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High activity of g-C_3N_4/multiwall carbon nanotube in catalytic ozonation promotes electro-peroxone process

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HIGHLIGHTS

- The composition with g-C_3N_4 improves electronic conductivity of CNT.
- The composition with g-C_3N_4 increases the activity of CNT in catalytic ozonation.
- Catalytic ozonation benefits for organics degradation in electro-peroxone process.
- The yield of hydroxyl radical is enhanced in this process.

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ABSTRACT

Three kinds of graphitic carbon nitride materials (bulk, porous and nanosheet g-C_3N_4) were composited with a multiwall carbon nanotube (MWCNT) by a hydrothermal method, and the obtained b-C_3N_4/CNT, p-C_3N_4/CNT and n-C_3N_4/CNT materials were used in the electrodes for electro-peroxone process. It was found that the n-C_3N_4/CNT composite exhibited the highest efficiency in oxalate degradation, though it performed the worst in the oxygen-reduction reaction for H_2O_2 production. The n-C_3N_4/CNT composite exhibited higher activity than CNT and other composites in catalytic ozonation experiments, due to the higher pyrrolic-N content modified on the CNT surface and higher surface area. It also has higher electron transfer ability, which benefited to the electro-reduction of both O_2 and O_3. The result confirmed that catalytic ozonation process was an important means to enhance the degradation efficiency in the electro-peroxone process, besides peroxone process and O_3-electrolysis.

1. Introduction

As an efficient advanced oxidation process (AOP), peroxone process has attracted great attention in the remediation of wastewater (De Witte et al., 2009; Wu and Englehardt, 2015; Deeudomwongsa et al., 2017; Meshref et al., 2017). Utilizing the reactive oxygen species (ROS) generated in the reaction between O_3 and H_2O_2 (Eq. (1)), rapid and complete mineralization of aqueous organic pollutants could be achieved. However, the potential risk arising from the transportation and storage of external added H_2O_2 became the bottleneck for the further development of the peroxone process (Guo et al., 2015). Moreover, the discharge of the unreacted O_2 for O_3 production caused waste of resources. The recently developed electro-peroxone process successfully prevailed over these deficiencies in peroxone process (Wang et al., 2015; Yao et al., 2017). H_2O_2 is in-situ produced from the oxygen-reduction reaction (ORR) via 2-electron pathway (Eq. (2)), which circumvents the risk of H_2O_2 transportation and storage and improves the utilization of O_2 at the same time (Bakheet et al., 2013; Zhang et al., 2016; Wu et al., 2017). Meanwhile, highly active ROS could also be generated from the O_3 electrolysis process (Kishimoto et al., 2005). The synergistic effect between the peroxone process and O_3 electrolysis could significantly enhance the degradation efficiency in the electro-peroxone process.

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$$H_2O_2 + O_3 \rightarrow \bullet OH + O_2^{\bullet-} + H^+ + O_2 \quad (1)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

Unfortunately, some drawbacks have been gradually revealed in term of the degradation experiments in the electro-peroxone process. Firstly, the reaction rate between O_3 and H_2O_2 was significantly affected by the solution pH, and alkaline solution was obviously benefited to the peroxone process (Von Sonntag and Von Gunten, 2012). However, carboxylic acids with low molecular weight were often produced as intermediates in the degradation of refractory organic compounds. This would lower the solution pH to decrease the degradation efficiency. Secondly, the relatively small size of electrode in a much larger volume of solution has limited ability in H_2O_2 dispersion and O_3-electrolysis, and thus leads to low utilization ratio of O_3. Moreover, the effect of peroxone and O_3-electrolysis are considered in the electro-peroxone process, but very few researches concerned the catalytic ozonation process. Synthesizing a cathode material by introducing the component with the activity of catalytic ozonation was a good choice.

Multiwall carbon nanotube (MWCNT) exhibits excellent electrocatalytic activity deriving from its sp^2 hybrid structure and honeycomb morphology (Ma et al., 2014), and graphitic carbon nitride (g-C_3N_4) is rich in nitrogen element. Doping nitrogen on carbon materials can significantly improve their activities in catalytic ozonation (Restivo et al., 2016; Liang et al., 2017). As a result, the g-C3N4/CNT composite is an ideal catalyst combining the activity of electrocatalysis and catalytic ozonation. However, study revealed that the oxygen reduction pathway was unexpectedly shifted to 4-electron resulting in the decrease of yield of H_2O_2, when composites were applied in the ORR (Gong et al., 2014). Consequently, this will have both positive and negative effects in the electro-peroxone process. It is meaningful to estimate the impact derived from the dual functions of the composite materials, also to evaluate the role of catalytic ozonation in the electro-peroxone process.

