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Catalytic activity of palladium nanocubes/multiwalled carbon nanotubes structures for methyl orange dye removal

O. Arciniega Cano[a], C.A. Rodríguez González[a,*], J.F. Hernández Paz[a], P. Amezaga Madrid[b], P.E. García Casillas[a], A.L. Martínez Hernández[c], C.A. Martínez Pérez[a]

[a] Universidad Autónoma de Ciudad Juárez, Av. del Charro # 450 Nte, col. Partido Romero, Cd. Juárez Chihuahua, CP 32310, Mexico
[b] Centro de Investigación en Materiales Avanzados, S.C., Departamento de Física de Materiales, Miguel de Cervantes 120, Complejo Industrial Norte, Cd. Chihuahua, Chih. México, C.P. 31136, Mexico
[c] División de Estudios de Posgrado e Investigación, Instituto Tecnológico de Querétaro, Av. Tecnológico de Querétaro, Av. Tecnológico s/n Esq. Gral. Mariano Escobedo, Col. Centro Histórico, 76000 Querétaro, Mexico

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A B S T R A C T

In this work, the synthesis and catalytic activity measurements of a nanostructured material formed by palladium (Pd) nanocubes supported on multiwalled carbon nanotubes (MWCNTs) for removing methyl orange as a model of organic contaminant from aqueous solution are presented. The nanocubes were synthesized by a reduction process of H_2PdCl_4 and a non-covalent method that involves a surfactant functionalization of the carbon nanotubes was used to produce the nanostructured material. Characterization was performed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV–vis. Results showed well dispersed Pd nanocubes, in the range of 15–25 nm, bonded onto the carbon nanotubes. The catalytic experiments exhibited 81.9% methyl orange removal after 8 min and 99% after 60 min using 1 mg of the nanostructured material per every 20 mg/L of the dye.

1. Introduction

Textile, food, leather, plastics, dyeing, printing and cosmetic are among the most contaminant industries due to release of hazardous effluents containing dyes with complex and highly persistent structures, which may lead to the contamination of the ecosystem. Also, they can cause severe health problems in human beings, since they exhibit high biotoxicity as well as potential mutagenic and carcinogenic effects [1,2].

A wide range of technologies are applied in order to remove dyes from colored effluents, some of them are physical (adsorption, reverse osmosis, ultrafiltration), chemical (chlorination, ozonation, precipitation, chemical oxidation processes, advanced oxidation processes, photocatalysis) and biological (microbiological or enzymatic decomposition, biodegradation) [3].

Noble metal nanoparticles (e.g. Platinum, Palladium, Rhodium and Ruthenium) have been successfully used as catalyst for different applications such as chemical synthesis, oil refining, storage of hydrogen, exhaust gas treatment and wastewater treatment due to their high specific surface areas, high ordered structures, densely populated unsaturated surface coordination sites, high oxidation activity and excellent mechanical and thermal strength [4,5]. The catalytic properties of metal nanoparticles (NPs) are determined by shape, size and composition. Shape control of metal NPs can provide a way to adapt their catalytic activity because shape defines the atomic disposition on the surface and it can maximize their performance in many catalytic applications [6]. Palladium plays an important role in a wide number of industrial applications and these applications demand the use of Pd in a finely divided state where the size and shape are important parameters to control in order to maximize its properties [7]. Pd nanocubes have been used as catalyst to enhance the properties in different studies such as oxygen reduction [8,9] and glucose sensing [10].

Since their discovery by Sumio Iijima in 1991 [11], carbon nanotubes (CNTs) have attracted great attention in multidisciplinary areas due to their unique mechanical, electronic and optical properties. In comparison with classical adsorbents such as activated carbon and clay, CNTs are more attractive because of their favorable physicochemical stability, high selectivity, and structural diversity. CNTs might be ideal sorbents for the dye removal from water [12–14]. Nanostructures made of carbon structures with noble metals NPís have been used for dye removal obtaining promissory

* Corresponding author.
E-mail address: claudia.rodriguez@uacj.mx (C.A. Rodríguez González).

