

Simple preparation of tungsten supported carbon nanoreactors for specific applications: Adsorption, catalysis and electrochemical activity



Vishal J. Mayani, Suranjana V. Mayani, Sang Wook Kim*

Department of Advanced Materials Chemistry, College of Science and Technology, Dongguk University–Gyeongju, Gyeongbuk 780-714, Republic of Korea

ARTICLE INFO

Article history:

Received 30 December 2014
Received in revised form 26 March 2015
Accepted 28 March 2015
Available online 4 April 2015

Keywords:

Adsorbent
Carbon tungsten composites
Electrode
Heterogeneous catalyst
Nanoreactors
Tungsten carbide

ABSTRACT

Porous carbon supported tungsten carbide nanoreactors, two sizes (~25 and 170 nm), were designed using economical petroleum pitch residue followed by tungsten (W) doping. X-ray diffractions showed both carbon tungsten composites (CTC-25 and CTC-170) contained tungsten subcarbide (W_2C) and monocarbide (WC) as the major and minor crystalline phases, respectively. The present study provides a multiple perspective of carbon tungsten composites (CTCs) for methanol oxidation (as an electrode), adsorption (as an adsorbent) and degradation (as a solid catalyst) of methylene blue (MB). The operational electrodes were designed from both CTCs and used as a catalyst in an electrocatalysis process. The electrocatalysts exhibited high and stable catalytic performance ($CTCE-25 > CTCE-170$) in methanol electro-oxidation. The newly synthesized W-doped carbon nanoreactors were used successfully as an adsorbent for MB and a heterogeneous catalyst for MB oxidation. Ordered CTC-25 and CTC-170 exhibited dynamic MB adsorption within 15 min and complete oxidation of MB in 25–40 min. A synergetic effect between tungsten carbide and the carbon cage framework was noted.

© 2015 Published by Elsevier B.V.

1. Introduction

The direct methanol fuel cells (DMFCs) are highly suitable for the growth of portable devices and transportation applications for energy generation between the range of fuel cells, due to its high activity at low temperatures and easy tackling of liquid fuel. The most promising materials for DMFCs are metal particles dispersed on carbon framework, these metal composites provides (i) high activity for methanol oxidation and (ii) water activation, which is essential for the removal of the adsorbed carbon monoxide generated during the methanol decomposition process [1]. Besides energy conservation, the environmental protection is an important aspect in the today's industry oriented world. The total expulsion of organic waste in the water resources is a critical environmental issue. Different analytical techniques and methods are available for the separation of dyes from the contaminated water, which includes photo-catalysis, ultrafiltration, adsorption, membrane and electrochemical processes. However, adsorption and catalysis are the significant techniques in terms of simplicity of design, ease of operation and flexibility. Metal associated carbon composites have

shown greater adsorption property along with catalytic behavior compare to pristine carbon for the removal of organic dyes from the polluted water [2,3].

In recent years, hybrid carbon composites with unique properties have been designed to meet the demands of multiple applications. These metal-doped carbon materials have potential in the field of energy storage, heterogeneous and electro-catalysis, and material science owing their individual porous structure and surface area, nano size, mass transfer capacity, and chemical and physical properties [4–7]. Pyrolysis fuel oil (PFO) residue-based pitch is considered the best alternative for the efficient and economical large-scale production of new template-based porous carbon networks and devices [8,9]. A chemically inert porous carbon cage (CC) developed from inexpensive petroleum pitch as a carbon source after extraction of naphthalene crystals and silica as a template can be used as a metal host, where energetic metal particles can trigger along the surface/to be filled inside the carbon framework [10–12]. Consequently, among the many techniques available for engineering metal carbon nanoreactors (MCNRs), the modern template method and metal doping approach can uniquely produce a wide range of different sized porous structures and well-defined morphologies with metal functionalities [13–15]. Reusable, inexpensive and eco-friendly MCNRs also have several additional features as well as the potential for tuning the

* Corresponding author. Tel.: +82 54 770 2216; fax: +82 54 770 2386.
E-mail address: swkim@dongguk.ac.kr (S.W. Kim).

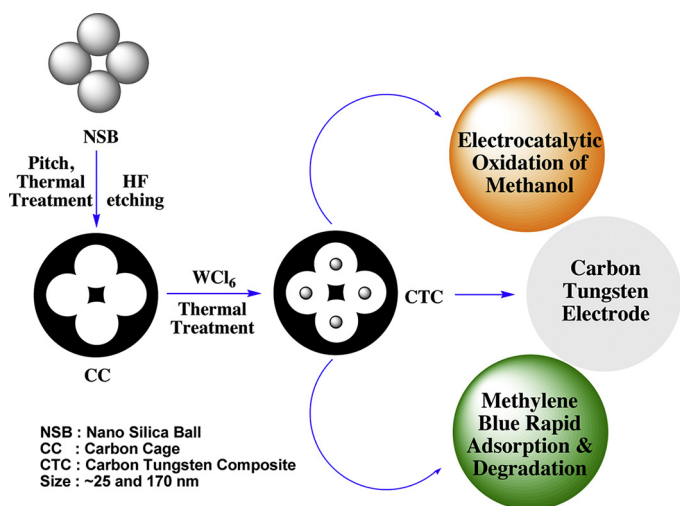


Fig. 1. Schematic illustration for the preparation of NSB, CC and CTC.

activity and selectivity of nanocomposites. Transition-metal composites (tungsten and molybdenum) have shown great significance over the past years because of their potential in applications as a sensor, photochemical device, fuel cell for power generation, adsorbent, heterogeneous catalyst or its host [16–18]. Therefore, the characteristic properties of transition-metal composites have been found to be similar to those of precious metals, such as platinum [19].