In this study, three kinds of hybrid materials b-C_3N_4/CNT, p-C_3N/CNT and n-C_3N_4/CNT were prepared by combing bulk g-C_3N_4, porous g-C_3N_4 and nanosheet g-C_3N_4 with MWCNT, respectively. Their morphology, texture, electronic conductivity and electrocatalytic performances in ORR were investigated in detail. The catalytic activities of the composites in electro-peroxone process were compared and the enhancement on the n-C_3N_4/CNT composite was analyzed by electrochemical characterization and catalytic ozonation experiments. The role of catalytic ozonation in the electro-peroxone process was also revealed.

2. Methods and materials

2.1. Chemicals and reagents

Melamine, N, N-Dimethylformamide (DMF), sodium oxalate, NH_4Cl, Na_2SO_4, H_2SO_4 and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Polyvinylidene fluoride (PVDF) was supplied by Alfa Aesar. MWCNT was purchased from Shenzhen Nanotech Port Co., Ltd., China, with a diameter of 10–20 nm and a length below 2 μm. Ultrapure oxygen (purity 99.999%) was provided by Beijing Qianxi Gas Co., Ltd., China. All chemicals were at least in analytical grade without further purification.

2.2. Materials synthesis and electrode preparation

Bulk g-C_3N_4 was prepared by pyrolysis of melamine (Xiao et al., 2016b). Typically, a certain amount of melamine was heated at 550 °C for 4 h with a heating rate of 10 °C min^{-1} in a muffle furnace. Porous g-C_3N_4 was prepared with a similar method, with addition of NH_4Cl as the pore-creating agent (Xiao et al., 2016c). Nanosheet g-C_3N_4 was obtained by thermal exfoliation of bulk g-C_3N_4 at 550 °C for 4 h with a heating rate of 3 °C min^{-1}. All g-C_3N_4 samples were protonated in 10 M HCl solution, washed with ultrapure water until a neutral pH of the solution was achieved, and finally dried in an oven at 60 °C for 12 h.

CNT was slightly oxidized by a modified Hummers method to modify functional groups (mainly carboxyl group) on the surface (Fig. SM-1) (Ma et al., 2014). The CNT was negatively charged after the surface modification, and it would easily combine with protonated C_3N_4 materials to produce composites by electrostatic attraction. In a typical synthesis, different protonated g-C_3N_4 materials were uniformly mixed with MWCNT in a solution of water (30 mL) and isopropanol (20 mL) at a mass ratio of 30/70, respectively. After a hydrothermal treatment at 120 °C for 48 h, the solids were collected and washed with ultrapure water, and dried at 60 °C for 12 h. The samples were labeled as b-C_3N_4/CNT, p-C_3N_4/CNT and n-C_3N_4/CNT according to the different kind of the g- C_3N_4.

To prepare the electrode used in electron-peroxone process, an appropriate ratio of the g-C_3N_4/CNT hybrid and PVDF were mixed in 5 mL of DMF and stirred for 12 h to ensure uniform dispersion. The mixture was uniformly dropped on the two-sided graphite slice with a size of 2 cm × 4 cm. The electrodes were dried in an oven at 120 °C for 12 h to completely remove DMF.

2.3. Materials characterization

The crystal structure of the composite materials was investigated by X-ray diffraction (XRD) with a Cu Kα irradiation. The morphology was characterized in transmission electron microscopy (TEM, JEM-2100). The Brunauer-Emmett-Teller (BET) surface areas of samples were measured on an automated gas sorption analyzer (Autosorb-iQ, Quantachrome). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi instrument (Thermo Fisher Scientific).

Their electrochemical performance in ORR was measured by a rotating ring-disk electrode device in an electrochemical workstation (CHI 760e, CH instrument, China). A saturated calomel electrode (SCE) and a platinum wire were used as the reference electrode and the counter electrode, respectively. The rotating ring-disk electrode with the composite material coated on the surface was used as the working electrode. The measurements were performed in O_2-saturated 0.05 M Na_2SO_4 solution. Electrochemical impedance spectroscopy (EIS) was investigated in $[Fe(CN)_6]^{3-/4-}$ solution with signal amplitude of 5 mV and a frequency range of 10^{-1} –10^6 Hz.

2.4. Degradation of sodium oxalate

The organics degradation in electro-peroxone process was performed in a columnar reactor (8 cm diameter and 11 cm height) with a two-electrode system. All experiments were carried out at pH 9 at 25 °C, because alkaline solution was beneficial to the reaction between O_3 and H_2O_2 (Von Sonntag and Von Gunten, 2012). A Pt sheet (2 cm × 2 cm) was used as the anode, and the cathode was the graphite electrode coated with various composite materials. The simulated wastewater was 250 mL solution with 2 mM of sodium oxalate and 0.05 M of Na_2SO_4. O_3 was continuously bubbled into the reactor with a flow rate of 100 mL min^{-1} and a concentration of 60 mg L^{-1}. Oxalate was analyzed by high performance liquid chromatography (HPLC, Agilent series 1260, USA) equipped with a Zorbax SB-Aq column and a UV–Vis detector qualified at the