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Sandwich-like Co_3O_4/MXene composite with enhanced catalytic performance for Bisphenol A degradation

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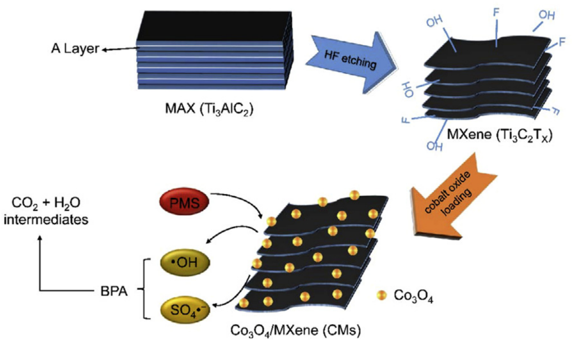
HIGHLIGHTS

- The Co_3O_4/MXene (CMs) composite was first presented for activation of PMS.
- CMs/PMS system exhibited dramatic catalytic activity for BPA degradation.
- Wide pH range and favorable Anti anionic property were achieved.
- Mechanisms and proposed pathway of BPA degradation in CMs/PMS system were revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

MXene, as an emerging group of two-dimensional layered material, attracted more and more attention due to its extraordinary physical properties. In this study, a sandwich-like Co_3O_4/MXene (CMs) composite was prepared via a one-step heating method and used as a novel catalyst to activate peroxymonosulfate (PMS) for Bisphenol A (BPA) degradation. The sample (CM-20%) achieved an efficient catalytic activity with 95% removal of BPA at 20 mg/L within 7 min. Meanwhile, the parameters in the degradation process were optimized. In particular, CM-20% obtained excellent BPA removal efficiency in a wide pH range (4–10). Anions like NO_3^- and Cl^- had a slight negative effect while HCO_3^- had a great negative effect on catalytic activity in CM-20%/PMS system. Notably, the catalyst exhibited a good performance after 5 consecutive runs and the leached cobalt ion was negligible. Electron paramagnetic resonance (EPR) analysis and quenching tests identified $SO_4^{\cdot -}$ and $^{\cdot}OH$ were the reactive species. The pathway of degradation was also detected by analyzing its intermediates using LC-MS. This work provides a new field of MXene composite material for PMS remediation of organic pollutant and widens the application of MXene in environmental remediation field.

1. Introduction

Endocrine disrupting compounds (EDCs), acting as a structurally diverse class of emerging contaminants, have generally been detected in water environments, which can affect the human endocrine systems with synthesis, secretion, transport, action or elimination of natural hormones in the body [1,2]. Among the series of EDCs, Bisphenol A (BPA) has attracted much attention due to its acutely toxic to the

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aquatic organisms [3,4]. Currently, sulfate radical ($SO_4^{\cdot -}$) based advanced oxidation processes (AOPs) emerged as an environmentally cost-effective technology for degrading most organic contaminants due to their higher redox potential (2.5–3.1 V) than that of the hydroxyl radical ($^{\cdot}OH$) (1.8–2.7 V) [5–8]. In $SO_4^{\cdot -}$ production, the chemical oxidants of peroxymonosulfate (PMS) and persulfate as precursors could be activated by heat [9], transition metal ions [10,11], UV [12], ultrasound [13] and electrochemical processes [14,15]. Transition metals (Co, Fe, Cu and Mn) exhibited superiority compared to other methods because of low cost and reusability [16]. Among them, the Co^{2+}/PMS system demonstrates the best performance that is even superior to traditional Fenton reaction at neutral pH and with lower dosage of reagents [10]. However, the cobalt leachate may result in metal pollutant and ecological toxicity [17]. Therefore, to achieve relatively higher stability, Co_3O_4-based AOPs have been extensively investigated. Since the activation of PMS by heterogeneous cobalt sources has been attracted great attention recently, incorporating Co_3O_4 on support is thrived to further improve the catalytic activity and stability [18].

Owing to the rich active sites and high surface areas, two-dimensional (2D) materials, such as graphene and zeolite nanosheets, have been considered as perfect catalyst support [18]. Recently, a novel kind of 2D layered materials, MXene, first reported in 2011 [19], prepared by removing A layers from $M_{n+1}AX_n$ (M represents an early transition metal, A is assigned to an IIIA or IVA group element and X is either C or N component, n = 1, 2, 3), has stimulated extraordinary enthusiasm due to hydrophilic surfaces, excellent electrical conductivities and environment-friendly characteristic. So far, the most studied MXene is $Ti_3C_2T_X$ (T_X represents surface groups such as -OH and -F) [20]. Some major industrial problems can be solved by the possible applications of MXene such as energy storage and Li-batteries [21]. The unique layered structure of MXene could provide more space for immobilization of functional nanomaterials and improve their distribution on MXene surface, which may grant the possible applicability of MXene as potential supporting materials for environmental remediation (e.g., catalysis, adsorption). Little is known, however, about possible applications for water purification [22]. It is reported that Fe_3O_4/MXene composites exhibited excellent performance for phosphate removal from wastewater [23]. Overall, MXene presents a promising prospect for pollutant removal, and gives an opportunity to extend the application for AOPs in environmental remediation field. However, to best of our knowledge, there is limited report on MXene used for AOPs, especially Fenton or Fenton-like reaction in organic contaminant degradation.

