x, and then decreased after attaining a maximum value at an optimal content (2.5 at.%) for degradation of aqueous Cr(VI) solution. The addition of Ca^{2+} promotes photocatalysis owing to its ionic bridging function in the form of $=TiOH^+$—Cr(VI)–Ca^{2+}—Cr(VI) linkages, while $SO_4{}^{2-}$ slightly inhibits the photo-reduction of Cr(VI), indicating good synergy of photocatalysis and adsorption even at higher ionic strength of electrolyte. The photocatalytic reduction of Cr(VI) is also significantly promoted by phenol and synergism between Cr(VI) reduction and degradation of phenol which is demonstrated by measuring the effect of multiple usage of Co-TNSs on its photocatalytic efficiency. Desorbed Co-TNSs (Co-TNSs-Des) are easily regenerated and reused for Cr(VI) removal with excellent performance. A possible alternate mechanism for the enhancement of photocatalytic activity under visible light irradiation is also proposed.

1. Introduction

The removal of toxic contaminants from water remains a huge challenge for industrial and municipal wastewaters as the deterioration of global environment is increasing. Wastewaters often contain a lot of inorganic and organic pollutants. The major inorganic pollutants are heavy metals such as Cr, Pb, Hg and Cd ions, which have become a serious problem in the aquatic environment due to their toxicity, bioaccumulation and persistence [1–6]. And organic pollutants like phenol, polychlorinated biphenyls in water also have been causing serious environmental problems [7–9]. The co-existence of organic matter and metal ions in wastewater is a common phenomenon, such as leather tanning, film making, wood processing, automobile manufacturing, petroleum refining industry wastewater, etc. The simultaneous removal of organic

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matter and metal ions from wastewater has particular significance to pollution control and remediation. Among various treatments of removing the pollutants from wastewaters, photocatalytic technology is known as a promising one due to its ability to mineralize most of the organic pollutants by using only luminous energy. TiO_2 has been proved to be the most representative and extensively used photocatalyst, owing to its high photo-activity, low cost, non-toxicity, high oxidation ability and relatively high chemical stability [10,11]. However, its relatively wide band gap (~3.2 eV) and the high recombination rate of the photo-generated electron-hole pairs hinder its large-scale applications [12,13]. Therefore, considerable efforts have been made to narrow the band gap to shift the absorption edge of TiO_2-based materials, deeper into the visible-light (VL) region of the electromagnetic spectrum, where the Sun's total irradiance lies nearly 42%.

To reach this goal, one of the challenges is to develop highly effective photocatalysts to accelerate the reactions. Recently, the manipulation of morphology of TiO_2-based photocatalysts has attracted attention of many researchers. As a result, TiO_2 has been reported in different morphologies in recent years, e.g., nanofibers, nanotubes, nanorods, nanosheets, and nanoflowers owing to their large specific surface area and small dimension effect [14–19]. Larger specific surface area allows photocatalysts to expose for the light effectively and lead better contact with more molecules of pollution thus efficient photocatalytic reaction. Smaller thickness of photo catalyst may be beneficial to improve the separation rate of photo-generated electron-hole pairs. Inspired by the natural photochemical process by leaves of plants with their two-dimensional (2D) structure that can efficiently convert sunlight to chemical energy through photosynthesis, developing and improving 2D TiO_2-based nanomaterial have attracted increasing attentions [20,21]. Comparing with other morphologies of TiO_2-based photocatalysts, 2D-nanosheets possess higher specific surface area and smaller thickness. These advantages make nanosheets be expected to exhibit excellent photocatalytic activity. Various methods have been attempted for the preparation of nanosheets so far, such as hydrothermal method, sol-gel method, chemical vapor decomposition (CVD) methods, etc. [22–26]. Hydrothermal method is one of the most popular methods due to its advantages of simpleness and convenience. TiO_2 nanoparticles (3D) take the form of nanosheets (2D) and finally nanotubes (1D) under hydrothermal conditions. Controlling the environment of the reaction, results in the synthesis of different nanostructures of TiO_2-based nanomaterial [27]. Our previous work shows that, TiO_2-based nanosheets (TNSs) with high specific surface area ($339\,m^2/g$) can be synthesized and the thickness of single nanosheet has reached to 4–5 nm. Moreover, UV–vis photocatalytic efficiency of TNSs is better than Degussa P25 during the degradation of Rhodamine B (RhB), methylene blue (MB), crystal violet (CV), etc. [27,28].

