



# Application of carbon aerogel electrosorption for enhanced Bi<sub>2</sub>WO<sub>6</sub> photoelectrocatalysis and elimination of trace nonylphenol



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## ARTICLE INFO

### Article history:

Received 1 August 2017

Received in revised form

22 September 2017

Accepted 2 October 2017

Available online 5 October 2017

## ABSTRACT

Carbon aerogel (CA) was used in electrosorption to enhance Bi<sub>2</sub>WO<sub>6</sub> photoelectrocatalytic process for trace amount (1 mg/L) nonylphenol (NP) elimination. The composite Bi<sub>2</sub>WO<sub>6</sub>/CA electrode fabricated with CA as adsorbent and Bi<sub>2</sub>WO<sub>6</sub> as photocatalyst was found to be effective to achieve the synergy of electrosorption and photoelectrocatalysis. At alkaline pH (>12), more than 90% of NP was adsorbed by applying potential larger than 0.6 V (vs. SCE), most of which was gathered on the electrode. Electrosorption was promoted with increasing of electric field intensity and pH. NP gathered on the electrode was degraded completely (99.3%) in the photoelectrocatalytic process due to electrosorption enrichment and well photocatalytic properties of the electrode. The degradation efficiency depended largely on the electrosorption process, thus the removal of NP was also affected by pH and applied potentials. The electrode achieved “self-cleaning” due to synergistic effect of electrosorption and photoelectrocatalysis: electrosorption was favorable for photocatalytic degradation and the photocatalytic degradation can renew the electrode after the adsorbed pollution was removed. Trace NP can be eliminated efficiently in real sample, and the final concentration of NP was below 6.4 μg/L, which meet the effluent standard of NP.

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## 1. Introduction

The usage and production of nonylphenol (NP) have been increasing rapidly, since it was first synthesized in 1940 [1]. Tons of NP was produced for production of nonylphenol polyethoxylates (NPEOs) [2], a surfactant which was used in a number of industrial products. Most of the products entered the aquatic environment, and easily decomposed into NP again. Thus NP is widespread in our environment, including river, lake, soil and sea [3,4]. As a kind of typical endocrine disruptor chemicals (EDCs), NP aroused people's attention gradually due to its potential threat to organisms. Furthermore, NP is bioaccumulative in aquatic organisms and can cause interference on the endocrine system by replacing endogenous hormone, which means it would be harmful to the organism even at low concentration [5,6].

Currently, the U.S. Environmental Protection Agency (EPA) has accepted the risks of NP and has prepared a guideline for ambient water quality that recommends NP concentrations in freshwater to

be below 6.6 μg/L and in saltwater below 1.7 μg/L [7]. The target is very challenging. Conventional wastewater treatment methods are inefficient at removing NP due to its refractory and toxic nature, and the relatively low efficiency of the current remediation processes. So, researchers are trying new solutions for rescuing by applying additional technologies. Biodegradation is economically cheap and simple, but it takes months for totally removal at the risk of poisoning bacteria [8–10]. Adsorption of NP by porous material is high effective and easily operated [11,12]. But the regeneration of adsorbent is difficult. Besides, NP is transferred from solution to the adsorbent in adsorption process, so the adsorbent may be hazardous to the environment once it was not well treated. Advanced oxidation processes (AOPs), appearing to be a promising alternative for totally transformation of NP, including H<sub>2</sub>O<sub>2</sub>/UV system [13,14], Fenton [15], photocatalytic degradation [16–18], etc. And photoelectrocatalysis is widely used in the treatment of environmental pollutants [19–21]. However, EDCs cannot be efficiently degraded due to the relatively low content, saying μg-ng/L.

Electrosorption is an alternative, effective, relatively unexplored method of enrichment that the pre-concentration process can force charged ions to transfer to the electrode with opposite charge

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driven by coulomb force [22–25]. Photoelectrocatalysis is a typical heterogeneous process [26–28]. The reaction rate depends largely on the concentration of reactant. So the combination of electro-sorption and photoelectrocatalysis has been used for ionized pollution degradation [29–31]. The dissociation constant ( $pK_a$ ) of NP was 10.7 [1], so NP dissociated into sodium nonylphenate under alkaline pH, i.e. the pollutant has a negative charge. In this condition, NP can be forced to transfer to anode during electro-sorption process. In the electro-sorption process, a good adsorbent is critical to capture the migrated NP. Carbon materials is a kind of material with excellent electrochemical properties and adsorption properties [32,33]. Carbon aerogel (CA) is one of the novel mesoporous carbon materials with carbon network that can be good substrates possessing good adsorption property and conductivity [34]. Besides the adsorbent, photocatalyst with good catalytic property is equally important for thorough NP elimination.  $\text{Bi}_2\text{WO}_6$  was found to possess excellent intrinsic physical and chemical properties [35,36], such as ferroelectric piezoelectricity, catalytic behavior, and non-linear dielectric susceptibility. Recently, many efforts were devoted to the controlled synthesis of  $\text{Bi}_2\text{WO}_6$ -semiconductor nanocomposites (such as  $\text{Bi}_2\text{WO}_6/\text{TiO}_2$  [37],  $\text{Bi}_2\text{WO}_6/\text{Ag}$  [38],  $\text{Bi}_2\text{WO}_6/\text{C}_3\text{N}_4$  [38]) to effectively decrease the probability of electron-hole recombination and enhance photocatalytic activities [39,40].

