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Full Length Article

Mitigation of low methane content landfill gas through visible-near-infrared photocatalysis over Y_2O_3:Er^{3+}/Graphene/TiO_2

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ABSTRACT

Untreated low methane (CH_4) content (less than 10%) landfill gas within the post-methanogenic stage is currently vented into the atmosphere, constituting an important source of anthropogenic greenhouse gas (GHG). Development of a proper mitigation process for low CH_4 gas is therefore necessary for landfills. In this study a special photocatalyst, Y_2O_3:Er^{3+}-TiO_2-0.05% graphene (GR), was synthesized by sol-gel method and then characterized; it showed a good response to visible-near-infrared (Vis–NIR) sunlight. The corresponding absorption edge was 354 nm, and upconversion fluorescence peaks of ultraviolet (364 nm) and violet (408 nm) emissions were acquired under 980 nm excitation. Y_2O_3:Er^{3+}-TiO_2-GR was developed and tested for removal of low CH_4 landfill gas under Vis–NIR light irradiation, and a maximum photodegradation rate of 45.1% for CH_4 was obtained using the photocatalyst Y_2O_3:Er^{3+}-TiO_2-0.05% GR with a light intensity of 2050 mW m^{-2}. The corresponding CH_4 content decreased from 10% to 5.5%, mitigating almost half of GHG during the post-methanogenic stage. The intermediate products of CH_4 degradation were CO, $^{\cdot}OH$, O^-, CO_2 and H_2O traced by *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). This research proposes a new approach for reducing the GHG effect of low CH_4 content landfill gas.

1. Introduction

CH_4 derived from landfills is an important source of greenhouse gas (GHG) emissions, totalling approximately 11–13% of anthropogenic CH_4 emissions [1,2]. CH_4 in landfill gas varies with extended disposal time, and no more than 50% of the total CH_4 in landfill gas can be collected in the methanogenic stage due to landfill gas fugitive and low value landfill gas [3]. Landfill gas with high content CH_4 is relatively straightforward to burn and is often used to generate electricity in modern landfill sites. It is difficult to directly burn landfill gas with a low CH_4 content, such as gas with less than 20% for example [4]. In addition, exploitation of low CH_4 landfill gas as a fuel, such as that typically existing in a landfill at the post-methanogenic stage or in small-scale landfills, is not viable owing to its lower heating value and higher investment requirement.

Landfill sites with a large surface area receive a high exposure to sunlight; therefore, the application of a photocatalyst within the CH_4 conversion process might offer a promising and viable solution. Traditional photocatalytic degradation technology relies on ultraviolet (UV) light, meaning that over 95% of available solar energy cannot be used in this process. The construction of highly efficient visible-near-infrared (Vis-NIR) light responsive photocatalysts is essential for effective photocatalysis. The incorporation of a metal atom [5–8], graphene (GR) [9], and upconversion (UC) material [10,11] in a traditional photocatalyst can contribute to viable utilization of solar energy. NIR accounts for a large fraction within sunlight [12–15], and rare-earth elements can transform low-energy photons to high-energy photons, thereby converting NIR sunlight into visible and UV light [16,17]. A photocatalyst doped with rare-earth elements can improve the utilization efficiency of sunlight. Rare-earth ions doped into semiconductors can acquire electrons to form two valence electrons, such as Er^{2+}, which can promote the separation of photoelectrons from holes [12]. GR may act as an electron bridge to promote the transfer of electrons between TiO_2 particles, which retards recombination and prolongs the carrier lifetime [18].

Some studies have shown the degradation potential of CH_4 under UV irradiation. For example, Villa et al. [19,20] reported the conversion of CH_4 to methanol in an aqueous solution under UV–visible light irradiation with WO_3, while László et al. [21] investigated the photocatalytic conversion of CO_2 and Ar under UV light over Au- and Rh-

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doped titanate nanotubes. Most of the studies were based on the reaction of high concentration CH_4 (20–100%) in aqueous solution under the protection of inert gas using UV light.

In this study photocatalysis was introduced into a landfill to reduce the CH_4 within low CH_4 content landfill gas. Special photocatalysts of TiO_2, Y_2O_3:Er^{3+}-TiO_2, and Y_2O_3:Er^{3+}-TiO_2-GR were prepared by the sol-gel method. Conventional analytical techniques could not be used as the concentration of intermediate products were low; therefore, *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to detect the change of functional groups on Y_2O_3:Er^{3+}-TiO_2-0.05% GR surface, and then to deduce the CH_4 degradation intermediate products. The photocatalytic degradation and mechanism of low CH_4 content (10%) landfill gas under Vis-NIR illumination by catalysis were systematically investigated, with the main objective of reducing the contribution of low CH_4 landfill gas on GHG emissions. The removal of CH_4 through the photocatalytic process within low CH_4 content landfill gas offers a promising solution for the GHG mitigation in landfills.

2. Methods

2.1. The synthesis of photocatalysts

The composite catalysts Y_2O_3:Er^{3+}-TiO_2-GR were synthesized by a sol-gel method (Fig. 1). To enhance UC contribution to photocatalytic activity, Y was chosen as a sensitizer to transfer its energy to Er; this approach of dual ion UC may increase optical absorption in the NIR. For a more detailed description of the synthesis of Y_2O_3:Er_2O_3 (Fig. S1), Y_2O_3:Er^{3+}-TiO_2 (Fig. S2) and graphene oxide (GO) see Experimental methods in Supporting Information.

