Research paper

Exceptional photocatalytic activities for CO_2 conversion on Al−O bridged g-C_3N_4/α-Fe_2O_3 z-scheme nanocomposites and mechanism insight with isotopesZ

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ABSTRACT

It's highly desired to design and fabricate effective Z-scheme photocatalysts by promoting the charge transfer and separation. Herein, we firstly fabricated the ratio-optimized g-C_3N_4/α-Fe_2O_3 nanocomposites by adjusting the mass ratio between two components through a simple wet-chemical process. The resulting nanocomposites display much high photocatalytic activities for CO_2 conversion and phenol degradation compared to bare α-Fe_2O_3 and g-C_3N_4. Noteworthily, the photocatalytic activities are further improved by constructing Al−O bridges, by 4-time enhancement compared to those of α-Fe_2O_3. Based on the steady-state surface photovoltage spectra, transient-state surface photovoltage responses, photoelectrochemical I-t curves and the evaluation of produced ·OH amounts, the exceptional photoactivities of Al−O bridged g-C_3N_4/α-Fe_2O_3 nanocomposites are attributed to the significantly promoted charge transfer and separation by constructing the g-C_3N_4/α-Fe_2O_3 heterojunctions and the Al−O bridges. Moreover, the charge transfer and separation of this photocatalyst have been confirmed to obey the Z-scheme mechanism, as supported by the single-wavelength photocurrent action spectra and single-wavelength photoactivities for CO_2 conversion. Furthermore, the mechanism of the photocatalytic CO_2 conversion has been elaborately elucidated through the electrochemical reduction and the photocatalytic experiments especially with isotope $^{13}CO_2$ and D_2O, that the produced H atoms as intermediate radicals would dominantly induce the conversion of CO_2 to CO and CH_4.

1. Introduction

The excessively exhausted gases, like carbon dioxide (CO_2) as a main greenhouse gas, are recognized to be the culprit causing the global climate change [1]. It's estimated that a double increase of the atmospheric CO_2 concentration would cause a global temperature rise of approximately 3 °C (with a probable uncertainty range of 2–4.5 °C) [2]. The accompanying freak weather, land desertification, sea level rise and widespread amphibian extinctions from epidemic disease hence would occur in high frequency [3–5]. Therefore, it's urgent to cut down the atmospheric CO_2 concentration effectively. In addition, as a vital link of carbon cycle, CO_2 could be utilized as the raw material to produce valuable chemicals [6,7]. Hence, it's rather meaningful to develop an efficient technique to convert CO_2 for reducing the greenhouse effect and producing value-added chemicals [8]. Moreover, organic contaminant pollution is another environmental threat for water body. As a typical contaminant among various organic ones, phenol greatly harms

the environment due to its high toxicity and bio-recalcitrant nature [9,10]. Therefore, it is highly desired to develop novel, green and sustainable technologies for CO_2 conversion and phenol degradation for the purpose of long-term development of human society.

Noteworthily, the photocatalytic technology is promising to solve the above-mentioned environmental problems, compared with the conventional technologies [11]. Photocatalysis is a clean and environmentally friendly process by utilizing solar energy, in which a semiconductor as the photocatalyst is excited by light to generate electrons and holes so as to induce reduction and oxidation reactions, respectively [12]. The chemical nature of the photocatalyst primarily leads to the efficiency of the photocatalytic process. Among distinct types of photocatalysts, single-metal oxides such as TiO_2, ZnO, SnO_2, WO_3, Bi_2O_3 and Fe_2O_3 are mostly investigated [13–18]. Since the visible light occupies 44% of the actual solar light spectrum, narrow-bandgap oxides capable of absorbing more visible light hence become the predominant choice. The narrow-bandgap α-Fe_2O_3 (band gap

energy equals 2.0-2.2 eV) is widely applied due to its low cost, high stability, non-toxicity and magnetism [19,20]. However, its photo-catalytic activities are limited mainly by the weak charge separation [21]. For this, several methods have been developed, such as nanostructured construction, heterojunctional fabrication and elemental doping [22,23].

Additionally, from the thermodynamics view of point, the low conduction band (CB) bottom level of α-Fe₂O₃ corresponds to the photo-induced electrons with the low energy, which is hardly capable of inducing reduction reactions with adsorbed H₂O, CO₂ and O₂. This is mainly responsible for its weak photocatalytic performance [24]. Unfortunately, the above-mentioned factor limiting the activity of α-Fe₂O₃ is often neglected. To overcome the shortfall, targeted modification strategies have been successfully developed to enhance the photocatalytic activities. For example, noble metals as co-catalysts could be integrated with α-Fe₂O₃ [25]. In this case, the photo-induced electrons immigrate to the metals serving as the catalytic sites. However, the high cost of noble metals limits the practical application. While another feasible strategy is to couple α-Fe₂O₃ with wide-bandgap semiconductors, like TiO₂, which could afford a high-level-energy platform to accept the photo-induced electrons from α-Fe₂O₃, hence improving the photocatalytic activities [26]. However, it is an uncommon electron transfer process from α-Fe₂O₃ to the wide bandgap oxides with a high-level conduction band, leading to the low efficiency. Therefore, it is much meaningful to develop a novel and effective strategy to significantly facilitate the charge separation of α-Fe₂O₃ in order to obtain enhanced photocatalytic performance.