In this work, we prepared  $\text{Bi}_2\text{WO}_6/\text{CA}$  electrode with good adsorption property and photocatalytic properties, and studied the performance of electro-sorption and photoelectrocatalytic degradation to NP. The electrode possessed good conductivity, high specific surface area and good adsorption performance. To improve the photocatalytic removal efficiency of low concentration NP, electro-sorption was employed to increase NP content on the catalyst surface. The higher the concentration, the faster the photoelectrocatalytic reaction rate. The applied potential can not only enrich NP, but also facilitate photoelectrocatalytic reaction by forcing the separation of photo-generated charges.

## 2. Experimental section

### 2.1. Preparation and characterization

CA was prepared through phenol formaldehyde condensation reaction [22]. Generally, resorcinol (1,3-dihydroxy benzene), formaldehyde, deionized water, and sodium carbonate were mixed in a molar ratio of 1:2:17.5: 0.0008. After forming homogeneous solution, the mixture was cast into a cuboid glass with interlayer distance of 5 mm, and cured at 30 °C for one day, 50 °C for one day, and 90 °C for 3 days. The resulting organic wet gel (RF) was immersed into acetone for 3 days to replace the water in wet gel. Then it was dried under ambient condition for 4 days to obtain massive dry gel with integrated structure. The aerogel was converted to CA by pyrolysis in a tube furnace, and the temperature was kept at 950 °C for 4 h in argon atmosphere with a flow rate of 200 mL/min. Then CA prepared above was activated in  $\text{CO}_2$  atmosphere at a flow rate of 30 mL/min at a tube furnace. The temperature of the tube furnace rose slowly to 850 °C and was maintained for 6 h.

$\text{Bi}_2\text{WO}_6$  nanosheets was synthesized through hydrothermal reaction [35]. 0.606 g of bismuth nitrate pentahydrate (1.25 mmol), 0.206 g of sodium tungstate dihydrate (0.625 mmol) and 0.5 g of PVP were mixed under intensely stirring, till the solution was homogeneous. Then the solution was transferred into 50 mL polytetrafluoroethylene-lined stainless autoclave and placed in a 180 °C oven for 24 h reaction. After the reaction, cooling the autoclave to room temperature and washing the mixture with deionized water and ethanol to obtain a white powder.

$\text{Bi}_2\text{WO}_6$  was loaded on F-doped  $\text{SnO}_2$  glass and CA by electro-phoretic deposition on constant voltage following a previously reported procedure [41].  $\text{Bi}_2\text{WO}_6$  powder (50 mg) was dispersed in 50 mL of acetone with iodine under ultrasonic for 20 min. CA (or FTO) and titanium plate were immersed in the solution in parallel at a distance of 2 cm. 30 V of voltage was applied between the electrodes for 10 min using a dc power supply. The coated area was about  $1.5 \times 2 \text{ cm}^2$ . Then the electrode was annealed in muffle furnace at 300 °C for 2 h.

The electrode was characterized by field emission scanning electron microscopy (Hitachi S-4800), transmission electron microscopy (JEOL, JEM-2100), X-ray diffraction (Bruker, D8) and BET analyzer (Micromeritics, TRISTAR 3000). The electrochemical experiments were carried out on electrochemical workstation (CH Instruments, CHI 660C) using a three-electrode system, with the as-prepared CA,  $\text{Bi}_2\text{WO}_6/\text{CA}$  and  $\text{Bi}_2\text{WO}_6/\text{FTO}$  as the working electrodes. The electrochemical impedance spectra of the electrodes were measured in a 5 mmol/L  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  solution. The photoelectrocatalytic properties of the electrode were measured in 0.1 mol/L  $\text{Na}_2\text{SO}_4$  solution.

### 2.2. Adsorption and degradation

The adsorption experiment of NP was carried out by applying a positive potential on the working electrode with surface area of  $1.5 \times 2 \text{ cm}^2$  to form a positive electricity field in 1000  $\mu\text{g}/\text{L}$  ( $4.55 \times 10^{-6} \text{ mol}/\text{L}$ ) NP for 8 h. Electro-sorption was carried out under a three-electrode system. Degradation experiment was carried out in a quartz tubular reactor placed inside a columniform electrochemical reaction cell with simulated sunlight (500 mW/ $\text{cm}^2$ ). The reactor was externally connected to circulating water to keep the reaction at constant temperature of 25 °C. The prepared electrode was employed as the working electrode separately with same working area, which was 3 cm away from the light source to construct a three-electrode system at +0.6 V.

### 2.3. Analysis

To detect the concentration of NP during reaction, samples was concentrated by liquid-liquid extraction. 50 mL of ethyl acetate was added to 100 mL of the reaction solution for extraction, and the extract was concentrated to 1 mL after repeating three times. The content of NP was then determined by HPLC. HPLC was performed using an Agilent Eclipse plus C18 ( $4.6 \times 100 \text{ mm}$ , 5  $\mu\text{m}$ ) column with a mobile phase of methanol: water = 90: 10, a flow rate of 1 mL/min, and a UV detector at 221 nm.

To detect the amount of residual NP on CA, the electrode was immersed in 50 mL of ethyl acetate in the dark for 12 h after drying at 60 °C. Repeating the above steps three times, the eluate was gathered and concentrated to 1 mL. The content of NP in the eluate was measured by HPLC too.

## 3. Results and discussion

### 3.1. Characterization of the electrode

As the SEM photograph shown in Fig. 1A, CA had three-dimensional porous network structure consisting of granular carbon nanospheres with diameter of 50–100 nm. It is well known that the adsorption capacity and catalytic activity of CA are closely related to their specific surface area. To improve the specific surface area of CA, it was activated at 850 °C using  $\text{CO}_2$ . As shown in Fig. 1B, after 6 h activation, looser structured CA was obtained. The size of the granular carbon nanospheres reduced to 30–50 nm, and the mechanical strength decreased slightly. As shown in Fig S1A, TEM

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