2.2. Photocatalytic degradation and degradation mechanism of CH_4

The photocatalytic degradation of CH_4 was conducted in a photocatalytic reaction system (Fig. S3 is a diagramatic representation of a photocatalytic reactor). The system was equipped with a photocatalytic reactor and a Vis-NIR light generator, including an SXE-300BF xenon lamp fitted with a UV filter ($\lambda > 400$ nm). The distance between the quartz reactor and xenon lamp was 4 cm. The titanium mesh loaded with 1 g catalyst was placed in the center of the reactor. Before illumination, the mixed gas was transported into the reactor, following which it was placed in the dark for 1 h to achieve an adsorption/desorption equilibrium between catalysts and the mixture gas. The mixed gas comprised CH_4 and CO_2 at a volume ratio of 1:9. The photodegradation experiments were conducted under Vis-NIR light irradiation with a humidity of 23–26% and a temperature of 23–30 °C. At periodic intervals, 1 mL of the mixed gas was extracted from the reactor and analyzed by gas chromatography (GC7900, Shanghai Tian Mei Scientific Instrument Co., Ltd.). Functional groups of intermediate products were tested with an *in-situ* DRIFTS gas analyzer (Thermo Nicolet 8700) equipped with a homemade quartz *in-situ* reactor. The scanning range of the *in-situ* infrared spectrometer was 400–4000 cm^{-1} and the process ran for 180 min.

2.3. Characterizations

The X-ray diffraction (XRD) patterns of the samples were measured using an automated Bruker D8 Advance X-ray Polycrystaline Diffractometer. Morphological observations were achieved by use of a JSM-7800Ffield emission scanning electron microscope (FESEM), a JEM-2100F transmission electron microscope (TEM), and Agilent-5500 atomic force microscopy (AFM). The energy-dispersive spectrometry (EDS) analysis of the samples was performed with a JSM-7800F FESEM. The absorption bands of the catalysts were determined with UV–Vis diffuse reflectance spectroscopy (DRS) and the diagonal of formula $Eg = (\alpha h\upsilon)^{1/2}$ was used to calculate the band gap (Eg). UC fluorescence spectra were measured with a Hitachi F-7000 fluorescence spectrophotometer equipped with a 980 nm semiconductor solid laser with tunable power.

3. Results and discussion

3.1. Properties of the photocatalysts

3.1.1. XRD and morphology analyses

The XRD patterns (Fig. 2a) indicated that all samples contained the anatase TiO_2 phase. The major diffraction peaks were located at 25°, 37°, 48°, and 63°, which match very well with the (1 0 1), (1 0 4), (2 0 0), and (2 0 4) planes of anatase TiO_2 (JCPDS card no. 84-1285), respectively. The XRD results indicated the absence of any other phases of TiO_2 and showed that the main diffraction peaks of the Y_2O_3:Er^{3+}-TiO_2-0.05% GR composites were similar to those of pure Y_2O_3:Er^{3+}-TiO_2 particles (JCPDS card no. 84-1285). The incorporation of Er and Y did not alter the crystalline phase, despite their ionic radii being larger

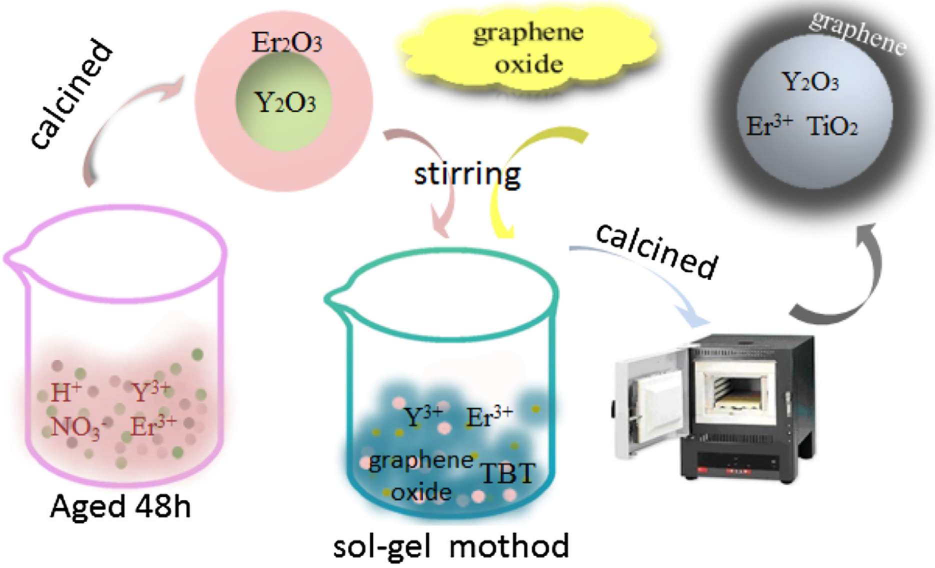

Fig. 1. Synthesis process of Y_2O_3:Er^{3+}-TiO_2-GR.