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Efficient UV–vis-infrared light-driven catalytic abatement of benzene on amorphous manganese oxide supported on anatase TiO_2 nanosheet with dominant {001} facets promoted by a photothermocatalytic synergetic effect

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ABSTRACT

The nanocomposites of amorphous manganese oxide (MnO_x) supported on anatase TiO_2 nanosheet with dominant {001} facets (TNS) with different Mn/Ti molar ratio were prepared by hydrothermal redox reaction of $KMnO_4$ and $Mn(NO_3)_2$ in the presence of TNS. The MnO_x/TNS nanocomposites were characterized by XRD, SEM, TEM, ICP, XPS, BET, and diffuse reflectance UV–vis-Infrared adsorption. MnO_x/TNS with the optimum Mn/Ti molar ratio of 0.40 exhibits highly efficient photothermocatalytic activity and excellent durability for the oxidation of the recalcitrant and carcinogenic benzene under the full solar spectrum irradiation from a Xe lamp. Remarkably, the CO_2 production rate of MnO_x/TNS enhances by 99 times as compared to TNS. Impressively, MnO_x/TNS also exhibits efficient photocatalytic activity with the visible-infrared irradiation, even with the infrared irradiation. The highly efficient photothermocatalytic activity of MnO_x/TNS under the full solar spectrum irradiation originates from the highly efficient solar light-driven thermocatalysis on MnO_x due to its strong absorption in entire solar spectrum region and the efficient thermocatalytic activity, which is considerably promoted by a photothermocatalytic synergetic effect. We put insight into the photothermocatalytic synergetic effect by CO temperature-programmed reduction of MnO_x/TNS in dark and with the solar light irradiation: the active species generated by the photocatalysis on TNS migrate to MnO_x via the MnO_x/TiO_2 interface, and accelerate the solar light-driven thermocatalysis on MnO_x in the nanocomposite.

1. Introduction

Anatase TiO_2 nanocrystal with dominant {0 0 1} facets has attracted enormous interests due to its unique physicochemical properties such as high surface energy, active unsaturated Ti atoms, etc., since Yang et al. reported the preparation of anatase TiO_2 single crystals with dominant {0 0 1} facets [1]. It has been widely used in photocatalytic environmental purification, photocatalytic hydrogen production, photocatalytic reduction of CO_2, selective photocatalytic synthesis of fine chemicals, dye sensitized solar cell, etc [2–7]. However, there are three major drawbacks to greatly hinder its wide photocatalytic application. The first is its low photocatalytic efficiency owing to the rapid recombination of photogenerated electron and hole. The second is its photocatalytic activation only by UV light due to its large band gap. The third is its prone deactivation due to the deposition of recalcitrant carbonaceous intermediates or the production of oxygen vacancies on the surface of TiO_2 nanosheets in the photocatalytic process [8,9]. Scientists have developed various strategies to resolve the three problems. The reported strategies of enhancing its photocatalytic efficiency involve: tuning the ratio of {001} and {101} facets of TiO_2 nanocrystals for preferential transport of photogenerated electrons and holes to different facets of the TiO_2 nanocrystals, thereby reducing the charge recombination [10–17], forming porous TiO_2 superstructure consisted of anatase TiO_2 nanocrystals with dominant {001} facets [18], forming unique anatase TiO_2 twin crystals with {001} facets [19], creating defects (e.g. oxygen vacancies) on {001} facets of anatase TiO_2 nanosheets [20,21], surface modification of TiO_2 with F to reduce the recombination rate of photo-generated electrons and holes, or enhance the adsorption of

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O_2 so as to promote the photogenerated electrons captured by the adsorbed O_2 [22,23],forming nanocomposites with of grapheme [24–27], 2D-MoS_2 [28], layered Ti_3C_2[29], quantum Cu(II) nanodot [30] to retard the recombination of photogenerated charge carriers and prolong electron lifetime, and so on.

The reported strategies of extending its photocatalytic response from UV to visible region include: doping by nonmetals such as nitrogen [31], carbon [33], co-doping by nonmetal and metal [34,35], forming nanocomposites with semiconductors with narrow band gap such as CdS [36], Bi_2O_3 quantum dots [37], CdSe quantum dots [38], and g-C_3N_4 [39], forming plasmonic photocatalyst of Au/TiO_2 [40] and Au-Pd/TiO_2 nanosheets [41], utilizing the interaction between reactant and TiO_2 nanosheet to form surface complex with visible photocatalytic response [42], etc. Among the reported strategies, only the plasmonic photocatalysts of Au/TiO_2 and Au-Pd/TiO_2 were reported to exhibit very low photocatalytic activity for photocatalytic H_2 production under near-infrared irradiation above 780 nm [42]. All other strategies just extend its photocatalytic response to visible region with maximum wavelength up to ~600 nm [31–39].

The reported strategies of improving photocatalytic durability of anatase TiO_2 nanocrystal with dominant {001} facets are very limited [8,43]. Xu et al. revealed the origin of deactivation of anatase TiO_2 nanosheet with dominant {001} facets, and reported a regeneration method by simply refluxing the deactivated TiO_2 nanosheet in water at 100 °C [8]. Stefanov et al. [43] reported a method of improving its photocatalytic stability for gas-phase photodegradation of acetaldehyde by controlling reaction condition such as humidity and temperature.

