



Fabrication and catalytic mechanism study of CeO₂-Fe₂O₃-ZnO mixed oxides on double surfaces of polyimide substrate using ion-exchange technique[☆]



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ABSTRACT

A series of CeO₂-Fe₂O₃-ZnO mixed oxides layers on double surfaces of polyimide film have been fabricated by direct ion exchange technique. The obtained products were thoroughly characterized by various techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), ultraviolet-visible (UV-VIS) absorption spectra and thermogravimetric (TG). The results confirmed that the CeO₂-Fe₂O₃-ZnO mixed oxides were successfully formed and dispersed uniformly on surfaces of polyimide film. The PI/CeO₂-Fe₂O₃-ZnO films displayed a wide visible-light absorption in the range of 400–710 nm and low energy gap at 1.55–1.75 eV. The initial decomposition temperatures of PI/CeO₂-Fe₂O₃-ZnO films were all larger than 550 °C. Moreover, the PI/CeO₂-Fe₂O₃-ZnO films possessed outstanding photothermocatalytic and microwave catalytic activity compared with PI/ZnO nanocomposite film. The removal efficiency of methyl orange with the PIZNNIFE-3 film under UV-VIS-80 °C-H₂O₂ condition and microwave (MW)-H₂O₂ condition in 12.0 min reached respectively up to 92.7% and 98.7%. The improved photothermocatalytic activity could be mainly attributed to the electrons and holes transfer and the thermal oxidation of Ce³⁺ ions. The high microwave catalytic activity was due to the effect of MW “hot spots”, microwave thermally induced electron/hole pairs and high thermal oxidation of CeO₂. This study introduces a new class of promising sunlight-driven photocatalytic nanocomposites with outstanding comprehensive performance.

1. Introduction

Semiconductor-based metal oxides are widely used in treatment of wastewater [1], especially dyes, due to their low cost, low toxicity, recyclability, and the ability to facilitate multi-electron transfer processes. However, single-component metal oxide has some drawbacks, such as the rapid recombination of photo generated charge carriers of ZnO [2–4], the low spectral responsive range of TiO₂ [5–7], the poor thermal and chemical stability of CeO₂ [8,9], et al. Mixed metal oxide has attracted increasing interests because its unique physical and chemical properties. Due to the synergistic effect of individual metal oxide, the drawbacks of individual metal oxide can be overcome and the catalytic activity can be improved.

Owing to the high value of exciting binding energy and suitable band gap (3.37 eV), ZnO exhibits high photocatalytic efficiency in degradation of organic pollutants. One major drawback of ZnO is the low quantum efficiency, which is due to very fast recombination of photo

generated electron-hole pairs [10–12]. Similarly, CeO₂ has a band gap (3.2 eV) similar to TiO₂ and holds promise as a suitable photocatalyst for the degradation of organic pollutants. More importantly, CeO₂ is one of the efficient thermocatalysts, owing to its remarkable Ce⁴⁺/Ce³⁺ redox properties giving rise to oxygen vacancies [13]. However, the use of pure CeO₂ in a heterogeneous catalytic reaction is still limited due to its poor thermal stability. The mixed metal oxides of ZnO and CeO₂ have been proposed as photocatalysts and redox mediators for organic pollutant detection and degradation. Fine ZnO/CeO₂-based particles with very small sizes exhibit unique UV-absorbing abilities, excellent catalytic activities [14–17]. Recently, a synergetic effect of photothermocatalysis was reported by several groups [18,19]. And, perhaps most impressively, with the synergetic effect of photocatalysis and thermocatalysis, significant enhancement in the catalytic activity of ZnO/CeO₂ mixed oxides was achieved under hot environments. However, a relative fast recombination of photo generated electron-hole pairs and a relative low thermal stability still limited the application of

