Chemical Engineering Journal 358 (2019) 389–397

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Plasmonic gold particle generation in layer-by-layer 2D titania films as an effective immobilization strategy of composite photocatalytsts for hydrogen generation

Qian Zhang[a,b], Yihe Zhang[a,*], Ke Xiao[a], Zilin Meng[b], Wangshu Tong[a], Hongwei Huang[a,*], Qi An[a,*]

[a] *Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, PR China*
[b] *School of Resources and Environmental Engineering, Shandong University of Technology, Zibo, PR China*

HIGHLIGHTS

- A surface-immobilized Au-2D titania nanosheets photocatalyst is reported.
- AuNP is generated in layer-by-layer titania nanosheet/polyelectrolyte matrices.
- The films with varying crosslinking degrees allow fine tuning efficiencies.
- The photocatalysts can be reused multiple times.

ARTICLE INFO

Keywords:
Titania nanosheet
Layer-by-layer
Au nanoparticle
Hydrogen generation

ABSTRACT

We propose a strategy for the surface immobilization of composite catalysts consisting of titania nanosheets (TNs) and Au nanoparticles (AuNPs) via the in situ generation of nanoparticles in a covalent LbL (Layer-by-layer) matrix followed by calcination. The thickness and compactness of the TNs and polymer film were finely adjusted to prepare AuNPs of varying sizes and densities, leading to surface immobilized composite catalysts with varying H_2 generating capacities after calcination. The optimized composite catalyst with the addition of 2.5 wt% Pt as cocatalyst presented high performance even comparable to the highest hydrogen generation efficiency by mobilizing particle catalysts containing TNs. The study demonstrates that a proper surface immobilization strategy not only facilitates catalysts application and collection, but also allows for catalytic efficiency to be enhanced by fine tuning the ratios and structures of each of the constituent components.

1. Introduction

Following the development of highly efficient photocatalysts, their controlled application and collection from solution environments after use have become increasingly important [1–4]. Residual photocatalyst that is scattered in an aqueous environment causes severe environmental and ecological problems because of their potent redox properties. In addition, although most photocatalysts are expected to be reused multiple times, efficient strategies for the application and recycling of catalysts remains severely underdeveloped. The immobilization of catalysts on substrates is originally considered to be a promising technique because it facilitates both the application of the catalysts in a controlled location or density and allowed for its collection after use [5,6]. During the application or collection processes, no external energy sources, such as magnetic field or ultrasonic waves, are needed to disperse or collect the catalysts, imposing advantages over the magnetically active composite catalytic particles [7]. The surface immobilization strategy has been explored for various photocatalysts. Such strategies include the use of P25 (Titania particles), BiOX or metal nanoparticles that use chemical vapor deposition, sol-gel methods and electrophoretic deposition; however, all these techniques have provided only limited success. This lack of success is due to previous studies in which surface modification of the catalyst remarkably decreased catalytic efficiency [8–14]. For newer 2D materials, their application and collection from solution using surface immobilization has not been widely studied. The main challenges in achieving superior performance for the surface immobilization of catalysts are the following: First, tight aggregation of the nanosheets must be avoided so as to preserve enough

---

* Corresponding author.
E-mail addresses: zyh@cugb.edu.cn (Y. Zhang), hhw@cugb.edu.cn (H. Huang), an@cugb.edu.cn (Q. An).

https://doi.org/10.1016/j.cej.2018.10.052
Received 20 July 2018; Received in revised form 19 September 2018; Accepted 7 October 2018

void space to allow mass transport of the reactants. Previously, when immobilizing titania particles on substrates using spin coating and sol-gel methods, the aggregation of particles and thus a reduction in the effective catalytic area was considered to be the main factor that suppresses the catalytic performance. In order to avoid this unwanted aggregation, the thickness and interfacial structures must be fine-tuned. Secondly, organic binders have been frequently employed to immobilize catalysts; however, the organic binders are consumed catalytically by photocatalytic active species and so compromise catalytic activity; this subsequently leads to the acceleration in the decomposition of the materials [15]. Thirdly, the immobilization of composite catalysts comprised of several different components requires control of the ratio of the components. Over-dosing of one of the components compromises electron transfer, leading to wasting of material and a reduction in the catalytic efficiency. In light of these difficulties, the surface immobilization of catalysts remains challenging and better strategies are urgently needed.

2D TiO_2 nanosheets (TNs) have demonstrated excellent catalytic power in various applications, including clean energy generation [16,17], pollutant degradation [18], and CO_2 fixation [19]. Among 2D catalysts, the use of TNs has received a lot of attention because of their high efficiency, low toxicity, low cost and chemical stability [20]. However, because pristine TNs could only absorb UV light, composite materials containing Au nanoparticles (AuNPs) were developed in order to render TNs active to visible light activity; this is due to the plasmonic effect of the AuNPs [21–23]. The composite TNs-AuNP catalyst has proved to be highly effective and have found use in various applications [24]. Thus, we chose TNs-AuNP as a model catalyst, which acts as a 2D semiconductor, to demonstrate an effective strategy for the surface immobilization of composite catalysts.

