

Shape-Controlled Synthesis of CeO₂ Nanotube Using P123 Triblock Copolymer and Its Application in Catalytic Ozonation

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Abstract—CeO₂ nanotube with improved catalytic properties has been synthesized by a simple precipitation method using P123 triblock copolymer as surfactant. The prepared samples were characterized by X-ray diffraction, Scanning electron microscopy and BET surface area analysis. The activity of the material in catalytic ozonation degradation of organic pollutants in textile wastewater was investigated. The results showed that the presence of P123 could improve the crystallization of CeO₂ particles and slightly enlarge their specific surface area. The catalytic efficiency of the as-prepared CeO₂ nanotube with P123 adjusted is higher than that of CeO₂ nanotube with urea treatment. The spent catalyst could be recycled with only slight decline in catalytic activity.

Keywords-nanotube CeO₂; P123; catalytic ozonation; mineralization of organics

I INTRODUCTION

Estimates indicated that about 2.8×10^5 tons of the textile dyes are discharged into water sinks through textile effluents annually [1]. With the increase in stringent legislation, discharge of even a small quantity (around 1 mg/L) of dye is not acceptable. Therefore, treatment of these textile effluents characterized by high COD (150-10000 mg/L), BOD (100-4000 mg/L), pH (6-10) and color content (50-2500 mg/L) has always been a major concern in the textile industry [2]. Conventional treatment methods, including adsorption, coagulation, filtration and biological treatment, have been proven unsuccessful to treat the organic dyes having complicated structures [3,4]. Ozonation, characterized by the features of no sludge formation, potential to perform decolorization and degradation in a single step and decomposition of residual ozone into water and oxygen, is considered as an efficient option for in-situ production of H₂O₂/HO[·] for dye degradation [5]. However, Ozone decomposition in water is strongly pH dependent and reactions of ozone with organic molecules usually lead to the formation of aldehydes and carboxylic acids that are resistant to ozone attack[4]. To overcome this problem, catalytic ozonation is an efficient alternative because controlled decomposition of ozone into HO[·] resulting in effective mineralization of dyes happened in the presence of catalysts [6].

Cerium oxide is an important component in many heterogeneous catalytic processes. One of its key characteristics is the ability to provide or remove oxygen in chemical reactions. Performance of catalytic ozonation can

further be improved in the presence of CeO₂ as it enhances the chances of in-situ HO[·] radical formation [7]. However, the different crystallographic faces of ceria present significantly different surface structures and compositions that may alter the catalytic reactivity [8]. For this, our previous paper demonstrated the activity of CeO₂ with different morphologies for ozonation of lemon yellow [9]. We observed that improvement in the performance of ozonation was due to the presence of CeO₂. Moreover, this improvement depends on morphology properties of CeO₂ i.e. pore volume and surface area and CeO₂ nanotube was found to have the highest catalytic efficacy.

Many researches found that the addition of P123 can act as both a reducing agent and colloidal stabilizer in the synthesis of nanomaterials having various sizes and shapes. Thus, in this work, CeO₂ was prepared using P123 as a crystal structure and physical property controlling agent. The performance of the catalytic ozonation system was evaluated in terms of the extent of mineralisation achieved when it was applied to treatment of a given textile wastewater.

II EXPERIMENTAL

A. Materials

Textile wastewater used in the catalytic ozonation experiments, was collected from JiangXi Worldbest JiangFang Textiles Printing & Dyeing CORP located in Nanchang, China. The original effluent has a COD of 150 mg/L and color of 500 (pH 7.5), containing reactive dyes. All chemicals used were reagent grade and were supplied by Xilong Chemical Co. Ltd China or Sinopharm Chemical Reagent Co. Ltd China.

B. Catalyst Preparation and Characterization

In a typical synthesis of CeO₂ nanotubes, 5.80 g of pluronic P123 block copolymer with molecule of 5800 was dissolved in 40mL mixture of ethyl alcohol and deionized water (V:V, 1:1) and 1.86 g of CeCl₃·7H₂O was then added. After vigorous stirring for 30 min, 3 mL NH₃·H₂O was dropwise added and the pH value of this solution was adjusted to 10. The formed suspension was transferred to a 50mL Teflon-lined stainless steel autoclave and kept at 160°C for 72 h, followed by cooling and filtration. The solid products were washed with deionized water and ethyl alcohol respectively for three times and dried at 60°C for 10h. The resultant product was a yellow powder signed as CeO₂-P123 nanotubes.

