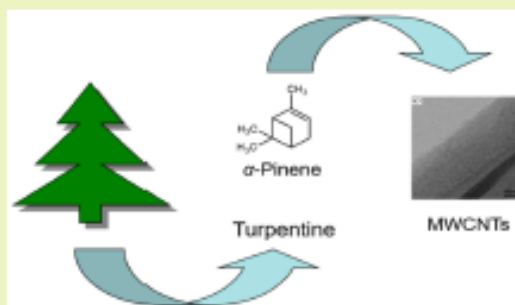


Parametric Study of the Synthesis of Carbon Nanotubes by Spray Pyrolysis of a Biorenewable Feedstock: α -PineneJ. Lara-Romero,^{*,†} T. Ocampo-Macias,[†] R. Martínez-Suarez,[†] R. Rangel-Segura,[†] J. López-Tinoco,[‡] F. Paraguay-Delgado,[§] G. Alonso-Núñez,^{||} S. Jiménez-Sandoval,[⊥] and F. Chiñas-Castillo[#][†]Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Avenida Francisco J. Múgica S/N, Edificio V1, Ciudad Universitaria, C.P. 58060, Morelia, Michoacán, México[‡]Departamento de Química y Bioquímica, Instituto Tecnológico de Lázaro Cárdenas, Avenida Melchor Ocampo No. 2555, C.P. 60950, Lázaro Cárdenas, Michoacán, México[§]Centro de Investigación en Materiales Avanzados, Unidad Chihuahua, Miguel de Cervantes Saavedra No. 120, C.P. 31136, Chihuahua, México^{||}Centro de Nanociencia y Nanotecnología, Universidad Nacional Autónoma de México, Km 107 Carretera Tijuana-Ensenada, C.P. 22800, Ensenada, Baja California Norte, México[⊥]Centro de Investigación y de Estudios Avanzados del IPN, Unidad Querétaro, Libramiento Norponiente No. 2000, C.P. 79230, Querétaro, México[#]Facultad de Ingeniería Mecánica, Instituto Tecnológico de Oaxaca, Avenida Ing. Víctor Bravo Ahuja No. 125, C.P. 68030, Oaxaca, México

Supporting Information

ABSTRACT: We present a parametric study on the growth of carbon nanotubes (CNTs) by spray pyrolysis of a biorenewable feedstock obtained from living pine trees, namely α -pinene. The analyzed variables were the type of catalyst, catalyst concentration, flow of reactants, and reaction time; all at a fixed temperature of 800 °C. The evaluation and optimization of these parameters was performed based on the yield and crystallinity of produced CNTs which were monitored by Raman spectroscopy, thermogravimetric analysis, X-ray diffraction, and high resolution transmission electron microscopy. Ferrocene as catalyst produced highly crystalline multiwalled CNTs while Co- and Fe-phthalocyanine produced nitrogen-doped CNTs. A ferrocene concentration of 37 mg/mL and 5000 sccm flow were the optimal conditions to obtain the highest yield of crystalline CNTs. The variation of time produced crystalline CNTs with different lengths without modifying their crystallinity. The growth kinetics of MWCNTs follows a Deal–Grove model which indicates that the growth is diffusion-limited and suggests that the root growth mechanism controls the growth process.

KEYWORDS: Carbon nanotubes, Spray pyrolysis, α -Pinene, Raman spectroscopy, Growth kinetics



INTRODUCTION

Carbon nanotubes (CNTs) play an important role in the development of nanomaterials due to their unique electrical, mechanical, and optical properties.¹ They are currently being used in various and diverse applications such as catalysts,^{2–4} sensors,^{5,6} fuel cells,^{7–9} lubricant additives,^{10,11} etc. Because of their enormous application potential, the production of large quantities of quality CNTs at low costs is highly desirable which must be achieved by controlling different parameters for a given synthesis method. Low cost methods such as chemical vapor deposition and spray pyrolysis offer excellent production yield with controlled features of the CNTs produced.¹² The combination of carbon source, the type of catalyst and the

reaction parameters such as temperature, flow, and reaction time are critical for the production of well-crystallized CNTs. In this direction, many reports considering the effect of different parameters on the synthesis of carbon nanotubes using different reacting systems can be found in the literature.^{13–18}

Several carbon species such as methane, acetylene, benzene, xylene, and toluene have been used as a feedstock to synthesize CNTs. These precursors are obtained from fossil fuel and are projected to diminish in the future making it necessary to look

Received: December 14, 2016

Revised: March 22, 2017

Published: March 30, 2017

Materials Research Express



PAPER

Occurrence of photoluminescence and onion like structures decorating graphene oxide with europium using sodium dodecyl sulfate surfactant