Layer-by-layer (LBL) self-assembly is a well-developed nanofabrication technique that exerts delicate control over the film component, thickness, and the interactions and ratios between various film-building components [25]. The technique is operationally simple and is gaining application at both laboratorial and industrial scales. TNs were immobilized on substrate surfaces using the LBL method [26,27]. However, the preparation of composite TNs-AuNP films with high photocatalytic performance is still challenging because of the multi-component nature of the catalyst. In previous studies, we developed a photochemical method for the preparation of covalently crosslinked LbL films of varying compactness, and demonstrated the film's adjustable compactness could be used for the in situ preparation of inorganic particles of varying size and density [28]. These developments made it possible to prepare catalytic LbL film consisting of multiple components.

In the current work, we report the preparation of a composite TNs-AuNP LbL film using a covalent LbL method followed by calcination. The films with varying compactness were then used as a matrix to generate AuNPs (Fig. 1(a)). Composite films of TNs-AuNPs with delicate structural control and AuNPs with varying densities and sizes, were thus obtained. Afterwards, the films were calcinated at 350 °C to partially carbonate the organic component to enhance the crystallinity of the inorganic components and enhance the film's electron transfer ability. Photocatalytic H_2 production from water indicated that the LbL assembly parameter remarkably influenced the catalytic efficacy, and the medially crosslinked composite film presented the highest photocatalytic performance. The optimized catalyst system presented high performance even comparable to the highest hydrogen generation efficiency by mobilizing particle catalysts containing TNs reported previously. In line with this idea, a novel catalyst immobilization strategy with high performance was proposed. Such structure not only reduces the recombination of the carries but also improves the utilization of solar energy. Meanwhile, the possibilities of practical application and recycling ability are improved. The accounting for the improved photocatalytic activity and the photocatalytic mechanism were discussed in this work. It is anticipated that our report will inspire the development of surface immobilized composite catalysts of all other 2D materials for a wide application.

2. Experimental section

2.1. Materials and characterization

Poly(allylamine hydrochloride) (PAH, Mw, 15000) was purchased from Sigma Aldrich. 4,4′-diazostilbene-2,2′-disulfonic acid disodium salt (DAS) was purchased from TCI Co., Ltd. NaOH, $HAuCl_4{\cdot}4H_2O$, H_2PtCl_6, $N_2H_4{\cdot}H_2O$, H_2O_2 (30 wt%), H_2SO_4, CH_3CH_2OH, CH_3COCH_3, $K_3Fe(CN)_6$ were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. $C_{12}H_{14}Cl_2N_2$ was purchased from Aladdin Co., Ltd. The two-dimensional titania nanosheet was obtained according to the reported literature [29].

UV–Vis absorption spectra were recorded using a UV-6100 UV–Vis spectrometer (Meipuda, Shanghai, China). The morphologies of multilayers were observed by field emission scanning electron microscopy (FE-SEM) (S-4800). Atomic force microscopy (AFM) tapping mode was used to test the thickness and microscopy of the samples. Photoluminescence (PL) spectra were measured on an F97XP fluorescence spectrometer with an excitation wavelength of 317 nm. X-ray diffraction (XRD) was performed on D/MAX-RC with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was characterized on a Thermo Scientific ESCALAB250 instrument with a monochromatized Al Kα line source (150 W). The binding energies were referenced to the C1s line at 284.8 eV from alkyl or adventious carbon. Cyclic voltammetry was performed on an electrochemical analyzer (CHI660B, China) with a three electrode system configuration with Pt wire as the counter electrode and Hg/Hg_2Cl_2 as the reference electrode.

2.2. Layer-by-layer assembly of PAH/TNs multilayers

The quartz substrate and silica wafer were cleaned in a H_2O_2 and H_2SO_4 mixed solution at volume ratio of 3:7 and washed with a large amount of deionized water. First, the quartz substrate was immersed in PAH solution ($1\ mg\ mL^{-1}$, pH = 9.0) for 15 min, washed with deionized water and dried under nitrogen. Secondly, the quartz substrate was immersed in 2D titania nanosheet solution ($0.8\ mg\ mL^{-1}$, pH = 9.0), washed with deionized water and dried under nitrogen. The quartz substrate was then alternatively immersed in PAH and titania nanosheet solution until the desired bilayers were obtained. The multilayers were recorded as $(PAH/TNs)_n$, with 'n' being the number of bilayers.

2.3. Photochemical crossing-linking of the multilayers

The multilayer $(PAH/TNs)_n$ were immersed in DAS aqueous solution ($5\ mg\ mL^{-1}$, pH = 3.8) for 10 s, 2 min and 20 min, and then subjected to UV irradiation to obtain multilayers with low, medium and high crosslinking degrees. The UV irradiation was performed under a 400 W high-pressure mercury lamp with an intensity of $2.5\ mW\ cm^{-2}$ for 300 s. After photochemical cross-linking, the multilayers were immersed in NaOH aqueous solution (pH = 12) for 3 min, then washed with deionized water and dried under nitrogen.

2.4. Loading Au nanoparticle on multilayered films

The multilayered films of varying crosslinking degrees were immersed in hydrazine hydrate (8 wt%) solution for 3 min. The multilayers were then immersed in an aqueous solution of $20\ mmol\ L^{-1}$ chloroauric acid ($HAuCl_4$) for 10 min, followed by washing with deionized water and dried under nitrogen. The multilayers were recorded as $(PAH/TNs)_n$-Au. At last, the film were calcined at 350 °C and recorded as $(PAH/TNs)_n$-Au-350 °C.