In order to compare the relationship between morphology and catalytic property, another CeO₂ nanotube was prepared by sol-gel method with Ce(NO₃)₃·6H₂O and urea as host [9] and it was signed as CeO₂-urea nanotubes.

C. Catalyst Characterization

The composition and crystalline phase of the nanotubes were studied with X-ray powder diffraction (XRD) equipped with intense CuK α radiation ($\lambda = 1.54059\text{\AA}$) in a continuous scan mode in the 2θ ranging from 10° to 70° . Their morphologies and microstructure were investigated with Nova Nano 450 scanning electron microscope (SEM) operating at an accelerating voltage of 80 kV. The Brunauer-Emmett-Teller (BET) surface (S_{BET}) areas of the samples were determined from nitrogen adsorption at 77 K on a Quantachrome Nova 2000e surface area and pore size analyzer.

D. Catalytic Ozonation Experiment

Catalytic ozonation experiments were carried out in a semi-continuous reaction mode under room temperature. Catalyst and textile wastewater were mixed in the reactor and then the ozone was bubbled into it through the porous plate of the reactor bottom. Samples were taken from the reactor every 20 minutes to measure the TOC. An aliquot of 0.1M Na₂S₂O₃ was subsequently added to the sample to quench the aqueous ozone remaining in the reaction solution. The samples were filtered through a Millipore filter (pore size 0.45 μm) and the TOC of the solution was analyzed by a Shimadzu CPHL-5000A TOC Analyzer.

III RESULTS AND DISCUSSION

A. XRD Analysis

The crystalline nature, phase, and purity of the as-prepared CeO₂ nanotubes were determined by X-ray diffraction (XRD). Fig. 1 shows the XRD patterns of both nanotubes. Both patterns exhibit peaks that correspond to (110), (200) and (220) planes at 29° , 33° and 48° , which match well with the diffraction data of standard CeO₂ powder (JCPDS card no 43-1002). However, a careful comparison shows these diffraction peaks in the pattern of CeO₂-P123 nanotubes are less sharp than in that of CeO₂-urea nanotubes. No diffraction peaks were found to be indexed as the (222) and (400) reflection but new diffraction peaks at 15° , 27° , 32° and 40° can be observed in the pattern of CeO₂-P123 nanotubes, which means the surface structure of CeO₂ changes during crystallization with the addition of P123. Of these new present planes, (100) and (201) planes are stable in spite of their weak catalytic activities, which is important in enhancing the stability of materials. Meanwhile, another new present plane (111) is structure with good activity, which plays great role in strengthening the catalytic activity.

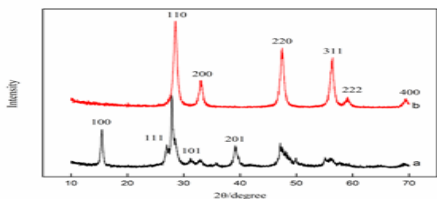


FIGURE I: XRD PATTERNS OF THE SAMPLES: CeO₂-P123 (A) AND CeO₂-UREA (B).

Further information about the crystallite size of these samples was obtained from Scherrer equation (Table 1). It is suggested that the average grain size decreased with the addition of P123, indicating that P123 had a depression effect on the grain growth.

B. SEM Analysis

The morphologies of products were examined by SEM. As shown in Fig 2, with the addition of P123, the nanotubes form and arrange more regular and the length of tubes are uniform and the aggregations seldom occur.

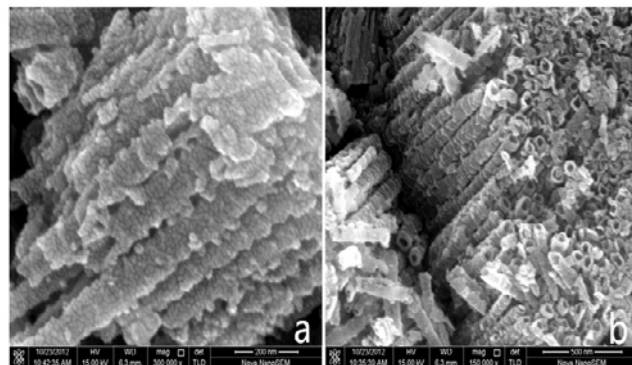


FIGURE II: SEM IMAGES OF CeO₂-UREA NANOTUBE (A), AND CeO₂-P123 NANOTUBE (B).