RECEIVED
11 May 2017REVISED
30 May 2017ACCEPTED FOR PUBLICATION
5 June 2017PUBLISHED
10 July 2017V J Cedeño¹, R Rangel² , J L Cervantes³, J Lara¹, J J Alvarado³ and D H Galván⁴¹ Programa de Doctorado en Ingeniería Química, División de Estudios de Posgrado, Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Z.C. 58060, Morelia, Michoacán, Mexico² División de Estudios de Posgrado, Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Z.C. 58060 Morelia, Michoacán, Mexico³ CINVESTAV-IPN, Unidad Mérida, Mérida, Yuc., Mexico⁴ CNYN-UNAM, Ensenada, B.C., MexicoE-mail: rrangel@umich.mx

Keywords: graphene oxide, decoration, europium, surfactant

Abstract

Graphene oxide decoration with europium was carried out using SDS (sodium dodecyl sulfate) as the surfactant. The reaction was performed in a microwave oven and subsequently underwent thermal treatment under hydrogen flow. The results found in the present work demonstrate that through the use of SDS surfactant aggregates of hemi-cylindrical and onion-like structures could be obtained; which propitiate an enhanced synergistic photoluminescence located at the red wavelength. On the other hand, after thermal treatment the aggregates disappear providing a good dispersion of europium, however a decrease in the photoluminescence signal is observed. The graphene oxide decorated with europium was characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Fourier infrared transform spectroscopy (FTIR), RAMAN spectroscopy, x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) techniques, showing the characteristic features of graphene oxide and europium.

1. Introduction

Constituted in a hexagonal lattice one atom thick, graphene is the most promising allotrope of carbon. Graphene is an excellent conductor of heat and electricity. It possesses a high mechanical strength (0.05 TPa), great flexibility and transparency [1–4]. As a consequence, graphene is being studied by many research groups for the preparation of new hybrid nanomaterials. A commonly used procedure for this purpose is the decoration of surfaces. The decoration is a process consisting of homogeneous and non-agglomerated dispersion of a metal on the surface of graphene. The purpose is to improve the transfer rate of electrons between the graphene and the deposited molecule. In this way it is sought to enrich the desired property; such as could be, the photoluminescence [5, 6]. In a general description, this procedure occurs through the oxygen-containing functional groups, which are adsorbed on a vacancy or defect, which subsequently interacts with the europium, promoting its anchoring to the graphene oxide surface. In this way, some properties considering different applications such as super-capacitors, solar cells, field-effect transistors, sensors and biosensors, hydrogen storage batteries, transparent electrodes, among others are modified [7–9]. In particular, rare earth metals such as europium deposited on graphene show luminescent properties, which can be valuable for biosensing or optoelectronics [10, 11]. One of the most useful methodologies in nanometals synthesis is the chemical reduction of metal salts in the presence of some stabilizing agent, such as surfactants; and the incorporation of microwave heating for a rapid assembly of nanostructures [12, 13]. The use of surfactant promotes the dispersion of the solid into the aqueous media, and helps to control the deposit and insertion of functional groups on the surface of graphene and thereby obtain ordered hybrid materials [14]. These surfactants possess amphiphilic properties. They own long, hydrophobic tail with short, hydrophilic head, which tends to be added, resulting in diverse morphologies, ranging from vesicles to and multilamellares to hemi-cylindrical and onion micelles [15, 16]. Besides the SDS (sodium dodecyl sulfate) surfactant is being used

Influencia del dopaje con Ce en las propiedades estructurales y optoelectrónicas de películas delgadas de ZnO

MANUEL GARCÍA MÉNDEZ*, ALVARO BEDOYA CALLE*, RICARDO RANGEL SEGURA**, VÍCTOR COELLO***

El óxido de zinc (ZnO) es un óxido transparente conductor (TCO) cuyas propiedades únicas hacen posible su uso como película delgada en diversas aplicaciones tecnológicas.¹⁻⁴ El ZnO tiene una estructura hexagonal tipo würtzita ($a_0 = 3.24$ Å, $c_0 = 5.20$ Å), un ancho prohibido directo, E_g , relativamente grande, de ~3.3 eV, por lo que es transparente en la región desde UV-Visible-Cercano IR y una energía excitónica grande, de 60 meV, que resultaría en una alta eficiencia en emisión de luz.^{5,7,8} El ZnO ha ganado un amplio interés en el ámbito científico y comercial como TCO alternativo al óxido de indio dopado con estaño (ITO).⁹ Entre sus ventajas se cuenta la posibilidad de modelado fino en sus propiedades, bajo costo, abundancia en la Tierra y compatibilidad con procesos de integración a gran escala (circuitos ULSD).^{5,10} Para fabricar ZnO en película delgada se han empleado varias técnicas, entre otras se pueden mencionar el depósito por láser pulsado,⁸ erosión iónica reactiva DC,^{4,5} depósito por capas atómicas,⁶ evaporación por cañón de electrones,¹¹ rocío pirolítico¹² y erosión iónica reactiva RF.¹⁴