Recently, a Z-scheme heterojunction strategy for α-Fe₂O₃ by simulating the natural photosynthesis to couple another narrow bandgap semiconductor has been well investigated [27–29]. For the Z-scheme photocatalyst, α-Fe₂O₃ and the coupled semiconductor would be simultaneously excited under light irradiation. Reasonably, the photo-induced electrons of α-Fe₂O₃ would transfer to the coupled semiconductor for recombining holes. Thus, residual holes in α-Fe₂O₃ exhibit strong oxidizing capacity, while the photo-induced electrons of the coupled semiconductor possess strong reducing capacity. Consequently, the designed Z-scheme α-Fe₂O₃-based photocatalyst would exhibit the much high photocatalytic activity [30]. To successfully construct a Z-scheme photocatalyst, the CB bottom level of the coupled semiconductor should be emphatically considered referring to the energy band structure of α-Fe₂O₃. Graphitic carbon nitride (g-C₃N₄) is a metal-free, robust, low-cost and visible light responsible polymeric semiconductor, which has been proven to be the appropriate candidate since its CB and valence band (VB) are positioned at −1.14 and 1.57 eV, respectively [31–33]. The g-C₃N₄/α-Fe₂O₃ nanocomposites have been reported to demonstrate much high activity compared with those of bare α-Fe₂O₃ and g-C₃N₄ [34–36]. Nevertheless, the specific electron transfer mechanism for this Z-scheme photocatalyst is still ambiguous to date and needed to verify with solid evidences.

Although the Z-scheme design has shown obvious advantages, the lattice mismatch of different constituents would hinder the charge transfer and separation, which is overlooked in most cases [37]. As a targeted approach, to build electron shuttling bridges between the semiconductors would address this mismatching problem. Generally, noble metals like Pd and Au as effective conductors could shuttle electrons for Z-scheme photocatalyst. However, it is unsatisfactory due to the high cost [38,39]. Thus, the cheaper electron bridges are needed to explore. Inspired by our previous works, the functional groups like −P-OH and −Si-OH could effectively connect constituents of the heterojunctional photocatalyst, such as ZnO/BiVO₄, TiO₂/Fe₂O₃ and TiO₂/g-C₃N₄, leading to the promoted charge transfer and separation and hence to enhanced photoactivities [40,41]. This indicates that the inorganic polyhydroxy groups like −Al-OH possibly serve as feasible electron bridges. Besides, the electron transfer mechanism for the Z-scheme photocatalyst with polyhydroxy group bridges has seldom been investigated. Therefore, it is urged to be raveled.

Under the light irradiation, the photo-induced electrons and holes of designed heterojunctional photocatalyst would induce CO₂ conversion and pollutant degradation with complex photophysical and photochemical processes [42,43]. It is widely accepted that the produced ·OH by oxidation between photo-induced holes and H₂O is regarded as the primary active species. The ·OH radicals would further evolve O₂ in CO₂ conversion and directly attack organics to induce the pollutant degradation, respectively [44,45]. Therefore, it's reasonable and feasible to investigate the photo-induced charge separation by measuring the amount of produced ·OH. Currently, most works mainly focus on the improvement of photocatalytic performance for CO₂ conversion, while detailed analysis on the reaction pathway and mechanism is ignored [46]. Naturally inferred, it's difficult for CO₂ to directly accept photo-induced electrons to get reduced since this process in water requires excited high-level-energy electrons below −1.9 V thermodynamically [47]. Thus, it's more possible for CO₂ to react with the produced H atoms by oxidation between photo-induced electrons and H₂O to gradually transform into CH₄ and CO [48]. However, the above inference still lacks convincible evidences. Therefore, it's rather meaningful to clarify the related process mechanism.

Based on the above considerations, we have successfully designed and fabricated the Al−O bridged g-C₃N₄/α-Fe₂O₃ Z-scheme nanocomposites as efficient photocatalysts for CO₂ conversion and phenol degradation. The promoted charge separation and transfer by constructing the g-C₃N₄/α-Fe₂O₃ heterojunctions as well as Al−O bridges has been evidenced by atmosphere-controlled transient-state surface photovoltage technique and measurement of produced ·OH amounts [49,50]. Comparing with P-O and Si-O bridges, Al−O ones indicate the strongest electron shuttling ability. Besides, the Z-scheme electron transfer mechanism has been verified by the single-wavelength photocurrent action spectra and single-wavelength photoactivities for CO₂ conversion. Moreover, it is suggested by means of electrochemical and isotope experiments that the produced H atoms as the active radicals would be much favorable to induce the reduction of CO₂ to CO and CH₄. Certainly, this work will help to understand the charge transfer and separation processes in the fabricated Z-scheme heterojunctions with deeper recognition, and provide reasonable design strategy for the α-Fe₂O₃-based photocatalysts applied in energy production and environmental remediation.

2. Experimental

All the chemicals in this study were of analytical grade and used as-received without further purification. Deionized water was used throughout the experiments.

2.1. Materials synthesis

Nanocrystalline α-Fe₂O₃ was synthesized by a phase-separated hydrolysis-solvothermal method. n-Butyl alcohol as the organic solvent and hydrated ferric nitrate Fe(NO₃)₃·9H₂O as the iron source were used. In a typical procedure, 10 mL of 5 wt.% ammonia solution was added into a 50 mL Teflon-lined autoclave and a 10 mL weighing bottle containing a solution of 0.8 g Fe(NO₃)₃·9H₂O in 8 mL n-butyl alcohol was placed in the autoclave with a support between the autoclave bottom and the weighing bottle. The Teflon-lined autoclave was kept at 140 °C for 6 h. After being cooled to the room temperature, the sample was washed for several times with ethanol and deionized water in turn and then dried in an oven at 80 °C to obtain nanocrystalline α-Fe₂O₃. The bare α-Fe₂O₃ is represented by F.

g-C₃N₄ was synthesized by heating urea in an alumina combustion boat at 550 °C for 4 h with a heating rate of 0.5 °C/min. After that, the furnace was cooled to the room temperature naturally. The obtained light-yellow product was grinded into fine powders for further experimental work.

To fabricate g-C₃N₄/α-Fe₂O₃, different amounts of g-C₃N₄ were