However, the photocatalytic efficiency of pure TiO_2-based nanosheets was relatively low, particularly under VL irradiation, due to the fast recombination rate of electron-hole pairs. In order to enhance the interfacial charge-transfer efficiency and utilize wider spectral range of solar energy, the TiO_2-based nanosheets catalyst has been modified by doping and manipulating nanomaterial composition [29,30]. Till date numerous efforts have been devoted to increase the separation efficiency of photo-generated charges and expand spectral response into VL region. Majority of the studies are focused on the modification of photocatalysts with metal and nonmetal additives as well as organic photo sensitizers [31–33]. Loading TiO_2-based nanosheets with CoO_x nanoparticles may be an efficient method to obtain high photocatalytic activity under VL irradiation owing to the photosensitizing effect of the CoO_x nanoparticles with narrow energy gap. The CoO_x nanoscale particles promote photosensitization, leading to the enhanced activity. However, these tiny CoO_x nanoparticles may easily suffer from leaching and runoff, leading to the poor durability. The structure and morphology of photocatalyst have received increasing attention owing to their remarkable influence on both the reactant adsorption and light absorbance. Meanwhile, the unique structure and morphology might also play key roles in determining the dispersion and the stability of loading against leaching during photocatalytic reactions.

In the present work, a novel visible-light-driven (VLD) CoO_x loaded TNSs with surface-enrich CoO_x nanoparticles with high photocatalytic activity were successfully synthesized by a facile one-pot hydrothermal approach. The CoO_x nanoparticles are highly dispersed on the surface of TiO_2-based nanosheets. The photocatalytic activities of the resultant Co-TNSs were evaluated by simultaneous photocatalytic detoxification of Cr(VI) and degradation of phenol. The Cr(VI) was selected as a reference metal ion since it is one of the most toxic ions present in the environment, posing toxicity to most organisms at the concentrations of higher than 0.05 ppm. Wastewaters generated from various industries contain aromatic compounds (e.g., Phenol, etc.) and their derivatives are toxic and thus have adverse effects on health and environment. Moreover, phenol has been known as an electron donor in the photocatalytic system; hence, phenol was selected as the oxidizable organic compound in a simultaneous photocatalytic oxidation-reduction reaction. The strong synergistic effect was demonstrated by simultaneous decontamination of Cr(VI) and phenol.

2. Materials and methods

2.1. Preparation of photocatalysts

Degussa P25 (TiO_2, 80% anatase, 20% rutile) is the product of Degussa Co., Ltd. The NaOH, cobalt nitrate ($Co(NO_3)_2$), HNO_3, acetone (C_3H_6O), phosphoric acid (H_3PO_4), 1, 5-diphenylcarbohydrazide ($C_{13}H_{14}N_4O$), ethyl alcohol (C_2H_5OH), H_2O_2, phenol, potassium dichromate ($K_2Cr_2O_7$), ammonium chloride (NH_4Cl), 4-amino-antipyrine ($C_{11}H_{13}N_3O$), $K_3[Fe(CN)_6]$ solution were provided by Sinopharm Chemical Reagent Co., Ltd, and coumarin was obtained from Alfa Aesar. All of the reagents were at analytically pure level and used without any further purification. Deionized (DI) water with a resistance of 4.25 MΩ cm was used in all experiments.

In a typical preparation procedure as shown in Scheme 1, 0.8 g P25 was dispersed in 50 mL of 10 mol/L NaOH solution under intense stirring. A certain amount of cobalt nitrate solution was dropped slowly into the suspension. After magnetically stirred for 1 h, the mixture was treated at 130 °C for 3 h in a 100 mL Teflon-lined autoclave. After the reaction, the autoclave was cooled down to the room temperature by water-cooling. The resultant white powders were washed with DI water until their pH reached 7, and followed by the proton exchange in 200 mL of diluted HCl solution. Finally, the powders were treated with DI water for several times and then dried at 70 °C for 12 h. The obtained samples were denoted by x-Co-TNSs, where x (x = 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, and 5.0%) representing the concentration of cobalt nitrate in the precursor solution. For comparison, unloaded TiO_2-based nanosheets (TNSs) were also prepared using the same process without adding any cobalt source.

2.2. Characterization of photocatalysts

The morphological features of the specimens were characterized by scanning electron microscopy (SEM) (SIRION, FEI, Netherlands), transmission electron microscopy (TEM) on JEOL TEM-2010 (HT) instrument, and high-resolution transmission electron microscopy (HRTEM) on JEM-2010 FEM. An atomic force