De las técnicas citadas, la erosión iónica reactiva asistida por radiofrecuencia (RF) es un procedimiento muy atractivo para fabricar películas delgadas de ZnO. Controlando parámetros de depósito (potencia de la fuente RF, presión de trabajo, flujo de gases) es posible obtener películas homogéneas, de espesor y texturizado homogéneo sobre áreas grandes de sustrato y con buena reproducibilidad, de propiedades compatibles a las requeridas para aplicaciones en dispositivos optoelectrónicos.^{5,14} Además, dopar al ZnO con una selección de elementos es un procedimiento que puede provocar modificaciones favorables en las propiedades estructurales y optoelectrónicas en las películas delgadas de ZnO.¹⁶⁻¹⁸

De los elementos disponibles para dopaje, el cerio (Ce) ha cobrado un interés especial, ya que las películas de ZnO dopadas con este elemento poseen propiedades óptimas para aplicaciones en dispositivos fluorescentes o electroluminis-

centes.^{19,20} En películas delgadas, el dopaje con Ce las vuelve emisoras de luz en la región UV o visible del espectro.^{21,22} En el caso de películas de ZnO dopadas con Ce, se ha reportado que cuando se excitan con luz UV, éstas emiten en el violeta, azul, verde y amarillo, dependiendo del porcentaje de dopado y calidad cristalina.^{16-18,21,22}

Dada la importancia y potenciales aplicaciones del ZnO como película delgada, es necesario contribuir con información precisa que permita incrementar el control sobre la sintonización de sus propiedades optoelectrónicas, en función de las condiciones experimentales de depósito, temperatura y dopaje.

En este trabajo se reportan los resultados obtenidos al fabricar y caracterizar películas delgadas de ZnO, sin dopar y dopadas con Ce (ZnO:Ce). Posterior al depósito, las películas se tratan térmicamente en una atmósfera de oxígeno con el objetivo de minimizar la presencia de defectos estructurales y vacancias de oxígeno, así como para mejorar calidad cristalina y orientación preferencial. Para su caracterización se emplearon las técnicas de difracción de rayos X, espectroscopia UV-Vis, fotoluminiscencia y espectroscopia de fotoemisión de rayos X (XPS). Se discuten los efectos que tiene la adición de Ce sobre las propiedades estructurales y optoelectrónicas del ZnO.

EXPERIMENTAL

Equipo experimental

Las películas de ZnO y de ZnO:Ce se fabricaron por erosión iónica reactiva asistida por RF. Se utilizaron dos blancos: uno

* Universidad Autónoma de Nuevo León.

** Universidad Michoacana de San Nicolás de Hidalgo.

*** Centro de Investigación Científica y de Educación Superior de Ensenada, Unidad Monterrey.

Contacto: mgarciamendez@cicfm.uaenl.mx

DENSIDADES Y VISCOSIDADES DE LÍQUIDOS IÓNICOS PUROS BASADOS EN LOS CATIONES SULFONIUM, IMIDAZOLIUM Y PYRROLIDINIUM Y EL ANIÓN BIS(TRIFLUOROMETILSULFONYL)IMIDE

Indira Yarely López Cortés^a, Mariana Ramos Estrada^a, Gustavo Iglesias Silva^b, Fernando Pérez Villaseñor^c

^a Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Francisco Mújica S/N, Morelia, Michoacán, CP 58000, México. mramos@umich.mx

^b Departamento de Ingeniería Química, Instituto Tecnológico de Celaya, Av. Tecnológico y A. García Cubas S/N, Celaya, Guanajuato, CP 38010, México.

^c Facultad de Ciencias Básicas Ingeniería y Tecnología, Universidad Autónoma de Tlaxcala, Av. Universidad No. 1, Tlaxcala, Tlaxcala, CP 90062, México

Resumen

Se determinaron las densidades y viscosidades de los líquidos iónicos puros 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonfyl)imide [Bmppyrr][NTf₂], triethylsulfonium bis(trifluoromethylsulfonfyl)imide [Et₃S][NTf₂], 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonfyl)imide [Amim][NTf₂] y 1,3-dimethoxyimidazolium bis(trifluoromethylsulfonfyl)imide [(OMe)₂Im][NTf₂] en un intervalo de temperatura de 278.15 a 343.15 K a presión atmosférica. Los resultados obtenidos de densidad se ajustaron a la ecuación propuesta por Gardas y Coutinho y los datos de viscosidad a las ecuaciones de Arrhenius y de Vogel-Fulcher-Tammann (VFT). La ecuación de por Gardas y Coutinho representa los datos experimentales con un porcentaje de error promedio absoluto de 0.000021%, 0.021147%, 0.044153% y 0.034780% para el [Bmppyrr][NTf₂], [Et₃S][NTf₂], [Amim][NTf₂] y [(OMe)₂Im][NTf₂], respectivamente. Para el caso de la viscosidad, el modelo de Vogel-Fulcher-Tammann y la ecuación de Arrhenius presentaron porcentajes de error promedio absoluto de 0.0696%, 0.0301% y 0.0388% para el [Bmppyrr][NTf₂], [Et₃S][NTf₂] y [Amim][NTf₂], respectivamente con la ecuación propuesta por Arrhenius, y de 0.0548%, 0.1150% y 0.1138% para el [Bmppyrr][NTf₂], [Et₃S][NTf₂] y [Amim][NTf₂] con la ecuación de Vogel-Fulcher-Tammann.

