Sensors and Actuators B 257 (2018) 48–59

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Carbon aerogel supported palladium-ruthenium nanoparticles for electrochemical sensing and catalytic reduction of food dye

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ARTICLE INFO

Article history:
Received 17 June 2017
Received in revised form
11 September 2017
Accepted 19 October 2017

Keywords:
Carbon aerogel
Pd-Ru nanoparticles
Supported nanocomposite
Sunset yellow
Electrochemical sensor
Dye degradation

ABSTRACT

A facile approach for the electrochemical determination and catalytic degradation of sunset yellow (SY) by using palladium-ruthenium nanoparticles incorporated carbon aerogel (Pd-Ru/CA) as catalyst is reported. The Pd-Ru/CA nanocomposite was prepared by sol-gel polymerization invoking the evaporation induced self-assembly (EISA) method and was characterized by various techniques such as XRD, SEM/TEM, N_2 physisorption/chemisorption, thermal analysis, and Raman, XPS, and EDS spectroscopies. The Pd-Ru/CA modified screen printed carbon electrode (SPCE) was found to show excellent performances for electrochemical detection and catalytic degradation of SY, surpassing the conventional HPLC method even in real samples. Effects of key experimental parameters such as type and pH of supporting electrolyte, and dye and interference concentrations on selectivity of the sensor during electrochemical detections were thoroughly assessed by CV and DPV methods The Pd-Ru/CA modified SPCE revealed excellent limit of detection (LOD) and analytical sensitivity of 7.1 nM and 3.571 μA μM^{-1} cm^{-2}, respectively. Moreover, as verified by UV–vis spectroscopy, the Pd-Ru/CA nanocomposite exhibited an extraordinary performance for catalytic degradation of SY with a pseudo-first order rate constant (k) of ca. 0.295 s^{-1}, making the proposed nanomaterial a suitable platform for prospective photo- and electro-catalytic applications.

1. Introduction

Transition metal nanoparticles (TMNPs), which exhibit unique optical, electronic, and catalytic properties, have drawn considerable attentions in the scientific research community as well as in prospective industrial applications [1]. Among them, palladium (Pd) and ruthenium (Ru) NPs represent two key elements in the noble metal group that have found many practical applications in fuel and energy storage [2–4], fuel cells [5], catalysis [6], and electrochemical sensors [7,8]. In particular, Pd-based bimetallic NP systems with changeable structures and morphologies were known to show enhanced catalytic and electrocatalytic activities [9–11]. For example, bimetallic Pd-Ru NPs were known to exhibit superior electrical, magnetic, optical, and catalytic properties compared to their monometallic counterparts, making them a new class of material with improved enhanced synergistic effects [12,13]. Moreover, it has been shown that their catalytic activities may be further enhanced by anchoring the bimetallic Pd-Ru NPs on catalytic supports such as graphene or graphene oxide [14], carbon nanotubes (CNTs) [15], or activated carbons [16]. In particular, carbon aerogels (CAs) are mesoporous materials with enriched porosity and high specific surface areas [17], which are favorable for many practical applications [18–20]. Moreover, being composed by a three-dimensional (3D) structural networks, CAs are also found to have excellent biocompatibility, good electric conductivity, extraordinary chemical and environmental stability, and strong adhesion ability, which are highly desirable for research and development of new-generation catalyst materials [21].

Several Pd-based bimetallic catalysts such as Pd-Cu [22], Pd-Ru [23], Pd-Ni and Pd-Co [24] have been found to exhibit superior cat-

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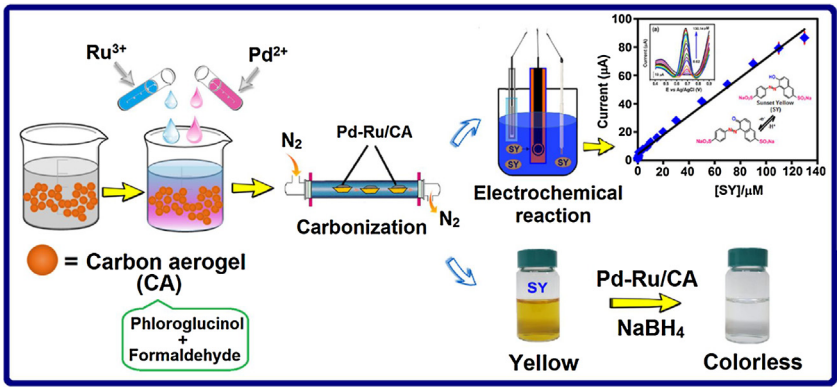
https://doi.org/10.1016/j.snb.2017.10.112
0925-4005/



Scheme 1. Schematic illustration of the preparation procedure and applications of the Pd-Ru/CA nanocomposite material.

alytic and electronic properties compared to their monometallic counterparts [25]. In particular, the Ru co-catalyst is an important electroactive element that tend to promote formation of oxygenated species at lower potentials, which in turn enhances the catalytic activity of the bi-functional catalyst [26]. Nonetheless, owing to the fact that the redox potential of Ru^{3+}/Ru^0 (0.62 V) is much smaller compared to that of Pd^{2+}/Pd^0 (0.95 V), and that the two elements readily belong to different crystalline phases [27], even though the bimetallic Pd-Ru nanomaterials exhibit size-dependent physicochemical properties, the synthesis and shape-control of Pd-Ru alloys remain as a challenging task [28].