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the ZnO/CeO₂ mixed oxides. Therefore, it is necessary to find novel ways how to combine other semiconductors to improve the catalytic efficiency of ZnO/CeO₂ mixed oxides. It has been proved that combining some semiconductors with different band gaps to form heterojunctions in photocatalytic systems could drive the photogenerated electrons and holes to the opposite directions, thereby minimizing their recombination [20,21]. In addition, a general way to overcome thermally induced negative effects was to introduce transition metal ion into the CeO₂ lattice to form the solid solution [22]. Fe₂O₃ is a narrow band gap (1.9–2.2 eV) semiconductor which is suitable to be coupled with ZnO to enhance the separation of photo-generated electron-hole pairs [23]. Fe₂O₃ is also a possible donor which can be used as a sensitizer under visible irradiation because it can be transfer electrons to wide band gap semiconductors such as TiO₂ and ZnO. Recently, some combinations of ZnO with Fe₂O₃ showed the increase photocatalytic activity by increasing the charge separation and extend visible response [24]. Also, as reported in other studies, by combining Fe₂O₃ and CeO₂ can improve the thermal stability and long-term catalytic stability of the pure CeO₂ [25–27]. Thus, we expect that the combination of Fe₂O₃ with ZnO/CeO₂ mixed oxides can be the viable option to overcome the aforementioned problems. To the best of our knowledge, there are few reports on CeO₂-Fe₂O₃-ZnO mixed oxides for the degradation of organic pollutants. Additionally, Fe₂O₃ and CeO₂ have a certain microwave absorption capacity. The conversion of microwave energy from the absorption energy into heat promotes the thermal catalytic efficiency of CeO₂. Thus, we also expect that the CeO₂-Fe₂O₃-ZnO mixed oxides have high microwave-induced catalytic oxidation activities.

It is very indispensable to enhance the desired properties of the CeO₂-Fe₂O₃-ZnO mixed oxides by dispersing them over a thermally stable support material. Polymeric materials are especially preferred due to excellent flexibility and easy machining according to the specific application shape [28,29]. Among them, aromatic polyimide (PI) has been considered to be one of the most important support materials, because of its excellent mechanical properties, thermal stability and chemical resistance [30,31]. Meanwhile, the PI supported mixed metal oxides has been demonstrated for enhancing photocatalytic efficiency, as a result of mixed metal oxides modifying by large conjugated aromatic structure of PI [32]. However, owing to the generated charges fast transfer from mixed metal oxides to PI, the energy efficiency of the PI supported mixed metal oxides is still low. The combination of Fe₂O₃ with ZnO/CeO₂ mixed oxides can increase the lifetime of excited electrons and holes and improve the interfacial charge transfer efficiency to adsorbed substrate. Therefore, it can be presumed that the CeO₂-Fe₂O₃-ZnO mixed oxides supported by PI are very useful for the catalytic oxidation of organic pollutants. On the other hand, immobilization of CeO₂-Fe₂O₃-ZnO mixed oxides on PI surface is an effective route to overcome disadvantages of being difficult to reclaim CeO₂-Fe₂O₃-ZnO mixed oxides nanoparticles from the reaction medium.

Diverse approaches were developed to prepare functional inorganic oxide nanoparticles [33–37]. Among them, the ion-exchange technique to prepare PI/metal oxide nanocomposites had its unique advantages [38–42]. The major advantage of ion-exchange technique lies in better dispersion that the nano-layer metal oxide can be dispersed uniformly on surfaces of polyimide film by the controlling of the size, thickness and distribution of the metal oxide nanoparticle. Another advantage is that altering distribution of the mixed metal ion in vertical and

horizontal PI matrix via ion exchange reaction can easily obtain heterostructured metal oxides on the surface of PI. Thus, we also expect that the fabrication of CeO₂-Fe₂O₃-ZnO nanoparticles onto polyimide surfaces can decrease the tendency of nanoparticle aggregation and improve the dispersion of CeO₂-Fe₂O₃-ZnO nanoparticles.