Introducción

Los líquidos iónicos (LIs) son sales cuyo punto de fusión se encuentra por debajo de los 373 K. En general, están formados por un catión orgánico aromático y un anión inorgánico [5]. Una de las propiedades más importantes de estos compuestos que los hace atractivos para aplicación en diferentes áreas de la industria e investigación, es que tienen una presión de vapor extremadamente baja, lo cual los convierte en sustancias prometedoras como solventes orgánicos en procesos de extracción o procesos de destilación extractiva [13]. Debido a su baja presión de vapor, han sido utilizados como sustituyentes de los compuestos orgánicos volátiles (COV) para reducir o eliminar los daños provenientes de estos compuestos y así contribuir a una menor contaminación ambiental [9]. Otra de las características principales de los LIs surge de su enorme variedad para modificar sus propiedades físicas y químicas combinando el tipo de catión y de anión presente en cada una de sus estructuras [7]. Por medio de una selección adecuada, el diseño de LIs permite el desarrollo de procesos y productos más eficientes [1]. En este sentido, el conocimiento de las propiedades termofísicas, como por ejemplo, la densidad y viscosidad, es de suma importancia desde el punto de vista de investigación, ya que la elección de un líquido iónico para alguna aplicación determinada se encuentra condicionado por su comportamiento termofísico [11]. Por ejemplo, las densidades experimentales son esenciales para diferentes aplicaciones en la ingeniería química, tales como el diseño de diferentes tipos de condensadores, rehervidores, trenes de separación o en recipientes de almacenamiento, así también en la determinación de flujo en tuberías y operaciones de transferencia

DENSIDADES DE LÍQUIDOS IÓNICOS BASADOS EN LOS CATIONES SULFONIUM E IMIDAZOLIUM Y EL ANIÓN BIS(TRIFLUOROMETHILSULFONYL)IMIDE Y SUS MEZCLAS CON 1-PROPANOL

Indira Yarely López Cortés^a, Mariana Ramos Estrada^a, Gustavo Iglesias Silva^b, Fernando Pérez Villaseñor^c

^a Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Francisco Mújica S/N, Morelia, Michoacán, CP 58000, México. mramos@umich.mx

^b Departamento de Ingeniería Química, Instituto Tecnológico de Celaya, Av. Tecnológico y A. García Cubas S/N, Celaya, Guanajuato, CP 38010, México.

^c Facultad de Ciencias Básicas Ingeniería y Tecnología, Universidad Autónoma de Tlaxcala, Av. Universidad No. 1, Tlaxcala, Tlaxcala, CP 90062, México.

Resumen

En el presente trabajo se investigaron las propiedades de exceso de los líquidos iónicos tryethylsulfonium bis(trifluoromethylsulfonyl)imide [Et₃S][NTf₂], 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Amim][NTf₂], 1,3-dihydroxyimidazolium [(OH)₂Im][NTf₂] bis(trifluoromethylsulfonyl)imide y 1,3-dimethoxyimidazolium bis(trifluoromethylsulfonyl)imide [(OMe)₂Im][NTf₂] con 1-propanol. Las densidades de los sistemas de mezclas fueron determinadas midiendo el periodo de oscilación en un densímetro de tubo vibrante de Anton Paar, en un intervalo de temperatura de 278.15 to 343.15 K a presión atmosférica. Los datos experimentales se ajustaron a la ecuación propuesta Redlich-Kister. Los volúmenes molares de exceso para los sistemas de [Et₃S][NTf₂] + 1-propanol y [Amim][NTf₂] + 1-propanol, presentaron resultados negativos en el intervalo de $x_{LI} < 0.9$, mientras que a concentración de $x_{LI} > 0.9$ se presentó un cambio de signo a valores positivos. Para el caso del [(OH)₂Im][NTf₂] + 1-propanol, los volúmenes molares de exceso el cambio de signo de negativo a positivo se observó a concentraciones de $x_{LI} = 0.4$ y 0.6 , mientras que para [(OMe)₂Im][NTf₂] + 1-propanol fue a $x_{LI} = 0.7$.

Introducción

Los líquidos iónicos (LI) son sales cuyo punto de fusión se encuentra por debajo de los 373 K. Están formados por un catión orgánico que generalmente es aromático y un anión inorgánico [2]. Una de las características principales de los líquidos iónicos surge de su enorme variedad para modificar sus propiedades físicas y químicas combinando el tipo de catión y de anión presente en cada una de sus estructuras. Debido a que los LI son relativamente sustancias nuevas y desconocidas, uno de los principales problemas que se presentan durante el diseño de procesos o para determinar nuevas aplicaciones de estos compuestos, es la ausencia de datos confiables de sus propiedades termodinámicas más importantes, tanto para LI puros como sus mezclas con diferentes solventes. En este contexto, las propiedades de los LI puros y sus mezclas pueden proporcionar información no solo acerca de la estructura del fluido, sino también información sobre las interacciones moleculares presentes en las mezclas, las cuales son la base para el mejoramiento de modelos termodinámicos y para la representación del comportamiento de los LI en cualquiera de sus aplicaciones [9]. Por ejemplo, en la industria química, se han utilizado mezclas de LI + agua como absorbente para la remoción de SO₂ [11]. Además, también se han utilizado mezclas de LI con diversos compuestos moleculares para ser utilizados como electrolitos en baterías de litio así como también en dispositivos electrónicos incorporados en vehículos eléctricos [12]. Por otro lado, también se han aplicado diversas mezclas de LI con alcoholes para la síntesis de otros líquidos iónicos, en procesos de extracción y para la generación de hidrógeno [10].