Sunset yellow FCF (SY), which contains an azo (−N=N−) group in its structure, is a petroleum-derived orange dye that has being widely used in food and beverage industry [29]. The azo linkage is the most labile portion of the dye molecule and is known to provoke enzymatic breakdown in mammals. Moreover, the toxic azo dyes tend to decompose easily to aromatic amines, which tend to induce carcinogenic side effects, hepatocellular damage, renal failures, headache, and children attention-deficit/hyperactivity disorder (ADHD) [30]. An excessive intake of SY (E110) may also cause allergies, diarrhea, and other symptoms [31,32], as such, azo dyes have been banned as food additives. In view of the fact that the control of food products should encompass qualitative and quantitative studies of the active as well as inactive ingredients, the control and detection of azo dyes such as SY have becoming the most demanding issues. The most common techniques invoked for detection of SY include electrochemical method [33], enzyme linked immunosorbent assay [34], high performance liquid chromatography (HPLC) [35], spectrophotometry [36], and so on. Among these techniques, electrochemical detection of SY is particularly advantaged by its easy setup, low-cost, quick response, and high sensitivity [37,38]. Nonetheless, while electrochemical sensors are known to be rather sensitive devices, they are normally drawback by narrow detection ranges.

We report herein a facile sol-gel route for the synthesis of Pd-Ru NPs incorporated carbon aerogel (Pd-Ru/CA) as an effective catalyst for sensitive electrochemical detection of SY, as illustrated in Scheme 1. The physicochemical properties of the as-prepared Pd-Ru/CA nanocomposite material were thoroughly characterized by a variety of different spectroscopic and analytical techniques. To the best of our knowledge, no relevant report on the fabrication of Pd-Ru/CA-modified electrode materials and their prospective application as SY sensors has been made. The electrochemical performances of the Pd-Ru/CA-modified electrode were compared with its monometallic counterparts with and without the presences of CA support and various potential interferences and were also tested for real samples. Moreover, the activity and kinetics for catalytic degradation of SY over the Pd-Ru/CA catalyst were also studied.

2. Experimental

2.1. Materials

Palladium(II) chloride anhydrous, ($PdCl_2$, *ca.* 59–60% Pd basis), ruthenium(III) chloride hydrate ($RuCl_3 \cdot xH_2O$ (*ca.* 40–49% Ru basis), and Sunset Yellow FCF (SY) were obtained commercially (Sigma-Aldrich) and were used without further treatment. Research grade reagents such as phloroglucinol (ACS, 99.98%), formaldehyde (37% in water), and hydrochloric acid (HCl) were purchased from Acros. The phosphate buffer solutions were prepared by using 0.05 M Na_2HPO_4 and NaH_2PO_4 solutions, while adjusting their pH values with 0.5 M H_2SO_4 and 2.0 M NaOH. All other chemicals used were analytical grade and all solutions were prepared using ultrapure water (Millipore).

2.2. Catalyst preparation

Carbon aerogels (CA) were synthesized by polycondensation of phloroglucinol-formaldehyde (Phl-F) by means of a modified sol-gel process reported elsewhere [8]. Typically, *ca.* 2.2 g of phloroglucinol was first dissolved in 8 mL ethanol and 1.0 mL HCl (0.01 M) mixture solution, followed by an ultrasonic agitation for about 10 min. Then, a total of 3.0 mL formaldehyde was added slowly into the above mixture solution in a dropwise fashion to obtain a homogeneous solution, which was then cooled in an ice bath for 2 h, followed by a gelation procedure at 40 °C for 24 h. Subsequently, the obtained Phl-F gel was aged at 80 °C for 24 h, washed with ethanol thrice, dried (at 60 °C), then subjected to a carbonization treatment under N_2 atmosphere with a heating rate of 5 °C min^{-1} till reaching 900 °C and maintained at the same temperature for 2 h. The CA supporting material was further thermally activated at 900 °C for 2 h under a continuous flow of N_2 and CO_2 gas with a flow rate ratio of 0.9:0.2 L min^{-1}.

The Pd-Ru NPs incorporated CA nanocomposites were also prepared by a similar sol-gel process. Typically, desirable amounts of Pd and Ru salt precursors with a Pd^{2+} to Ru^{3+} molar ratio of 2:1 were introduced into the Phl-F gel solution under stirring condition for at least 30 min. The subsequent procedures for curing, carbonization, and cooling were identical to that for the synthesis of CA support alone. The final nanocomposite material so fabricated is denoted as Pd-Ru/CA.

2.3. Fabrication of the Pd-Ru/CA-modified electrode

Typically, *ca.* 3.0 mg of the as-synthesized Pd-Ru/CA was first dispersed in 1.0 mL water and sonicated for 2 h. Then, *ca.* 8 μL of the substrate was withdrawn and drop-casted onto the surface of the screen printed carbon electrode (SPCE). The binder-free Pd-Ru/CA-