Currently, nano sized (~25 and 170 nm) carbon cages were prepared via a simple, effective and modified soft templating replication route based on a previous study, which allows the substantial production of ordered porous carbon cages (CCs) using economical PFO based pitch as carbon source after extracting naphthalene crystals [10,20]. Later, new and ordered carbon tungsten composites (CTC-25/170) were prepared easily by the simple thermal doping of tungsten on CC. The study provides a novel and multiple perspectives of CTCs as adsorbents, electrodes and heterogeneous catalyst for methylene blue (MB) adsorption, direct methanol fuel cell (DMFC) electro-oxidation and MB catalytic degradation, respectively. The electrocatalysts exhibited high and stable catalytic performance (CTCE-25 > CTCE-170) for methanol electro-oxidation. The W-doped nano-catalysts have also shown fast MB adsorption along with excellent MB catalytic oxidation. Ordered CTC-25 and CTC-170 exhibited dynamic MB adsorption within 15 min and complete oxidation of MB in 25–40 min. The large pores of the carbonaceous composite material CTC render it a potential heterogeneous catalyst and adsorbent.

2. Materials and methods

Fig. 1 represents a schematic illustration of the preparation of carbon tungsten composites (CTC-25 and CTC-170) and its precursors. The detailed methods for CTCs, carbon tungsten composite electrodes (CTCE-25 and CTCE-170), methanol electrocatalysis, MB adsorption and oxidation are given in the supporting information.

2.1. Materials

Reagents such as methanol, ethanol, toluene, ammonium hydroxide (Dae-Jung Chemicals & Metals Co., Ltd., Korea), tetraethylorthosilicate (TEOS), tungsten (VI) hexachloride (WCl_6), Nafion solution, methylene blue (Aldrich, USA), sulfuric acid (Junsei Chemicals Co., Ltd., Japan), 30% H_2O_2 (Wako Pure Chemicals Industries Ltd., Japan), and hydrofluoric acid (J.T. Baker, USA) were used

as received. Pyrolysis fuel oil (PFO) was obtained from Yecheon Naphtha Cracking Center (YNCC), Korea.

2.2. Characterization and measurements

Hybrid metal nanocomposites of tungsten with two sizes (~25 and 170 nm) were characterized by powder X-ray diffraction (PXRD, Phillips X'pert MPD diffractometer, Almelo, The Netherlands) over the 2θ range (10–80) at scan step 0.02° . Fourier transform infrared (FT-IR, Perkin-Elmer Spectrometer, Massachusetts, USA) spectroscopy was conducted out using a KBr self-supported pellet technique. Microanalysis of the products was determined out using a CHN analyzer (CE instruments, UK) and the metals entering into the carbon cage were determined by inductively coupled plasma–optical emission spectroscopy (ICP–OES, JY Ultima 2CHR). The thermal stability of the material was determined by thermogravimetric analysis (TGA, SDT600, TA instrument, USA). The BET surface area was completed by N_2 adsorption–desorption data measured at 77 K using a volumetric adsorption set up (Micromeritics ASAP-2010, USA). The pore diameter of the samples was determined from the desorption branch of the nitrogen adsorption isotherm employing the Barret–Joyner–Halenda (BJH) model. The microstructural evaluation of these samples were examined by scanning electron microscopy coupled with energy dispersive spectroscopy (SEM–EDS, LEO-1430, VP, UK) and transmission electron microscopy (TEM, JEM 2011, Jeol Corporation, Japan). MB centrifugation and adsorption were performed by centrifugation (Hanil Science Industrial Co., Ltd., Korea) and UV–vis spectroscopy (Varian Cary 4000, USA), respectively. Methanol oxidation was measured by electrochemical studies of CTCE-25 and CTCE-170 electrodes using cyclic voltammetry (CV, WonATech Zive SP2 Electrochemical Workstation, South Korea).

2.3. Synthesis of carbon tungsten composite (CTC-25/170)

Typically, 1.2 g of tungsten hexachloride (WCl_6) was dissolved in 50 mL of ethanol and 6 g of CC-25/170 was added slowly. The reaction mixture was sonicated for 30 min. The resulting mixture was stirred $60^\circ C$ for 2 h to allow homogeneous mixing and later air dried overnight at $100^\circ C$ in an oven. The solid was placed on a quartz reactor in a furnace and then treated in a N_2 atmosphere at $1000^\circ C$ for 3 h.

2.4. Preparation of carbon tungsten composite electrode (CTCE-25/170)

The working electrodes were designed by dispersing a small quantity of the electrode sample (CTC-25/170) in 1 mL of distilled water and $10\ \mu L$ of a 5 wt.% Nafion solution. The dispersion was ultrasonicated for 15 min and placed on a glass carbon electrode for W-doping. The excess water was evaporated slowly followed by the further addition of $10\ \mu L$ of 5 wt.% Nafion solutions to the resulting electrode for the electrode coating and the solvent was slowly evaporated. Carbon tungsten composite electrodes (CTCE-25 and CTCE-170) were used as the working electrode for electrocatalysis (Fig. 2A and B).

2.5. Methanol oxidation using cyclic voltammetry measurement

Electrochemical methanol oxidation analysis was carried out using newly developed electrodes (CTCE-25 and CTCE-170) as the working electrode. Platinum and $Ag/AgCl/3\ M\ NaCl$ were used as the counter and reference electrodes, respectively. CV was performed to examine methanol electrochemical oxidation using an electrolyte solution of 0.5 M H_2SO_4 and 1 M CH_3OH .

Download English Version:

<https://daneshyari.com/en/article/5355179>

Download Persian Version:

<https://daneshyari.com/article/5355179>

[Daneshyari.com](https://daneshyari.com)