With this background, the aim of the present work was to study the effect of the PI supported CeO₂-Fe₂O₃-ZnO mixed oxides on catalytic oxidation of organic pollutants. Accordingly, the PI supported CeO₂-Fe₂O₃-ZnO mixed oxides were, for the first time, prepared by ion-exchange technique. The effects of initial Ce, Fe and Zn ion loading in different proportions on microstructure, thermal properties, and catalyzed properties of the final PI supported CeO₂-Fe₂O₃-ZnO mixed oxides were also studied.

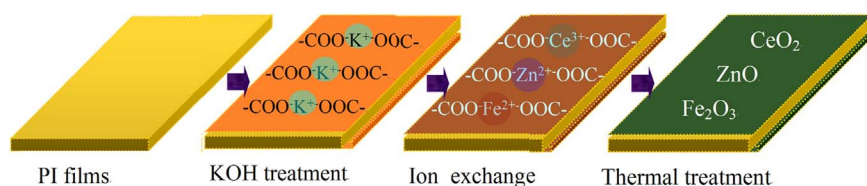
2. Experimental

2.1. Materials

Polyimide (a-BPDA, s-BPDA, 4,4'-ODA and PDA) films with thickness of 50 μm were prepared by our laboratory. The preparation procedure for polyimide films is referred to our previously work [30]. The co-poly (amic acid)s (PAAs) were synthesized by adding solid of a-BPDA (0.02 mol) and s-BPDA (0.08 mol) to a stirred mixture solution of 4,4'-ODA (0.01 mol) and PDA(0.09 mol) in DMAC in a nitrogen atmosphere at 0 °C. The reaction mixture was stirred for 0.5 h at this 0 °C, after that it was heated to room temperature and stirred for 48 h. The obtained PAAs solutions were coated onto clean, dry plate-glass and then dried at 60 °C for 2 h in an air-convection oven. The coatings were cured by heating under mild thermal conditions in follow stages: at 100 °C for 40 min, 125 °C for 30 min, 145 °C for 20 min, 185 °C for 10 min, 220 °C for 20 min, 260 °C for 20 min, 300 °C for 40 min, 330 °C for 20 min, 350 °C for 20 min. The PI films were rinsed by ultrasonic cleaning for 10 min in deionized water and dried in ambient environment prior to use. Zinc nitrate (Zn(NO₃)₂·6H₂O), Cerium nitrate (Ce(NO₃)₃·6H₂O), Ferrous nitrate (Fe(NO₃)₂·6H₂O) and Potassium hydroxide(KOH) was purchased from Shanghai Chemical Reagent Plant. All chemicals were analytical grade and used without further purification.

2.2. Preparation of composite films

The procedures for preparing PI/CeO₂-Fe₂O₃-ZnO films are illustrated in Scheme 1. The determination of the preparation conditions is based on the relevant literature [39,41] and previous experiments. First, PI films were treated by 2 mol/L aqueous KOH solution at 50 °C for 5 h to perform alkaline-induced hydrolysis resulting in the cleavage of the imide rings and the formation of carboxylates, and then washed with deionized water and blown dry with air. The surface modified films were next immersed into Zn(NO₃)₂, Ce(NO₃)₃ and Fe(NO₃)₂ mixed solution (0.1 mol/L Zn(NO₃)₂, Zn:Ce:Fe = 1:0:0, 2:1:1, 4:1:1,6:1:1 and 8:1:1, molar ratio) at room temperature for 3 h under the batch ultrasonic condition to incorporate Zn, Ce and Fe ions into the films through an ion-exchange reaction between potassium and Zn, Ce and Fe ions. After ion exchange, the films were rinsed by deionized water to remove the surface residual mixed solution and dried in ambient atmosphere. Finally, the precursor films were reimidized by slowly heating to 410 °C within 3 h in a forced air oven and were kept at 410 °C for 4.5 h, in which the hydrolyzed polyimide surface was reimidized coupled, the



Scheme 1. Schematic process for the PI supported CeO₂-Fe₂O₃-ZnO mixed oxides preparation.

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