J.A. Montes-Gutierrez¹ / R. García-Gutierrez¹ / M. Barboza-Flores¹ / R. Meléndrez¹ / R. E. Cabanillas¹ / O. E. Contreras² / G. A. Hlrata² / R. Rangel-Segura³

Micro-Structures of Nanodiamonds Grown on Silicon by Hot Filament Chemical Vapor Deposition

¹ Universidad de Sonora, Hermosillo, Sonora, Apdo. Postal 5-088, C.P. 83000, México, E-mail: rgarcia@cifus.uson.mx

² Centro de Nanociencia y Nanotecnología, Universidad Nacional Autónoma de México, Apdo. Postal 14, C.P. 22800, Ensenada, Baja California, México

³ Posgrado en Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Michoacan, México

Abstract:

A method to grow homogeneous micro-sized diamond clusters on silicon by Hot-Filament Chemical Vapor Deposition in a homemade reactor is reported in this work. Thermal decomposition of a $\text{CH}_4\text{:H}_2$ mixture gases was carried out in a horizontal quartz-tube reactor at 2200 °C filament temperature and 1000 °C substrate temperature at relative low pressure around 150 Torr depositing diamonds on silicon wafers. The diamond micro-structures are formed by nano-crystalline diamonds, they have a rounded shape and a narrow particle size distribution around a micrometer. The diamond micro-structures synthesized in this work showed a strong Raman shift signal, a peak at 1330 cm^{-1} typical of the diamond and a single optical trap was localized nearby 300 °C by Thermoluminescence analysis indicating that these diamond micro-structures could be a good thermoluminescent dosimeter material. Due to their excellent properties, diamonds obtained by this technique should find application in the biomedical and optoelectronic industry.

Keywords: biosensors, dosimetry, nano-diamonds, thermoluminescence

DOI: 10.1515/ijcre-2017-0088

Received: May 27, 2017; **Accepted:** October 26, 2017

1 Introduction

Micro- and nano-diamonds synthesized by Hot-Filament Chemical Vapor Deposition (CVD) are promising material for numerous applications due to their excellent properties such extreme mechanical hardness, broad optical transparency from deep-UV to the far-IR, good electrical insulation, excellent thermal conductivity, and resistance to chemical attack and intense radiation (Gracio, Fan, and Madaleno 2010). Micro- and nano-sized diamonds have been applied for their thermoluminescence properties in dosimetry and, due to its harmlessness and bio-compatibility also have been used recently in the industry of biosensors (Mochalin et al. 2012). Beside, diamond has atomic number ($Z = 6$) similar to atomic number biologic tissue ($Z = 7.4$), this property make it a suitable material for bio-mechanical applications (Rebisz et al. 2004a). In this work, thermoluminescence provided information of impurity defects in diamond crystallites that are used for quantitative determination of electron and hole traps, this property make micro-diamonds a successful material for dosimeters. Moreover, Raman spectroscopy and Scanning Electron Microscopy (SEM) are the techniques most frequently used for characterization of diamond (Chow et al. 2000; Merkulov et al. 2001). Diamond has been grown as films, columns, micro-crystallites, nano-crystallites and ultra-nano-crystallites (Auciello et al. 2004). In this research Raman spectroscopy provided the information about the crystalline quality and discriminated different structures, such as diamond films, micro-crystallites and nano-diamond carbon compounds. Likewise, SEM provided the morphology and size of the nanodiamonds synthesized by this technique.

2 Experimental procedure

In this work a home-made hot filament chemical vapor deposition (HFCVD) reactor has been used to grow nanodiamonds on silicon wafer. A schematic diagram of the HFCVD reactor is shown in Figure 1. The growth

Densities and Viscosities for Binary Liquid Mixtures of *n*-Undecane + 1-Propanol, + 1-Butanol, + 1-Pentanol, and + 1-Hexanol from 283.15 to 363.15 K at 0.1 MPa

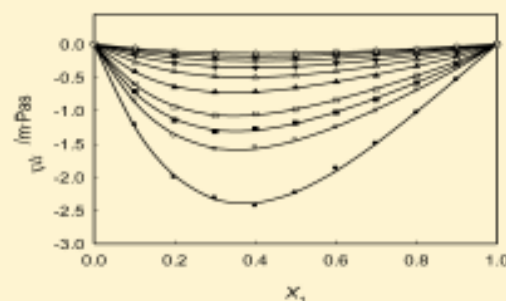
Gustavo A. Iglesias-Silva,* Adriana Guzmán-López, and Guadalupe Pérez-Durán

