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Au/carbon as Fenton-like catalysts for the oxidative degradation of bisphenol A

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ABSTRACT

The development of a new method for the degradation of bisphenol A (BPA) in aqueous solution is highly desired. Oxidative degradation using hydroxyl radicals (OH•) is an efficient approach for the remedy of toxic organic compounds. This paper describes the design and utilization of a new Fenton system consisting of the Au/styrene based activated carbon catalyst and hydrogen peroxide (H_2O_2) for the degradation of BPA under non-photo-induced conditions. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) results showed that the negatively charged Au nanoparticles were evenly distributed in a range 3.9–6.4 nm dominated with (1 1 0) facet. The generation of OH• over Au catalysts through the decomposition of H_2O_2 was evidenced using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) trapped electron paramagnetic resonance (EPR). The experimental results suggested that the conversion of BPA was affected by several factors such as the loading amount of Au, pH value, reaction temperature and the initial concentration of H_2O_2. In an optimum experiment, BPA could be degraded from 110 to 10 ppm within 12 h. The active sites was envisaged to be negatively charged Au atoms at the interface between Au particles and carbon support, the carbon surface is enriched with dangling carbon atoms as evidenced by the O_2-temperature programmed desorption (TPD) technique. A mechanism including the redox between $Au^{\delta-} \leftrightarrow Au^{\circ}$ during the decomposition of H_2O_2 has been proposed.

1. Introduction

Bisphenol A (BPA; 2,2-bis-(4-hydroxy phenyl)-propane) is regarded as a potential "endo-crinedisruptor" by the US Environmental Protection Agency (EPA) [1]. Up to date, most of studies on the environmental issues caused by BPA have been contributed to the occurrence, ecological risk, estrogenic activity and the effects on the health of human and animals. As an additive or contaminate, BPA can be detected in food [2], water [3], paper (including paper products, currencies, etc.) [4] and plastic products [5]. It has shown the effects of estrogen-like on gene imprinting and sexual differentiation when accumulating in human body [6]. The degradation of BPA naturally needs more than 90 years [7]. That means the pollution resulted from BPA or other chemicals with similar structure can last for several decades once it is released into water or soil [6]. Presently, several methods have been developed for the removal of BPA from aqueous solution, for instance, biochemical oxidation, absorption, electrochemical oxidation, wet chemical oxidation, ozonation, sonochemical oxidation and so forth [8–16]. The biodegradation approach, as a process widely used in industrial scale, needs several weeks or longer [12]. Therefore the development of a fast and simple method for the degradation of persistent organic compounds, especially for BPA, is still a tremendous challenge. Among all these methods, Fenton system shows the highest efficiency in the oxidation of organic compounds. In addition, as a model organic contaminate, BPA can be a category of organic compounds with benzyl rings, which is still difficult to be removed by the conventional methods.

The Fenton process as an advanced oxidation process (AOP) has long been used for the remedy of waste water and contaminated soil [17]. According to the radical (Weiss–Harber) mechanism, hydrogen peroxide (H_2O_2) can be decomposed into hydroxyl radical (•OH) by ferrous ions catalyst. •OH has the second highest oxidant potential (2.7 eV in an acidic solution) in nature and can oxidize organic compounds in aqueous rapidly [18–20]. However, the cost for this process could be too high in practical application because of the production of undisposable sludge, the continuous lost of the chemicals (mainly iron salt) and the narrow range of operation pH value (2.5–3.5) [21]. Nowadays, the heterogeneous Fenton agent was indicated as an ideal solution to these problems

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[22,23]. Solid iron-based catalysts [24] have showed comparable catalytic performance to the conventional Fenton catalyst (Fe^{2+}); however, the leaching of iron generally leads to a significant deactivation. Therefore, the development of novel heterogeneous Fenton system with enhanced stability is strongly desired, it would be of great importance for both environmental protection and chemical synthesis.

Au catalysis attracts tremendous attention since the seminal discovery on the superior performance of Au nanoparticles in 1980s [25,26]. Au-based catalysts have proven active for low-temperature oxidation, hydrogenation, water–gas shift, electrochemical reaction and so forth [27–34]. We have reported that Au/hydroxyapatite could be an alternative Fenton-like catalyst, which degrades H_2O_2 to •OH [35]. More recently, Garcia's group [36–39] has reported that a nanodiamond supporting Au (Au/OH-npD diamond) could be a Fenton catalyst for the metabolism of organic compounds under light irradiation [36]. The reaction was assumed to proceed through a photochemical process including a photo-induced electron ejection on the catalyst surface and the electron-transfer from Au to H_2O_2 [37]. Indeed, Au atoms can be excellent electron-donor or -acceptor under certain circumstances; in particular, this property can be used for the production of •OH by H_2O_2 decomposition. Au-Fenton catalysts have a great advantage compared to solid Fe-Fenton catalysts because Au is "inert" in nature and unlikely leaching under various reaction conditions.

