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Degradation photocatalysis of tetrodotoxin as a poison by gold doped PdO nanoparticles supported on reduced graphene oxide nanocomposites and evaluation of its antibacterial activity

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ABSTRACT

In this project, synthesis of pure and gold doped PdO-reduced graphene oxide nanocomposites by sonochemical and deposition-precipitation process was performed and characterized using X-ray diffraction (XRD), transmission electronic microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The specific surface area of synthesized un-doped and Au doped PdO-RGO nanocomposites is 83.2, 109.1 $m^2\ g^{-1}$ and total pore volume is 0.31, 0.40 $cm^3\ g^{-1}$, respectively. With Tetrodotoxin as a target pollutant, photocatalytic system of UV + photocatalyst + H_2O_2 was set up. Some influencing parameters, including H_2O_2 dosage and initial pH value were investigated and the stability of the photocatalyst was also studied during the photocatalysis. The optimum values of operating parameters were found at an initial pH value of 5.0, a H_2O_2 dosage of 0.15 $mmol/L^{-1}$ and photocatalyst dosage of 0.08 g. Under the optimal conditions, the highest removal rate of Tetrodotoxin achieved 95%. Compared with the traditional photo-Fenton system, the UV + photocatalyst + H_2O_2 system can not only improve the degradation efficiency of Tetrodotoxin, but also reduce the dosage of H_2O_2 and thus reduce the processing cost. Antibacterial properties of un-doped and Au doped PdO-RGO nanocomposites were investigated by gram negative bacteria *Escherichia coli* and gram positive *Staphylococcus aureus*. The results showed that the antibacterial activity enhanced by Au PdO-RGO nanocomposites.

1. Introduction

Tetrodotoxin (TTX) is a potent neurotoxin. Its name derives from Tetraodontiformes, an order that includes pufferfish, porcupinefish, ocean sunfish, and triggerfish; several species that carry the toxin. Although tetrodotoxin was discovered in these fish and found in several other aquatic animals, it is actually produced by certain infecting or symbiotic bacteria like *Pseudoalteromonas*, *Pseudomonas*, and *Vibrio* as well as other species found in the animals.

TTX is extremely toxic. The Material Safety Data Sheet for TTX lists the oral median lethal dose (LD_{50}) for mice as 334 μg per kg [1]. For comparison, the oral LD_{50} of potassium cyanide for mice is 8.5 mg per kg [2]. demonstrating that even orally, TTX is more poisonous than cyanide. TTX is even more dangerous if injected; the amount needed to reach a lethal dose by injection is only 8 μg per kg in mice [3]. The toxin can enter the body of a victim by ingestion, injection, or inhalation, or through abraded skin [4].

Photocatalytic process belongs to advanced oxidation technology, which can oxidize and decompose non-degradable organic pollutants in water into H_2O, CO_2 and inorganic salts, etc. This method has developed rapidly in recent 30 years and shows its unique advantages on the treatment of a lot of poisonous and harmful organic pollutants [5–7]. Photocatalyst is the core of photocatalytic technology and metal sulfide nanocomposite is a new type of semiconductor photocatalyst [8–10]. It utilizes the excellent properties of different semiconductor components effectively and overcomes the defects of traditional single material itself. Modification of catalyst enhances its catalytic activity, improves the reaction rate, and broadens its response range to visible light [11,12].

Recently, carbon materials, transition metal oxides and con-ducting polymers are using as main pillars for electrodes. Carbon materials exhibit superior chemical stability, electrical, mechanical properties and large surface area while the conducting polymers offer high pseudo capacitance, light weight, low cost, controllable electrical conductivity and high energy density [13–15]. In order to obtain high-performance electrode material with high capacitance and good cyclic stability. A nanocomposite of conducting polymers, transition metal oxides and carbon-based materials have been investigated [16,17].

Palladium oxide is the most important catalyst that is used for various reactions in the laboratory and industry. It has been used for catalytic oxidation of benzyl alcohol [18], sensing of OH radicals [19], oxidation

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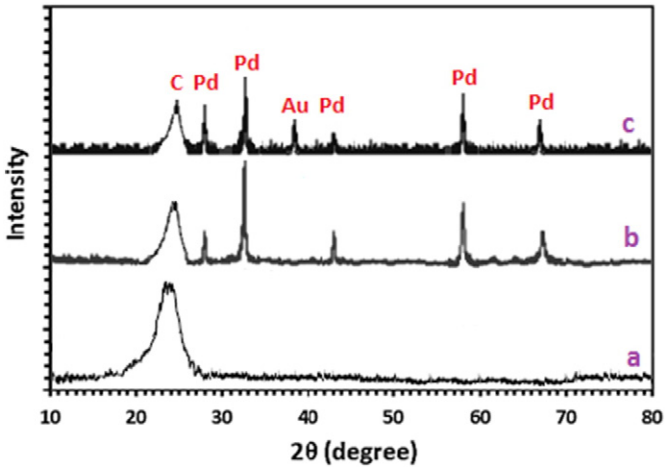

Fig. 1. XRD patterns of reduced graphene oxide (RGO) (a), PdO-RGO nanocomposites (b), and Au doped PdO-RGO nanocomposites (c).

of hydrocarbons [20], photocatalytic degradation of bacterial indicators [21]. Many researchers have recently been focused on examination of metal oxide nanoparticles with metal nanoparticles deposited on oxide surfaces, embedded within porous network or encapsulated in its matrices since such materials have wide applications in diagnostics, catalysis and photocatalysis [22]. Among of metallic NPs, Au nanoparticles have attracted much attention on potential applications due to their nonlinear optical properties, irresistible magnitude and quick response [23]. Then, removal or decompose of TTX is very important. The novelty of this work is synthesis of gold doped PdO-reduced graphene oxide nanocomposites for degradation this pollution.