Departamento de Ingeniería Química, Instituto Tecnológico de Celaya Celaya, Guanajuato CP 38010, México

Mariana Ramos-Estrada

Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Mich. CP 58030, México

ABSTRACT: This paper presents densities and viscosities of binary mixtures of *n*-undecane with 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol from 283.15 to 363.15 K at 0.1 MPa over the entire composition range. Densities come from a vibrating tube densimeter, while viscosities are from a pellet microviscometer. A three-body McAllister equation correlates the kinematic viscosities together with an equation based upon a quadratic mixing rule for the Gibbs energy of activation. The excess molar volumes and viscosity deviations calculated from the experimental data have positive and negative deviations from ideality over the temperature range, respectively.



1. INTRODUCTION

Densities and viscosities of mixtures are essential in industrial applications that involve mass, and heat transfer. Alcohols and their mixtures are used as solvents or in the manufacture of perfumes and brake fluids. This work is a continuation of our work of *n*-alkanes + 1-alcohols.¹ Thermodynamic properties of *n*-alkanes + *n*-alcohols have been measured to explain the way in which the alcohol structure is modified with the addition of *n*-alkane. This modification has been suggested to be due to a partial destruction of the structure formed by the hydrogen bonding of the pure 1-alcohol during the mixing process. Densities and viscosities of binary mixtures of *n*-undecane + 1-alcohols are scarce. Densities of *n*-undecane with ethanol have been measured by Pádelo et al.² To the best of our knowledge, densities with *n*-undecane + 1-propanol, + 1-butanol, 1-pentanol, and 1-hexanol does not exist in the literature. Viscosities for the binary mixtures of this work also have not been measured previously.

This work reports the densities and viscosities for binary mixtures of *n*-undecane with 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol at 0.1 MPa from 283.15 and 363.15 K over the entire composition range. A Redlich–Kister³ type equation correlates excess molar volume and viscosity deviations. The McAllister⁴ and Nava-Rios et al.⁵ equations are used to represent the kinematic viscosities.

2. EXPERIMENTAL SECTION

Samples. The samples were supplied by SAFC for *n*-undecane (≥99 in mass fraction %), Sigma-Aldrich for 1-propanol anhydrous (99.7 in mass fraction %), 1-butanol (99.8 in mass fraction %), 1-pentanol (≥99 in mass fraction %), and 1-hexanol (≥99 in mass

Table 1. Sample Information

chemical name	source	CAS No.	initial purity mass fraction	purification method	analysis method ^a
<i>n</i> -undecane	SAFC	1120-21-4	0.99	none	GC
1-propanol	Sigma-Aldrich	71-23-8	0.997	none	GC
1-butanol	Sigma-Aldrich	71-36-3	0.998	none	GC
1-pentanol	Sigma-Aldrich	71-41-0	0.99	none	GC
1-hexanol	Sigma-Aldrich	111-27-3	0.99	none	GC

^aGas chromatography provided by the supplier.

fraction %). The samples have been prepared using an analytical balance (Ohaus model AS120S) with an accuracy 0.1 mg. Substances are used as received and kept in airtight containers. Table 1 shows the specifications of the samples.

Apparatuses and Procedures. A vibrating tube densimeter (Anton Paar, DMA 5000) was used to measure the density with a stated reproducibility by the manufacturer of 1×10^{-6} g·cm⁻³ for the density and 0.001 K for the temperature. The densimeter is excited by a harmonic electromagnetic force and then senses the change of the oscillating frequency. An oscilloscope measures the resonance frequency of the tube. Densities are related to the harmonic oscillation period considering Hook's law. The densimeter is calibrated by the manufacturer using two reference fluids: ultrapure

Special Issue: In Honor of Kenneth R. Hall

Received: February 11, 2016

Accepted: June 17, 2016

Published: July 6, 2016

Photoluminescence on cerium-doped ZnO nanorods produced under sequential atomic layer deposition–hydrothermal processes

J. L. Cervantes-López¹ · R. Rangel²  · J. Espino² · E. Martínez³ · R. García-Gutiérrez⁴ · P. Bartolo-Pérez⁵ · J. J. Alvarado-Gil⁵ · O. E. Contreras⁶

Received: 6 October 2016 / Accepted: 19 December 2016
© Springer-Verlag Berlin Heidelberg 2016

Abstract Doped and undoped ZnO nanorod arrays were produced combining atomic layer deposition and hydrothermal processes. First, a ZnO layer with preferential orientation normal to the *c*-axis was grown on the substrate by means of the decomposition of diethylzinc; subsequently, the nanorod arrays were produced through solvothermal process using a solution of $\text{Zn}(\text{NO}_3)_2$ as precursor. Doped ZnO nanorods were produced using $\text{Ce}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{H}_2\text{O}$ as dopant agent precursor. Undoped and Ce-doped ZnO nanorod arrays showed high-intensity photoluminescence. The doping concentration of $x = 0.04$ ($\text{Zn}_{1-x}\text{Ce}_x\text{O}$) displayed the highest photoluminescence. Undoped ZnO showed an intense UV peak centered at 382 nm with a narrow full wide half maximum of 33 nm. Ce-doped ZnO PL spectra contain three bands, one signal in the UV region centered at 382 nm, other centered at 467 nm in the near-green region and other one emission centered at 560 nm. The results herein exposed

demonstrate the capability to produce high-quality ZnO and $\text{Zn}_{1-x}\text{Ce}_x\text{O}$ films.