In this study, Au nanoparticles dispersed on various carbon supports were prepared, characterized and used as solid Fenton catalysts for the degradation of BPA under mild conditions. In particular, the origin of active sites over Au/C catalyst was explored using multi techniques.

2. Experimental

2.1. Synthesis of the carbon material

2.1.1. Styrene-based activated carbon (SRAC)

A commercial polystyrene-based ion-exchange resin sphere (Rohm & Haas, USA) was used for the preparation of SRAC. Generally, it was carbonizated at 1073 K for 2 h in gaseous N_2, followed with an activating process at 1073 K for 60 min in water stream.

2.1.2. Pitch-based spherical activated carbon (PSAC)

The preparation of PSAC was followed the method introduced by Liu et al. [40]. Coal tar pitch was purified by HCl, and stabilized with 30 wt% naphthalene.

The obtained spheres were then carbonized at 1173 K for 0.5 h with a ramping rate of 10 K/min in a flow of N_2. The carbonized materials were activated at 1173 K for 2 h in a steam of 30 mL/min.

2.1.3. Carbon nanofiber (CNF)

A chemical vapor deposited (CVD) method was used for the preparation of CNF. A Ni/Al_2O_3 catalyst was selected for this system, and CO/H_2 (80/20) mixed gas flow was the carbon source. After 16 h for the nanofiber growth, the purification of the obtained materials was carried out with the concentrated NaOH.

2.1.4. Ordered mesoporous carbon (FDU-15)

The route for the synthesis of FDU-15 was followed the method proposed by Meng et al. [41]. Hexadecane and decane (a mole ratio of 1.55) was used as the source of carbon. After blending for 24 h at 338 K, the slurry precursor was obtained. Then, it was vacuum dried. With the ramping rate of 1 K/min to 623 K, the sample was calcined in N_2. Finally, the carbonized was carried out at 1073 K in a N_2 flow of 30 mL/L for 3 h.

2.2. Preparation of the catalyst

The introduction of Au nanoparticles followed the same procedure [42]. $Au(en)_2Cl_3$(en: 1,2-ethanediamine) was employed as the precursor, which could be adsorbed to SRAC at room temperature with pH 3.0. The obtained samples were washed with MilliQ (18.25 MΩ) water and then dried at 313 K overnight. The heat treatment was proceeded subsequently at 573 K in a H_2 flow of 30 mL/min for 30 min. The obtained catalyst was sealed in a dark vessel.

2.3. Catalytic test

The aqueous solution of BPA (~100 ppm) was prepared with MilliQ water (18.25 MΩ). The pH value was adjusted using 0.01 M HCl. The catalyst was added into the solution after forming a mixture of BPA, H_2O_2 and HCl in a thermostatic batch reactor. The reactor was tightly covered by aluminum foil for the evaluation of the influence of solar-light. In all the cases, aliquots of 2 mL were taken at interval of 1 h, and filtered by a 0.22 μm nylon membrane before analysis. The concentration of BPA was measured by a HPLC (Perkin Elmer Flexar) that was equipped with a Spheri-5 C18 column and UV detector with the wavelength 275 nm [10]. The variation of H_2O_2 concentration during reaction was analyzed colorimetrically using a UV–vis spectrophotometer after complexation with a $TiOSO_4/H_2SO_4$ reagent [43].

2.4. Characterization

2.4.1. Scanning electron microscopy (SEM)

The measurements were carried out at a FEI NOVA NanoSEM 450 scanning electron microscopy, which was operated at the accelerating voltage of 15 kV and the detector current of 10 mA. The collection was taken at a high vacuum mode (1×10^{-3} mbar). The size of the beam spot was 3 μm.

2.4.2. N_2 adsorption–desorption

N_2 adsorption and desorption isotherms were collected on a ASAP 2010 (Micromeritics, USA) at 77 K. Prior to the measurement, all samples were degassed at 573 K until a stable vacuum of ca. 5 m Torr was reached. The pore width distribution curves were calculated from the adsorption branch using a DFT method. The specific surface area was assessed using the BET method from adsorption data in a relative pressure range from 0.06 to 0.35. The conversion factor between the volume of gas and liquid adsorbate is 0.0015468 for N_2 at 77 K, when they are expressed in cm^3/g and cm^3 STP/g, respectively.

2.4.3. X-ray diffraction (XRD)

XRD was performed using Riguku D/max 2550 diffractometer, with accelerated voltage 40 kV and detector current 100 mA. Cu-K_α radiation was used for a continuous scanning with the step-size of 0.02° over a 2θ range 10–80°. The scan speed was 4°/min.

2.4.4. Transmission electron microscopy (TEM)

The measurements were performed on a JEOL-2000, which was operated at 200 kV accelerating voltage. The catalyst was first carefully grounded at an agate mortar to 30 μm. Then the fine sample was ultrasonically suspended in ethanol. One drop of this slurry was deposited on a copper microgrid without carbon coating. The liquid phase was evaporated before the grid was loaded into the microscope. The Au particle size was estimated on the basis of 300 particles.