In this study, un-doped and gold doped PdO-reduced graphene oxide nanocomposites was synthesized by sonochemical and deposition-precipitation process method and followed as a photocatalyst. The photocatalytic system of UV + photocatalyst + H_2O_2 was set up under ultraviolet (UV) irradiation. The effects of H_2O_2 dosage, initial pH value, and photocatalyst dosage on TTX degradation efficiency were investigated.

2. Materials and Methods

2.1. Reagents and Characteristic Apparatus

Raw materials used in the present study were procured from Sigma-Aldrich, Ltd.

A transmission electron microscopy (TEM, JEM- 2100F HR, 200 kV), and X-ray diffractometer (XRD) Philips X'Pert were used to characterize the adsorbent for its morphological information. Raman spectra were examined with an Ar ion CW laser (514.5 nm) as the excitation source by using a LabRAM HR UV/vis/NIR spectrometer (Horiba Jobin Yvon, France). The XPS spectra were recorded by a Kratos Axis Ultra DLD XPS system.

2.2. Preparation of Pure and Au Doped PdO-RGO Nanocomposites

Graphene oxide (GO) nanosheets were synthesized using the modified Hummer's method, as described elsewhere [24]. For preparation of RGO, 100 milliliter of 50% N_2H_4 was added into the GO suspension, and it was stirred and refluxed in a silicon oil bath at 100 °C for 12 h. Finally, the synthesized RGO was washed with distilled water and ethanol several times and dried.

The PdO-RGO nanocomposites were prepared using by sonochemical method. Predetermined amount of the RGO (50 mg) were added separately, to the aqueous solutions of $Pd(NO_3)_2 \cdot 2H_2O$ dissolved in 1 milliliter ionic liquid 1-butyl-3-methylimidazolium tetrafluorobo-rate ([bmim]BF_4), with the total volume of 100 milliliter. The mixtures were irradiated with high-intensity ultrasound radiation with 480 W cm^{-2} input power and working frequency of 24 kHz. During the reaction, the mixture temperature was at 50–55 °C. Then the mixture was sonicated in ethanol to remove the excess impurities and extracted from the ionic liquid by a centrifuge process.

Gold deposition was performed using a simple deposition-precipitation method. Typically about 1 g of the PdO-RGO nanocomposites was dispersed in 100 milliliter aqueous solution of $HAuCl_4 \cdot 3H_2O$. The solution temperature was slowly increased to 80 °C, and the pH was adjusted to a value of 9 using a 0.42 M urea solution. The reaction was then carried out for another 16 h at the constant temperature of 80 °C under gentle stirring. After the completion of the reaction the precipitate was separated from the solution mixture by centrifugation and was repeatedly washed with deionized water and then with absolute ethanol to remove the chloride ions. The solid precipitate was then dried under vacuum at room temperature for 24 h and finally calcined at 300 °C at a rate of 10 °C/min for 4 h in air.

2.3. Photocatalytic Performance

TTX was as the target of degradation in photocatalytic reaction under mercury lamp radiation with 100 W of UV power. The reaction device consisted of a metal shelter, power regulator, light source with 3.96 mW·cm^{-2} (at 254 nm) of the light intensity, glass reactor, and magnetic stirrer. Glass reactor was cooled by quartz protection cold trap which had not only a high penetration rate of UV, but also took

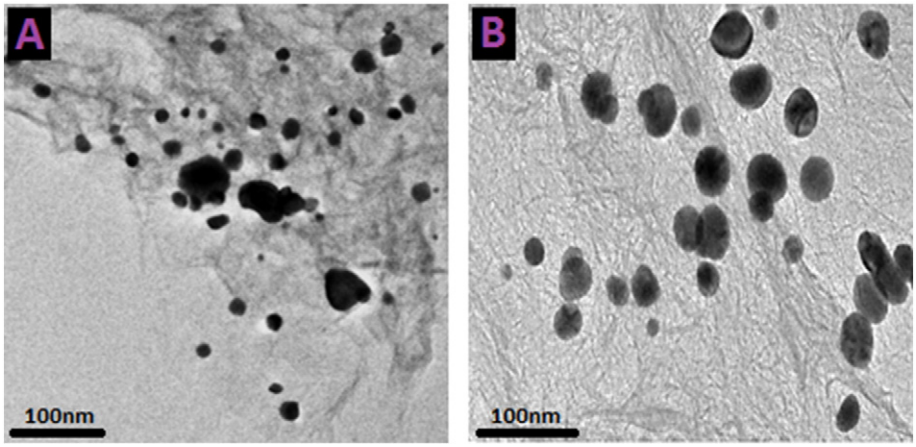

Fig. 2. TEM images of PdO-RGO nanocomposites (A), and Au doped PdO-RGO nanocomposites (B).