1 Introduction

ZnO wurtzite hexagonal phase is one of the most important functional materials due to its excellent physicochemical properties and its diversity in terms of morphology, properties and applications [1, 2]. The excellent properties of ZnO include direct band gap (3.37 eV), measured at room temperature with high exciton binding energy (60 meV). Recently, ZnO has been extensively studied because of its potential application in gas sensor arrays [3], solar cells [4], photodetectors [5], light-emitting diodes, laser systems [6], to name a few.

Considering the production of nanostructures based on a specific material, the morphology is a key factor in providing differences in comparison with the bulk compound. On this regard, an important feature attributed to ZnO is that it can be shaped into different nanostructures such as nanorods, nanowires, nanoplatelets and nanotubes, which are synthesized through various methods [7]. For instance, thin films have been produced by means of spray pyrolysis [4], radio frequency magnetron sputtering [8], pulsed laser deposition (PLD) [9], laser molecular beam epitaxy (MBE) [10], metal-organic chemical vapor deposition (MOCVD) [11], atomic layer deposition (ALD) [12]. In order to produce ZnO films with uniform thickness and grain size, atomic layer deposition technique has been employed which possesses the basic advantage of surface control during growth [12]. ALD may be regarded as a special modification of the CVD technique. It is based on surface reactions, which are accomplished by sequential dosing of gaseous precursors on substrates.

✉ R. Rangel
rrangel@umich.mx

¹ Programa de Doctorado en Ingeniería Química, División de estudios de Posgrado, Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Mexico

² División de Estudios de Posgrado, Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Z.C 58060 Morelia, Mich., Mexico

³ CIMAV, Unidad Monterrey, Monterrey, N. L., Mexico

⁴ Departamento de Investigación en Física, Universidad de Sonora, Hermosillo, Sonora, Mexico

⁵ Departamento de Física Aplicada, Cinvestav-IPN, Unidad Mérida, Mérida, Yuc., Mexico

⁶ CNYN-UNAM, Ensenada, B. C., Mexico

Materials Research Express



CrossMark

PAPER

Indium-doped ZnO nanorods grown on Si (1 1 1) using a hybrid ALD-solvothermal method

J L Cervantes-López¹, R Rangel², M García-Méndez³, H Tiznado⁴, O Contreras⁴, P Quintana⁵, P Bartolo-Pérez⁵ and J J Alvarado-Gil⁵

¹ Programa de Doctorado en Ciencias en Ingeniería Química, Facultad de Ingeniería Química, Universidad Michoacana de SNH., Morelia, Mich., Z.P. 58030, Mexico

² División de Estudios de Posgrado, Facultad de Ingeniería Química, Universidad Michoacana de SNH., Morelia, Mich., Z.P. 58030, Mexico

³ Facultad de Ciencias Físico-Matemáticas, Universidad Autónoma de Nuevo León, Mexico

⁴ Centro de nanociencias y nanotecnología (CNYN-UNAM), Ensenada Baja California, Nuevo León, Mexico

⁵ Departamento de Física Aplicada, CINVESTAV-IPN, Unidad Mérida, Mérida, Yucatán, Mexico

E-mail: rrangel@umich.mx

Keywords: nanorods, ZnO, atomic layer deposition, indium oxide

Abstract

Atomic layer deposition (ALD) followed by microwave hydrothermal processing was successfully employed for producing doped and vertically aligned ZnO nanorod arrays with different aspect ratio. Firstly, a textured ZnO layer with preferential orientation normal to the *c*-axis was formed on substrate (1 1 1) silicon single crystals by means of the ALD technique. This was achieved through the decomposition of diethylzinc at 190 °C and 3.289×10^{-4} atm, which provided an adequate template with nucleation sites, favoring further growth of vertical nanorods. Subsequently, nanorod array growth was produced on the same surfaces through solvothermal synthesis using as promoter a solution of $\text{Zn}(\text{NO}_3)_2$. In addition, growth of indium-doped ZnO nanorods over the substrates was produced by using $\text{In}(\text{CH}_3\text{COO})_3$ as a doping agent. The method presented allows good quality ZnO and $\text{Zn}_{1-x}\text{In}_x\text{O}$ thin films to be obtained. Photoluminescence spectra show clear evidence of the inclusion of indium in the ZnO matrix. The higher intensity ratio $\text{Zn}_{0.96}\text{In}_{0.04}\text{O}/\text{ZnO}$ was increased 40-fold, demonstrating such an effect.

