



Full Length Article

Photocatalytic removal of NO by Z-scheme mineral based heterojunction intermediated by carbon quantum dots

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ABSTRACT

A novel photocatalyst integrated with carbon quantum dots (CQDs), SmFeO₃ and attapulgite (ATP) clay mineral was synthesized by sol-gel/impregnation method which was successfully applied for NO removal under solar light irradiation. The textural and optical properties of the materials were analyzed by various characterizations. Results indicated the SmFeO₃ nanoparticles were uniformly loaded on the ATP support and both coherently interacted with CQDs. The amount of CQDs had significant effect on the NO conversion, while 5 wt% incorporation achieved the highest 90% conversion rate. An indirect Z-scheme mechanism was proposed that the CQDs performed as an intermediate between SmFeO₃ and ATP for the charge transfer while the high redox potential was maintained. In addition, the ATP fiber showed not only UV-responsive property in Z-scheme structure, but also excellent adsorption effect for gas molecules.

1. Introduction

As one of the primary air pollutant, NO imposes health risk for humans including respiratory diseases, acid rain, photochemical smog and solid particles PM2.5. Therefore, efficient methods for control of NO emission are urgently needed. It is widely accepted that photocatalysis has become a burgeoning approach for the pollution abatement [1–3], which is expected to be an environment-friendly, cost-effective and efficient oxidation process for NO_x removal. Up to date, strenuous efforts have been put to employ semiconductor nanomaterials for photocatalytic degradation of NO_x [4,5]. For instance, M.J. Hernández Rodríguez et al. [6] synthesized a TiO₂-based photocatalyst coupled with gold by sol-gel method, and found that 0.3 wt% Au modified TiO₂ oxidized NO to NO₂ with high degradation rates. Huang et al. [7] obtained hierarchical porous ZnWO₄ microspheres by ultrasonic-spray pyrolysis for NO_x removal. Wang et al. [8] has prepared layer-structured Bi₂O₂CO₃/g-C₃N₄ heterojunction for photocatalytic of NO in air. In particular, perovskite-type oxides have exhibited great potential due to its high catalytic activity, strong oxidizing ability and chemical stability [9,10]. Although photocatalytic activity of perovskite-type oxides have been extensively studied, such as pure LaMnO₃ [11], Cu doped LaCoO₃ [12], Ag/LaFeO₃ [13] etc, few studies have been reported on NO_x photocatalytic conversion. In our previous work [14,15], attapulgite clay supported LaFeO₃ perovskite oxides

doped with Mn was obtained, and found that the formation of “solid solution/coprecipitation” heterostructure demonstrated excellent photo-selective catalytic reduction of NO_x. As another important member in perovskite family, SmFeO₃ owns narrow bandgap which displays promising photocatalytic activity for degradation of inorganic and organic pollutants [16]. However, the pure SmFeO₃ has considerable drawbacks such as large particle size, fast recombination of electron-hole pairs and poor adsorptive performance [17,18]. As a natural clay mineral, ATP has been known with abundant active sites and large specific surface area, making it as a good candidate for adsorbent and the supported catalyst [19]. More importantly, pure ATP has been reported to exhibit absorption in the ultraviolet light region which enable it as a UV responsive semiconductor to some extent [20]. Thus, it is feasible to couple SmFeO₃ with ATP to form SmFeO₃/ATP heterojunction, which favors the efficient separation of electrons and holes.

On the other hand, generally more negative conduction band (CB) potential and more positive valence band (VB) potential render higher reduction and oxidation capabilities [21,22]. For the traditional type of semiconductor heterojunctions, the obvious disadvantage is that the oxidation-reduction capabilities of photogenerated electrons and holes are weakened after charge transfer. Given the virtue of efficient spatial separation of electrons and holes pairs, artificial heterogeneous Z-scheme systems maintained with strong reduction/oxidation abilities can be realized [23]. Among all Z-scheme photocatalytic systems, all-

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solid-state Z-scheme photocatalyst by using solid electron mediators including noble-metal (Pt, Au, Ag) particles as electron mediators have been explored extensively [24], however the high cost and complex preparation limits their wide applications. Alternatively, carbon quantum dots (CQDs) have attracted much more attention due to its low cost and easy accessibility [25,26]. In recent years, CQDs have been proven to be an excellent solid electron mediator in the Z-scheme photocatalytic systems, such as BiVO₄/CQDs/CdS and CQDs/WO₃, demonstrating enhanced photocatalytic activities for water splitting and photocatalytic hydrogen production, respectively [27,28]. Therefore the CQDs may play significant role in the mineral based Z-scheme nanocomposite materials by efficiently achieving high redox potential thus enhance the photocatalytic activity.

In the present work, we rationally designed all-solid-state CQDs/SmFeO₃/ATP Z-scheme nanocomposites which possessed high oxidation-reduction potential on photocatalytic oxidation NO. Moreover, the effect of CQDs on photocatalytic oxidation rate of NO under solar light irradiation is comprehensively investigated by tuning the loading amounts of CQDs. Finally, the possible electron transfer and NO oxidation reactions in CQDs/SmFeO₃/ATP photocatalyst are investigated to unravel the reaction mechanism.