C. Nitrogen Adsorption Test

The nitrogen adsorption-desorption isotherms of the CeO₂ nanotubes are depicted in Fig. 3. As can be seen, with a typical H₂ hysteresis loop, the isotherms belong to type IV Langmuir adsorption [9]. In the low pressure section gentle adsorption amount increases at this time of N₂ adsorbed in a single layer in a multilayer mesoporous surface when the pressure in the $0.6 < P/P_0 < 1$. Large pore capillary condensation phenomenon of adsorption can be suggested.

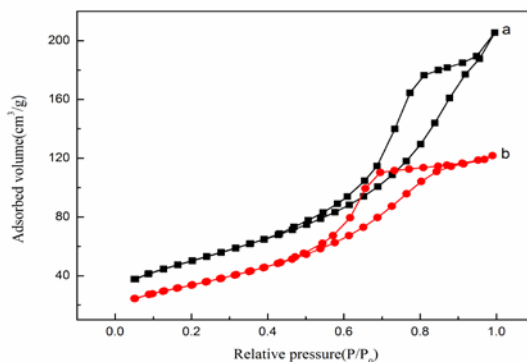


FIGURE III: N₂ ADSORPTION-DESORPTION CURVE: CeO₂-UREA NANOTUBE (A), AND CeO₂-P123 NANOTUBE (B).

From Table 1 it can be seen that the surface area of CeO₂-P123 nanotube is 180.04 m²/g, which was much higher than that (120.20 m²/g) of reference CeO₂ nanotube (CeO₂-urea). It is apparent that the introduction of P123 reduces the coalescence of neighboring particles.

TABLE I: TEXTURAL PROPERTIES OF THE MATERIALS.

Sample	Crystallite size (nm)	S_{BET} (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
CeO ₂ -urea	33.41	120.20	6.05	0.19
CeO ₂ -P123	18.23	180.04	7.06	0.32

D. CeO₂ Catalytic Ozonation

Fig. 4 provides the mineralization curves of organic pollutants in textile wastewater as a function of reaction time in the O₃, CeO₂-P123/ O₃, CeO₂-urea/ O₃ and Activated carbon (AC)/ O₃ processes. As shown, the total organic carbon in textile wastewater decreased with the increasing reaction time in ozonation alone, ozonation/ CeO₂-P123, ozonation/ CeO₂-urea, and ozonation/AC. Compared with ozonation alone, TOC removal was significantly accelerated in the presence of catalysts and the removal rates of TOC reached 70.5% in 120 min in ozonation/AC and ozonation/CeO₂-P123. As for the cases of comparative CeO₂ nanotube catalysts, similarly, they showed different growth of TOC removal efficiency in catalytic ozonation. The TOC removal rate was 65.2% and 80.5% in catalytic ozonation for CeO₂-P123 and CeO₂-urea catalysts, respectively. Based on the measured surface properties of CeO₂-P123 and CeO₂-urea samples, it seemed that the CeO₂-P123 sample with high surface area may have a high density of surface hydroxyl groups. This was because the high surface area of catalyst tended to increase the interaction with H₂O leading to the formation of more surface hydroxyl groups[10-11].

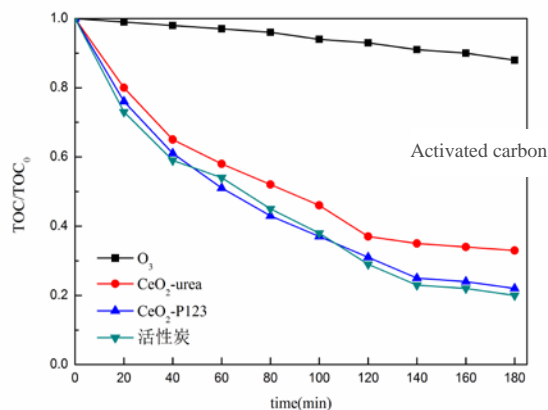


FIGURE IV: CATALYTIC PROCESSES FOR THE MINERALIZATION OF ORGANIC POLLUTANTS IN TEXTILE WASTEWATER (CATALYST: 0.5 G, OZONE DOSAGE: 15 MG/MIN).

IV CONCLUSIONS

With CeCl₃·7H₂O as cerium source and P123 as soft template agent, a CeO₂ nanotube was synthesized using hydrothermal method, and the sample was characterized in composition, morphology and surface properties. The sample's efficiency in catalytic ozonation of organic pollutants in textile wastewater was also investigated when compared with those of activated carbon and CeO₂ nanotube which was made by combining Ce(NO₃)₃·6H₂O and urea. The CeO₂-P123 nanotubes exhibited the highest activity in TOC removal,

which could substitute activated carbon for catalytic ozonation of organic pollutants in textile wastewater.

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