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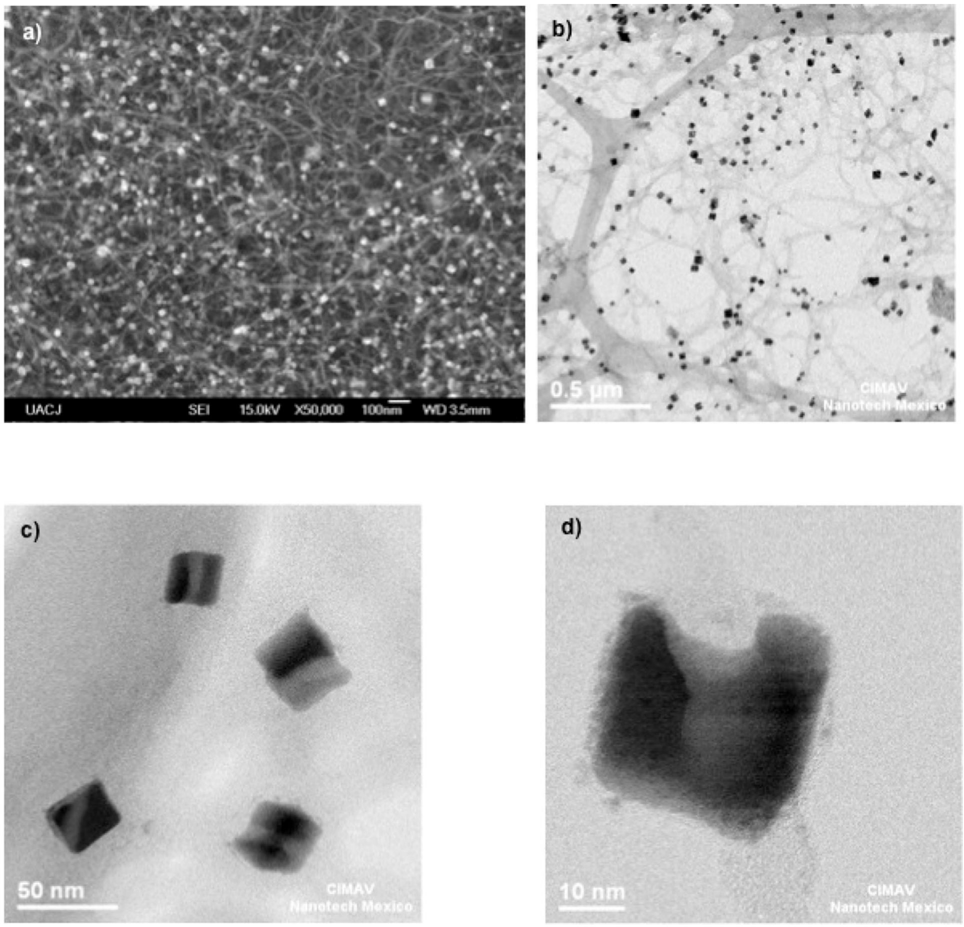

Fig. 1. SEM (a) and TEM (b–d) images of MWCNTs/Pd nanostructured material.

results [15]. There are several studies where carbon nanotubes are decorated with Pd NPs. Usually the surface of carbon nanotube is acid treated in order to create carboxylic, and hydroxyl groups for subsequent metal nanoparticles anchoring [16]. The principal problem with this method is that both electrical conductivity and corrosion resistance of carbon nanotubes would be reduced, and also can lead to poor dispersion of metal nanoparticles [17]. Another way to activate carbon nanotubes is by using wrapping materials (polymers, organic materials or surfactants), this non-covalent method causes less or even no damage to the structure of carbon nanotubes [18]. The correct organic material selection for wrapping will result in good metal NPs dispersion on the carbon nanotubes.

In this study, a MWCNTs/Pd nanocubes material was synthetized using a non-covalent method for methyl orange (MO) removal in aqueous solution under magnetic stirring. MO dye was chosen as contaminant due to it is a common azo dye. Azoic dyes are the 50% of the whole dyes used at the industry [19]. The synthesis of the material, catalytic properties of Pd and MWCNTs adsorption are discussed.

2. Experimental

2.1. Materials

Multiwalled carbon nanotubes produced by Chemical Vapor Deposition (MWCNTs, length: 100 nm, diameter: 5–7 nm, batch # MKBQ3087V), Cetyltrimethylammonium bromide (CTAB, 99%) and L-ascorbic acid (AA) were purchased from Sigma-Aldrich; Palladium (II) chloride ($PdCl_2$, anhydrous, 59.5% as Pd) was obtained from Alfa Aesar; Methyl orange was obtained from Matheson Coleman & Bell.

2.2. Instrumentation

Morphology and elemental chemical composition of the samples were examined with a Jeol JSM7000F scanning electron microscope (SEM) and a Jeol JEM-2200FS transmission electron microscope (TEM) coupled with an energy dispersive spectrometer (EDS). The XRD patterns of samples were obtained on a Panalytical X'Pert PRO powder X-Ray diffraction instrument with Cu Kα radiation (λ = 0.15418 nm) over the range 2θ = 10–100° at 40 kV and 20 mA. X-ray photoelectron spectroscopy (XPS) was carried out on a XPS Perkin Elmer spectrometer. Ultraviolet visible spectra (UV–vis) analysis was done on a StellarNet UV–vis-NIR spectrometer.

2.3. Preparation of MWCNTs/Pd nanostructure

A non-covalent method using CTAB as surfactant was used to allow the anchoring and growth of Pd nanocubes on the carbon nanotubes. First, 1.6 mg of MWCNTs was dispersed in 20 ml of CTAB (12.5 mM) and then sonicated for 20 min in order to allow the CTAB adsorption on the MWCNTs. In this process the hydrophobic part of the CTAB is adsorbed onto the MWCNTs surface by Van der Waals interaction [17]. Afterwards, 1 ml of H_2PdCl_4 (10 mM) was added under magnetic stirring at 95 °C allowing the anchoring of the CTAB hydrophilic segment to the Pd precursor [17,20]. Lastly, after 5 min 160 µl of AA (100 mM) was added to the mixture to produce a spontaneous reduction and stirred for 30 min. The mixture was then

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