Most of the published works about the anatase TiO_2 nanosheet with dominant {001} facets focused on the photocatalytic degradation of water pollutants (especially, dyes) and photocatalytic production of H_2. There have been only few works about the anatase TiO_2 nanosheet with dominant {001} facets for the photocatalytic degradation of volatile organic compounds (VOCs) [6,9,22,23,42–44], which are major components of air pollutants emitted in very large scale from various industrial processes related to the production and utilization of paints, organic chemicals, etc. To achieve the application of TiO_2 nanosheet with dominant {001} facets in the efficient abatement of VOCs using renewable solar energy, it is highly desirable but great challenging to develop a novel strategy of significantly improving its photocatalytic activity as well as durability, or/and efficiently extending its photocatalytic response from UV to visible region, even to infrared region. Very recently, we found a photothermocatalytic synergetic effect that can significantly enhance the catalytic activity and the durability of TiO_2 nanosheet with dominant {001} facets for the gas-phase abatement of benzene [45]. However, the TiO_2 nanosheet with dominant {001} facets only utilize UV light and the heating effect of infrared light for photocatalytic abatement of benzene. Herein, we prepared a novel nanocomposite of amorphous manganese oxide supported on anatase TiO_2 nanosheet with dominant {001} facet (MnO_x/TNS). By forming the MnO_x/TNS nanocomposite, both the photocatalytic activity and durability of anatase TiO_2 nanosheet with dominant {001} facet are significantly improved, and its photocatalytic response is efficiently extended from UV to whole solar spectrum region. The MnO_x/TNS nanocomposite exhibits highly efficient photothermocatalytic activity for the oxidation of the recalcitrant and carcinogenic benzene under the full solar spectrum, visible-infrared, or infrared irradiation. Remarkably, the CO_2 production rate of the MnO_x/TNS nanocomposite enhances by 99 times as compared to the pure TiO_2 nanosheet. The highly efficient photothermocatalytic activity of the MnO_x/TNS nanocomposite under the full solar spectrum irradiation is attributed to the highly efficient solar light-driven thermocatalysis on the amorphous manganese oxide considerably promoted by a photothermocatalytic synergetic effect. We put insight into the solar light-driven thermocatalysis and the photothermocatalytic synergetic effect.

2. Experimental section

2.1. Preparation

Anatase TiO_2 nanosheet with dominant {001} facets, denoted as TNS, was prepared by a hydrothermal reaction of $Ti(OBu)_4$ in the presence of HF at 180 °C according to the procedure reported in our previous work.[42] The BET surface area of the anatase TiO_2 nanosheet is 95.7 $m^2\,g^{-1}$. The percentage of the dominant {001} facets is estimated by the average thickness and length to be 72.3% [42].

The MnO_2/TiO_2 composites were prepared according to the following procedure. 1.0 g of anatase TiO_2 nanosheet was added into 50 mL of distilled water in a beaker, then ultrasonicated for 60 min until it was well dispersed. 0.1319 g of $KMnO_4$ and 0.1494 g of $Mn(NO_3)_2$ (50 wt%) solution with a $KMnO_4/Mn(NO_3)_2$ molar ratio of 2:1 were added into the suspension, and ultrasonicated for 10 min until they were dissolved. The beaker was covered with polyethylene film, and then placed into an electrical oven at 90 °C for 12 h. The precipitate formed in the solution was filtered, washed with distilled water, and dried in the electrical oven at 90 °C for 12 h. The obtained MnO_x/TiO_2 sample with the Mn/Ti molar ratio of 0.10 is denoted as MnO_x/TNS-A.

The MnO_x/TiO_2 samples with higher Mn/Ti molar ratio of 0.20, 0.40, and 0.60 were prepared by the same procedure as MnO_x/TNS-A except for adding the higher amount of $KMnO_4$ and $Mn(NO_3)_2$ (50 wt%) according to the same $KMnO_4/Mn(NO_3)_2$ molar ratio of 2:1. The obtained MnO_x/TiO_2 samples were denoted as MnO_x/TNS-B, MnO_x/TNS-C, and MnO_x/TNS-D, respectively.

The pure manganese oxide sample was prepared by the same procedure as MnO_x/TNS-A except for no adding TiO_2 nanosheet.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the samples were obtained on a Rigaku Dmax X-ray diffractometer using Cu Ka radiation. SEM image and energy dispersive X-ray spectroscopy (EDX) mapping of elements were obtained on an ULTRA PLUS-43-13 scanning electron microscope. The chemical composition of the samples was analyzed by inductively coupled plasma/optical emission spectroscopy (ICP-OES, PerkinElmer Optima 4300DV). Transmission electron microscopy (TEM) images were observed on a JEM-100CX electron microscope. Diffusive reflectance UV–vis-IR (DRUV-Vis-IR) absorption spectra were recorded on a UV-3600 spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurement was performed on a VG Multilab 2000 X-ray photoelectron spectrometer using Mg Ka radiation. BET surface area was measured on an ASAP2020 using N_2 adsorption at −196 °C.

CO temperature programmed reduction (CO-TPR) of the MnO_x/TNS-C sample in dark or with irradiation was measured in a quartz tube reactor on TP-5080 multifunctional adsorption apparatus equipped with a TCD detector. A quartz window was connected to one of the end of the quartz tube reactor. A Xe lamp (CHF-XM500), which has a spectral profile similar to the solar spectrum,[46] was put in the front of the quartz window. For measured the CO-TPR of the MnO_x/TNS-C sample under the irradiation with wavelength above 480 nm, a long wave pass cutoff filter of 480 nm was placed between the Xe lamp and the quartz window. The detailed procedure was reported in our previous work [47,48].