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Nitrogen-doped bamboo-like carbon nanotubes with Ni encapsulation for persulfate activation to remove emerging contaminants with excellent catalytic stability

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ABSTRACT

Nitrogen-doped bamboo-like carbon nanotubes encapsulated with nickel nanoparticles (Ni@NCNTs) were feasibly fabricated by a one-pot pyrolysis route. The characterization techniques revealed the surface morphology, structure and chemical composition of the as-prepared catalysts synthesized in different conditions. Ni@NCNTs were employed as both adsorbents and catalysts for activating persulfate to remove an emerging pollutant, antibiotic sulfachloropyridazine. The nitrogen modification enhanced both adsorption capacity and catalytic ability of Ni@NCNTs and proved to be a promising alternative to metal oxides and other carbon catalysts. Moreover, Ni@NCNTs showed an excellent stability because of nitrogen heteroatom doping and Ni nanoparticle encapsulation. Electron paramagnetic resonance (EPR) and classical radical quenching tests discovered a simultaneous radical/non-radical mechanism in Ni@NCNTs/persulfate system. The results indicated that the novel nano-architectured catalyst materials can show emerging functionalities for environmental remediation processes.

1. Introduction

Worldwide drinking water scarcity has become more intense because of the wide water contaminations, which appears as one of the most critical challenges in the world. Many water treatment techniques have been employed to cope with the rapid deterioration of water pollution in terms of the discharge quantity and ever-increasing complexity [1]. Recently, emerging contaminants, for instance pharmaceuticals and personal care products (PPCPs), have attracted tremendous attention. Their intrinsic properties, the continuous and fast development of new species, ubiquity in all surface waters, difficulty of complete remediation and tardy action in early days, as well as lack of understanding of their possible jeopardization to the environment, have brought out great issues to the development of remediation technologies [2,3].

As a representative and main contributor of PPCPs, sulfonamide antibiotics have been intensively used in animal husbandry and human medicine owing to their low cost and good therapeutic effect [4–8]. As a pharmaceutical product, sulfonamides are extremely recalcitrant to complete natural biodegradation because they are biological active [9]. Many studies have detected various sulfonamide compounds in aqueous environment. Even at a low level, a continuous and long-term exposure to such chemicals could lead to appreciable adverse effects on human health [10]. Therefore, the complexity, fine water solubility and trace amount have made them difficult to reach complete degradation via traditional wastewater treatment measures in wastewater treatment plants (WWTP) [11,12]. Recently, advanced oxidation processes (AOPs) have attracted massive attention as they are very effective for the degradation and mineralization of refractory organic pollutants in the aquatic environment [13]. Typically, AOPs are involving oxidants and superoxides such as ozone, oxygen, hydroperoxide, and various radicals that are capable of destroying target organics to harmless species. Hydroxyl radicals ($^{\cdot}$OH) have been most consequently observed in AOPs such as Fenton reaction, UV oxidation and ozonation owing to their superior oxidation ability towards organic pollutants with almost no selectivity [14,15]. Yet, the drawbacks of many $^{\cdot}$OH-related Fenton-like reactions, such as excess sludge production, narrow pH (~3) requirement and metal leaching, are the bottleneck limits.

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Comparably, strong oxidizing sulfate radical ($SO_4^{\cdot -}$) offers an excellent alternative to hydroxyl radical ($^{\cdot}OH$) because $SO_4^{\cdot -}$ has a higher oxidation potential (2.5–3.1 V) than hydroxyl radicals (2.7 V) and a better flexibility of pH tolerance [15–17]. Analogous to Fenton-like oxidation reactions, sulfate radicals can be obtained by activating persulfate (PS) through various activation methods, such as UV-light irradiation, heating, carbon catalysis, metal ion and metallic oxide catalysis, for organic contaminant degradation [18–21]. Among the catalysts used in AOPs, carbon-based nanomaterials stand out owing to the exceptional adsorption capacity, catalysis ability and environmentally friendly nature [22]. Graphene oxide, reduced graphene oxide, carbon nanotubes, and nanodiamonds have been employed in water treatment as an excellent alternative to metal-based catalysts and shown great competitiveness in terms of avoiding metal toxics and associated contamination [23]. However, pristine carbocatalysts suffer from poor stability in heterogeneous reactions, and the heteroatom doping with N, S, P or B into carbon honeycomb network offers an effective strategy to tackle such an issue [24–32].

Herein, we demonstrate a one-pot facile synthesis of high quality N-doped carbon nanotubes with nickel nanoparticle encapsulation (Ni@NCNTs) via direct pyrolysis of melamine as carbon/nitrogen co-precursor and nickel chloride as a Ni source. The prepared product presented a high N-doping level (6.6%) and successful Ni encapsulation. In addition, due to the synergistic effect of N-doping and Ni decoration, the catalytic oxidation and reusability were dramatically enhanced comparing with CNT and N-CNT in activation of PS to effectively remove sulfachloropyridazine (SCP) in water. Electron paramagnetic resonance (EPR) and quenching tests were used to investigate the mechanism of PS activation and SCP oxidation.