2. Experimental

2.1. Materials

Sm(NO₃)₃·6H₂O and Fe(NO₃)₃·6H₂O were provided by Sinopharm Chemical Reagent Co., Ltd, China. ATP was provided from Jiangsu Nanda Zijin Technology Group Co., Ltd. (Changzhou, China). C₆H₈O₇·H₂O and (CH₂OH)₂ were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. All reagents were of analytical grade and used without further purification.

2.2. Synthesis of carbon quantum dots (CQDs)

CQDs were synthesized according to the method reported in the literature [29]. Typically, 0.5254 g (2.5 mmol) citric acid was dissolved in 12 mL deionized water and stirred to form a clear solution. Then the solution was transferred into a 100 mL Teflon lined stainless steel autoclave. The sealed autoclave was heated to 160 °C in an electric oven and kept for 8 h. The upper solution was collected and centrifuged at 8000 rpm for 5 min. The solid CQDs can be obtained by freeze-drying.

2.3. Synthesis of SmFeO₃/ATP

SmFeO₃/ATP was synthesized by a sol-gel method. 1.75 g of samarium nitrate, 1.59 g of iron nitrate and 1.6 g of citric acid were dissolved in 100 mL deionized water and put into 250 mL breaker, then 100 mL of deionized water and 3 mL ethylene glycol were added to the mixture under ultrasonic dissolving. The mixed solution was maintained at 80 °C under stirring for one hour, followed by the addition of 1 g of ATP. The composite catalyst was obtained after calcined at 600 °C for 2 h.

2.4. Preparation of CQDs/SmFeO₃/ATP

CQDs/SmFeO₃/ATP were synthesized by an impregnation method. In a typical preparation, 1 g of SmFeO₃/ATP was added into 10 mL water after ultrasonic stirring for 1 h at room temperature. 0.01 g of CQDs is added to the as-obtained SmFeO₃/ATP solution by magnetically stirring for 30 min and impregnated for 24 h. The resulting solid was collected by filtration, and dried at 60 °C. The obtained powder was denoted as 1 wt% CQDs/SmFeO₃/ATP nanocomposite. Hereafter, the other samples with different mass of CQDs (2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt% and 7 wt%) were prepared using the same method.

2.5. Characterization

The XRD patterns were taken on a X-ray diffractometer equipped with a Cu anode (D/Max 2500 PC, Rigaku Corporation, Japan), running at 60 kV and 30 mA with 2θ range between 10° and 80° at a scan rate of 0.05° per second. The TEM images were obtained using a transmission electron microscope (JEM-2100, JEOL, Japan), working at 200 kV. The UV-vis diffuse reflection spectra were obtained for the dry-pressed disk samples using a Scanning UV-vis spectrophotometer (UV-vis DRS, UV-2700, Japan) equipped with an integrating sphere assembly, using 100% BaSO₄ as a reflectance sample. The photoluminescence (PL) spectrum was carried on a fluorescence photometer (LS45) with the excitation wavelength of 450 nm. The Fourier transform infrared (FT-IR) spectra were used on a Spectrum 100 spectrometer (PE, USA). The X-ray photoelectron spectroscopy with Al-KαX-ray (hν = 1486.6 eV) radiation operated at 150 W (XPS, Thermo ESCALAB 250, USA) was used to investigate the surface properties. The electron spin resonance (ESR) spectra were recorded at ambient temperature by a JES FA200 spectrometer. The photoelectric analysis was performed on an

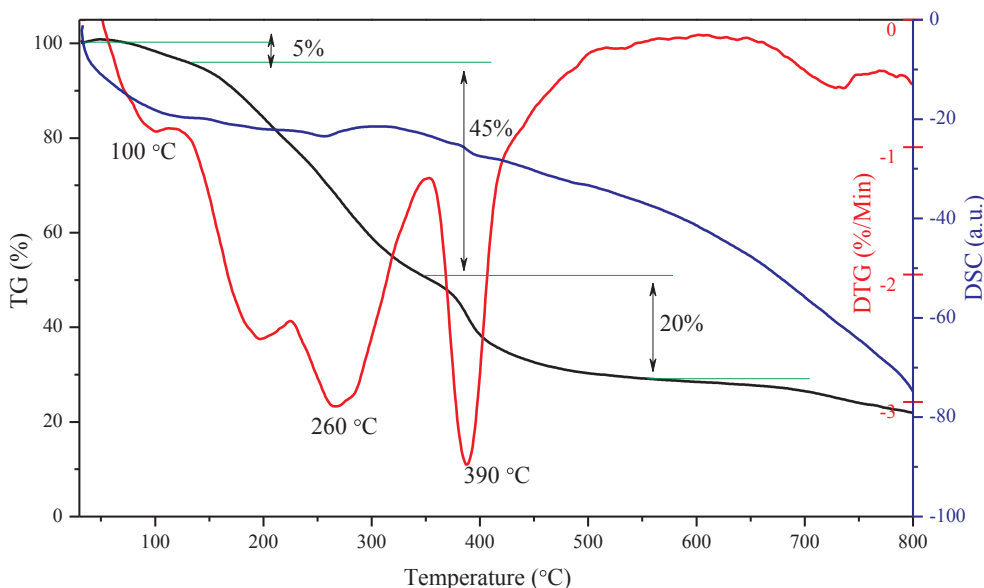


Fig. 1. TG-DSC curves of as-prepared SmFeO₃/ATP gel.

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