1. Introduction

The fabrication of nanodevices, which is very important nowadays, is directly related with the syntheses of nanomaterials, which aims at improving their physical, chemical and mechanical properties. An important issue for research is to study the improvement in the electrical and structural properties of certain devices through the syntheses of nanostructures, proposing facile techniques and low temperature processing [1]. As an example, the fabrication of hierarchically structured nanowire/nanoparticle composites presents an advantageous structure, one that allows nanoparticles to provide large surface areas for dye adsorption, whilst the nanowires can enhance the light harvesting, the electron transport rate, and the mechanical properties of the films [1]. In that sense, ZnO nanostructured materials have received considerable attention from diverse research groups due their remarkable performance as a base for the development of materials for electronics, optics and photonics [1, 2]. Their excellent properties include direct band gap energy of 3.37 eV, at room temperature, and a high exciton binding energy of about 60 meV. Moreover, ZnO thin films have been grown using several techniques, including electrochemical deposition [3], magnetron sputtering systems [4], spray pyrolysis [5], the thermal evaporation method [6], metal-organic chemical vapor deposition [7] and atomic layer deposition (ALD) [8].

The ALD technique has been employed to generate uniform thickness and grain size ZnO thin films due to its well-known inherent advantage of high quality control of the surface sample during the growth [9]. ALD may be regarded as a special modification of the CVD technique. It is based on sequential saturating surface reactions, which are accomplished by alternate dosing of gaseous precursors on substrates. The unique mechanism of film formation provided by ALD offers several advantages over other technologies. Among them, their remarkable capability of maintaining ultra-uniform thin deposited layers, and the simplicity of the reactor design and

Tailoring surface and photocatalytic properties of ZnO and nitrogen-doped ZnO nanostructures using microwave-assisted facile hydrothermal synthesis

R. Rangel¹  · V. Cedeño¹ · A. Ramos-Corona¹ · R. Gutiérrez² · J. J. Alvarado-Gil² · O. Ares² · P. Bartolo-Pérez² · P. Quintana²

Received: 24 March 2017 / Accepted: 11 July 2017
© Springer-Verlag GmbH Germany 2017

Abstract Microwave hydrothermal synthesis, using an experimental 2^3 factorial design, was used to produce tunable ZnO nano- and microstructures, and their potential as photocatalysts was explored. Photocatalytic reactions were conducted in a microreactor batch system under UV and visible light irradiation, while monitoring methylene blue degradation, as a model system. The variables considered in the microwave reactor to produce ZnO nano- or microstructures, were time, NaOH concentration and synthesis temperature. It was found that, specific surface area and volume/surface area ratio were affected as a consequence of the synthesis conditions. In the second stage, the samples were plasma treated in a nitrogen atmosphere, with the purpose of introducing nitrogen into the ZnO crystalline structure. The central idea is to induce changes in the material structure as well as in its optical absorption, to make the plasma-treated material useful as photocatalyst in the visible region of the electromagnetic spectrum. Pristine ZnO and nitrogen-doped ZnO compounds were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), specific surface area (BET), XPS, and UV-Vis diffuse reflectance spectroscopy. The results show that the methodology presented in this work is effective in tailoring the specific surface area of the ZnO

compounds and incorporation of nitrogen into their structure, factors which in turn, affect its photocatalytic behavior.

1 Introduction

Organic compounds are present in countless chemical processes. Among them, it is usual to find that a large amount of byproducts are generated, which often come from an organic source. Some of these processes produce species, which modify, among other characteristics, the color of the water discharge effluents, having frequently a negative impact on the environment. In particular, those effluents usually alter important parameters such as the chemical demand of oxygen (COD). Therefore, it is important to develop materials which can be helpful in developing methodologies which attenuate, at least to some extent, the effects of pollution caused by such compounds. Common means to attain this objective are the advanced oxidation processes (AOP); exhibiting high reactivity and non-selectivity, which made them applicable in a great variety of situations [1–3]. Although TiO_2 has shown to be, in many cases, the most efficient photocatalyst for advanced oxidation processes, other compounds such as ZnO have also proven to be a viable alternative [4, 5]. In particular, ZnO has been shown to be more efficient, in comparison to TiO_2 , in specific applications such as the treatment of wastewater arising from pulp bleaching [6–8]. One of the limitations of ZnO is its large energy gap (3.37 eV); therefore, the wavelength that promotes activation of this semiconductor is close to 368 nm, which corresponds to near-UV radiation. However, it has been shown that in some cases, the relevant absorption features of some compounds can be shifted towards the visible by

✉ R. Rangel
rrangel@umich.mx

¹ División de Estudios de posgrado de la Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Gral. Francisco J. Múgica S/N, Ciudad Universitaria, 58030 Morelia, Michoacán, Mexico

² Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional- Unidad Mérida, Antigua Carretera a Progreso Km 6, Cordemex, 97310 Mérida, Yucatán, Mexico