2. Experimental

2.1. Chemicals and materials

Nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, 98%), phenol (99%), sulfachloropyridazine (99%), 5,5-dimethyl-1-pyrroline (DMPO), Potassium persulfate, and hydrochloride acid (32%) were obtained from Sigma-Aldrich. Multi-walled carbon nanotubes (MWCNTs) were purchased from Timesnano, China. Graphene oxide (GO) was prepared via a modified Hummers' approach and reduced graphene oxide (rGO) was fabricated by annealing the obtained GO in a tubular furnace under nitrogen atmosphere at 700 °C for 1 h. Nitrogen doped reduced graphene oxide (N-rGO) was prepared through a hydrothermal approach, as detailed in previous studies [32–34]. All the chemicals were of analytical grade or higher and used as received without further purification. Deionized (DI) water was used in all the experiments.

2.2. Synthesis of nitrogen-doped carbon nanotubes with nickel encapsulation (Ni@NCNTs)

Nitrogen-doped carbon nanotubes with nickel encapsulation were fabricated by a controlled pyrolysis process using melamine and nickel chloride hexahydrate as carbon/nitrogen and nickel precursors, respectively. In a typical synthesis, melamine ($C_3N_6H_6$, 10 g) were dissolved in 20 mL of DI water at 65 °C under continuous stirring for 1 h until melamine was dissolved completely. $NiCl_2{\cdot}6H_2O$ as a nickel precursor with designed loading (1, 2, 3.3, or 7 g) was introduced to the melamine solution to form a homogenous greenish solution. Later, the mixed solution was heated and kept at 80 °C overnight to completely remove water. The resulting precipitates were placed inside a tube furnace and allowed nitrogen gas to flow through for three hours to purge out the air residue. And then the samples were annealed at 700, 800 or 900 °C for 6 h under N_2 atmosphere with a heating rate of 5 °C min^{-1}. After the pyrolysis, the sample was naturally cooled down to room temperature. Finally, the resultant black product was ground to fine powders, followed by thoroughly washing with excessive concentrated hydrochloride acid (32%), by stirring in the acid solution for 6 h. The obtained precipitates were then washed with ethanol and DI water for a few times until the clear solution pH achieved at the value of 7. The as-prepared catalysts were denoted as Ni@NCNT-T-M (where T represents the calcination temperature and M represents the initial weight ratio of melamine to nickel chloride), for instance Ni@NCNT-700-3 means Ni@NCNTs with 3:1 melamine to $NiCl_2{\cdot}6H_2O$ and heated at 700 °C.

2.3. Catalyst characterization

The crystal structure of the samples determined by X-ray powder diffraction patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) at 40 mA and 40 kV with a scanning speed of 0.2° (2θ) min^{-1}. The Raman spectra were obtained using a laser with an excitation wavelength of 785 nm at room temperature on a Renishaw Raman microscope. The surface contents and types of carbon, nitrogen and metals were measured by X-ray photoelectron spectroscopy (XPS) on a VG Multi lab 2000 spectrometer (Kratos AXIS Ultra DLD) with Al Kα radiation as the X-ray source (300 W). The C 1s line at 284.6 eV was applies as a calibration to correct the binding energies. By deducting the Shirley-type background, the core level spectra were deconvoluted into their components with Gaussian-Lorentzian (20:80) shape lines using the CasaXPS software. The Brunauer – Emmett – Teller (BET) specific surface area and pore-size distribution of the samples were determined by N_2 adsorption-desorption at −196 °C using a Micrometrics Tristar 3000. The samples were degassed in a vacuum at 110 °C overnight before the tests. The morphologies of the carbon samples were characterized using scanning electron microscopy (SEM; FEI Verios XHR 460) and transmission electron microscopy (TEM; JEOL 2100). The thermal stability was collected by the thermogravimetric analysis (TGA) using a TGA/DSC1 STAR^e system, Mettler-Toledo thermal analyzer under flowing air. The reactive radicals were detected by electron paramagnetic resonance (EPR) on a Bruker EMS-plus instrument with DMPO as a spin-trapping agent, and the Xeon software (Bruker) was used to analyze the quantitative information. The Ni concentration in reaction solutions was evaluated by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

2.4. Adsorption and catalytic oxidation of SCP solutions

SCP adsorption was performed in a 500 mL conical flask at 25 °C, unless other temperature specifically mentioned. Typical adsorption experiments were carried out by dispersing the Ni@NCNTs samples (0.2 g L^{-1}) in SCP (20 mg L^{-1}, pH = 7) solutions. At determined intervals, 1 mL of solution was withdrawn and immediately filtered by a 0.22 μm Millipore syringe filter to remove the solid particles.

2.5. Catalytic oxidation of SCP solutions

The degradation experiments were conducted by introducing designed amount of PS into the reaction solutions when the adsorption/desorption equilibrium was reached. After the reaction was initiated, 1 mL of solution was extracted at planned time intervals, and then injected into an UHPLC vial mixed with 0.5 mL methanol as the quenching agent. Each experiment and analysis was repeated twice and the results were reproducible with relative errors less than ± 5%. The concentrations of SCP were analyzed with an UHPLC system (Thermo-Fisher Scientific 3000) using an UV detector at a detection wavelength of 270 nm. An Acclaim RSLC C-18 column (2.2 μm) was used as a separation column. The mobile phase was a mixture of diluted acetic acid and methanol (70:30, v/v) with a flow rate of 0.3 mL min^{-1} and 20 μL of injection volume [32]. Total organic carbon (TOC) was measured using a Shimadzu TOC-5000 CE analyzer for a few selected samples. For TOC measurement, 10 mL sample was withdrawn at a designed