Herein, we firstly demonstrated a facile synthesis route to attain a unique sandwiched Co_3O_4/MXene (CMs) composite as a heterogeneous catalyst to activate PMS for BPA removal. The structure of nanocomposites was characterized by scanning electron microscope (SEM) and transmission electron microscopy (TEM). The distribution of Co_3O_4 nanoparticles on the surface of MXene was investigated using SEM mapping. CM-20% achieved an excellent catalytic activity with 95% degradation of BPA at 20 mg/L within 7 min, which was much more efficient than the most of reported catalysts. Effect of parameters (initial pH, concentration, reaction temperature, PMS dosage and anions) on catalytic efficiency of CMs was studied in detail. Furthermore, quenching tests and electron paramagnetic resonance (EPR) analysis were employed to identify the reactive radicals ($SO_4^{\cdot -}$ and $^{\cdot}OH$). A plausible mechanism of BPA degradation was investigated based on LC-MS.

2. Experimental

2.1. Chemicals

Titanium aluminum carbide (Ti_3AlC_2, purity ≥98%, 200 mesh) was purchased from Forsman Company (Beijing, China). Hydrogen fluoride (HF, 40%) was purchased from J&K Chemical (Shanghai, China). Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), Bisphenol A (BPA) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH), ethanol, methanol, tert butyl alcohol (TBA), sodium nitrate ($NaNO_3$), sodium carbonate ($NaHCO_3$) and sodium chloride (NaCl) were purchased from Nanjing Chemical Reagent Co., Ltd. Potassium peroxymonosulfate (available as Oxone, PMS, $KHSO_5{\cdot}0.5KHSO_4{\cdot}0.5K_2SO_4$) was obtained from Sigma-Aldrich. 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) was supplied from J&K Scientific. All the chemicals and materials were used as received without further purification. Deionized water (Millipore) was used in all experiments.

2.2. Preparation of CMs

MXene phase synthesis followed Naguib et al. with hydrouoric acid (HF) [19,24]. Typically, 3 g of as-purchased Ti_3AlC_2 was immersed in 35 mL HF and sealed in a polytetrafluoroethylene cup for 72 h at 313 K. After this procedure, Al layer was selectively etched from Ti_3AlC_2. The obtained material was washed and centrifuged by deionized water for several times to remove the residue impurities until pH > 5.5, and then dried in vacuum oven at 333 K overnight until reaching a constant weight.

The CMs composites were synthesized by a simple impregnation and evaporation method. To obtain catalyst with different Co_3O_4 contents, 1 g $Ti_3C_2T_X$ and different mass of $Co(NO_3)_2{\cdot}6H_2O$ (0.35, 0.7, 1.05 g) were mixed into 5–6 mL deionized water. The mixture was stirred vigorously at 333 K to evaporate the water. The obtained products were grounded into powder and heated to 473 K for 12 h with the ramping rate of 2 K/min in an ambient environment. After cooling to room temperature, the obtained catalysts were washed by deionized water for three times to remove the residue impurities, and labeled as CM-X (X was denoted as 10%, 20% and 30% according to the Co_3O_4 proportion of MXene quality). Meanwhile, CM-0 was also obtained by calcined $Ti_3C_2T_X$ at 473 K for 12 h in air without adding $Co(NO_3)_2{\cdot}6H_2O$. The pure Co_3O_4 was prepared according to our previous work [25].

2.3. Characterization

The X-ray diffraction (XRD) patterns were recorded by X-ray powder diffractometer with Cu Kα (λ = 1.5418 Å) radiation. N_2 adsorption/desorption isotherms were conducted by using a Micromeritics ASAP-2020 analyzer at liquid nitrogen temperature (−196 °C). The specific surface areas were measured using the Brunauer–Emmett–Teller (BET) method. Scanning electron microscopy (SEM) analysis was performed on an FEI Quanta 250F system. Transmission electron microscopy (TEM) analysis was operated on an FEI Tecnai 20 electron microscope with 200 kV. Energy dispersive X-ray spectroscopy (EDS) analysis was performed by using an energy dispersive X-ray spectrometer. The X-ray photoelectron spectroscopy (XPS) analysis was obtained using a PHI Quantera II ESCA System with Al Ka (1486.8 eV).

2.4. Batch experimental procedure

All the degradation experiments were carried out in a 200 mL beaker with a constant stirring at 350 rpm. In a typical reaction of BPA degradation, 100 mL aqueous solution containing 20 mg/L of BPA and 0.3 g/L of PMS were prepared. The pH value of the reaction medium was adjusted by 0.1 M HNO_3 and 0.1 M NaOH. After that, 10 mg CMs was added. 750 μL samples were taken out from reaction mixture at different time intervals and quenched with methanol, analyzed to determine the concentration of BPA. The zeta potential of the catalysts was conducted via a Zeta meter (ZetaPALS, Brookhaven Instruments, USA). Total organic carbon (TOC) was operated using a TOC analyzer (vario TOC, Elementar). All controlled experiments were carried out in the same conditions. During the cycling tests, CMs catalyst was collected by centrifugation and washed with deionized water after each