Ultrasonics Sonochemistry 17 (2010) 726–729

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

In situ sonochemical hydrolysis and deposition of composite layers of ionic liquid entrapped in colloidal silica network and their application as sensors for various gases

David S. Jacob [a], Avner Rothschild [b,1], Harry L. Tuller [b], Aharon Gedanken [a,*]

[a] Department of Chemistry and Kanbar Laboratory for Nanomaterials at the Bar-Ilan University Center for Advanced Materials and Nanotechnology, Bar-Ilan University, 52900 Ramat-Gan, Israel

[b] Crystal Physics & Electroceramics Laboratory, Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

ARTICLE INFO

Article history:
Received 16 August 2009
Received in revised form 7 December 2009
Accepted 15 December 2009
Available online 22 December 2009

Keywords:
Ionic liquids
Gas sensor
Silica hydrolysis
Ultrasound
Interdigitated electrode

ABSTRACT

An efficient one-step process for forming uniform solid-like layers of ionic liquid (IL) entrapped in colloidal silica network on interdigitated electrodes (IDE) using ultrasonic deposition is described in this communication. The electrical response of such layers deposited on insulating substrates fitted with interdigitated electrodes was measured upon exposure to different gases (H_2, NO_2, CO, and CH_4) in air demonstrating reversible and sensitive response at 100 °C.

1. Introduction

Room temperature ionic liquids (RTIL) are known for their useful electrochemical properties due to their electrolytic nature and high thermal stability [1]. These properties give rise to prospective applications in chemical and gas sensors, [2–8] batteries, [9] and fuel cells [10]. For example, IL coated on quartz crystal microbalance (QCM) transducers [2–4] or on langasite crystal resonators [5] were used as a sensors for organic vapors such as ethanol, acetone, toluene, and benzene. Microcantilevers coated with IL were also used as sensors for aqueous and organic vapors [6]. The sensing mechanism of these sensors is based on changes of the viscosity of the IL coating upon exposure to the analyte giving rise to a shift in the resonance frequency. In addition, IL were also deposited onto polymer membranes and their electrical resistance was found to be sensitive to gases such as O_2 [7,8]. In this work we report on the preparation of solid-like IL/silica composite layers deposited on alumina substrates fitted with platinum IDE and explore their gas sensing behavior.

In recent articles we described the preparation of conductive silica spheres filled with IL and means to control their surface morphology under different reaction conditions using a sol–gel process [11,12]. We found that the conductivity of pressed pellets of these spheres originates from the entrapped IL [11,12]. In this communication we describe a simple and efficient process for preparing composite layers of IL entrapped in the interstices in a solid network of silica particles and report on their electrical conductivity response to changes in the surrounding gas atmosphere.

The solidification of IL received an upsurge of interest as a means to fabricate conductive layers of ionogel materials. Ionogel materials are prepared by the in situ polymerization of suitable monomers and cross-linkers in IL [13], where the IL plays an important role in the electrical and mechanical behavior of the composite material [13]. Recently, Watanabe et al. studied the gelling behavior of composite layer comprising silica nanoparticles dispersed in IL [14]. They found that gelling occurs due to the formation of a network of interconnected silica particles where the IL fills the interstices between them. The conductivity of the composite material remained nearly the same as that of the pristine IL. In another study Roger et al. used IL as chemical additive in the synthesis of silica sol–gel materials with and without co-solvent [15].

Recently it was shown that ultrasonic waves can be used for depositing nanoparticles on flat and curved solid substrates such as ceramic [16], glass [17], polymers [18], textiles [19], metals

* Corresponding author.
E-mail address: gedanken@mail.biu.ac.il (A. Gedanken).
[1] Present address: Department of Materials Engineering Technion-Israel Institute of Technology, Haifa, Israel.

1350-4177/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultsonch.2009.12.015

Fig. 1. Gas sensor prototypes mounted on Al_2O_3 holders. (Note: The illustrated sensors resemble the ones used in this study.)

and paper. The deposition is performed either in a one-step or two step processes. In the one-step process the nanoparticles are fabricated sonochemically and subsequent to their production they are thrown at the solid surface by microjets formed after the collapse of the acoustic bubble. In the two step process commercially purchased nanoparticles are "thrown" at the solid surface by the microjets, and the ultrasonic waves are used only for "throwing stones" at solid surfaces. Our synthesis method is different from previous studies in that instead of dispersing silica particles in the IL we use a sonochemistry sol–gel process that leads to in situ precipitation of silica particles from silica precursor mixed in IL followed by network formation of silica particles where the IL fills the interstices between them. Thus the conductive silica nanoparticles are fabricated and thrown onto the IDE surface. This novel one-step process provides simple and versatile means to deposit solid-like composite layers of IL/silica as described in the following [20].

2. Experimental

The composite IL/silica layers were deposited on alumina substrates from a solution of IL and silica precursor using ultrasonic radiation. Fifteen grams of the IL 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIPF_6$, 99%, Solvent Innovation GmbH) were mixed with 1 ml of tetraethyl orthosilicate (TEOS, 99.9%, Aldrich). The solution was inserted into a three necked glass cell along with the alumina substrates and sonicated for 1 h at ~60 W/cm^2 and 20 kHz. The reaction temperature was maintained at 40–60 °C. Subsequently the substrates were taken out of the cell and washed with acetonitrile and ethanol to remove the excess IL attached to the substrate, followed by drying in vaccum (−1 bar pressure).

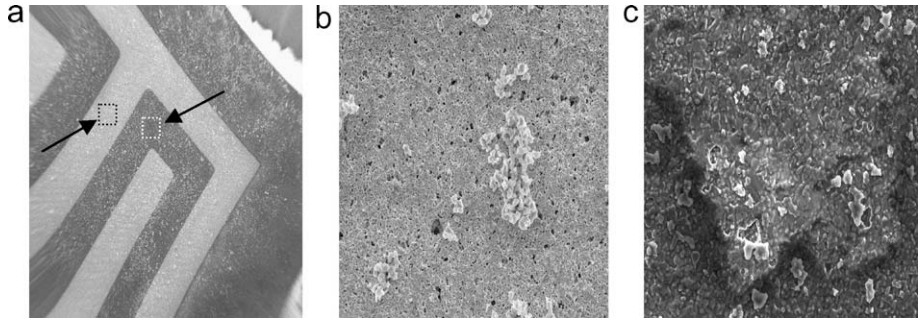

Fig. 2. HRSEM images of the coated substrate at low (a) and high magnifications (b and c), (12 mm length scale bar = 25 μm). The image in (b) was taken from an area above the Pt electrode and in (c) from an area above the bare alumina substrate, as indicated by the arrows in (a).

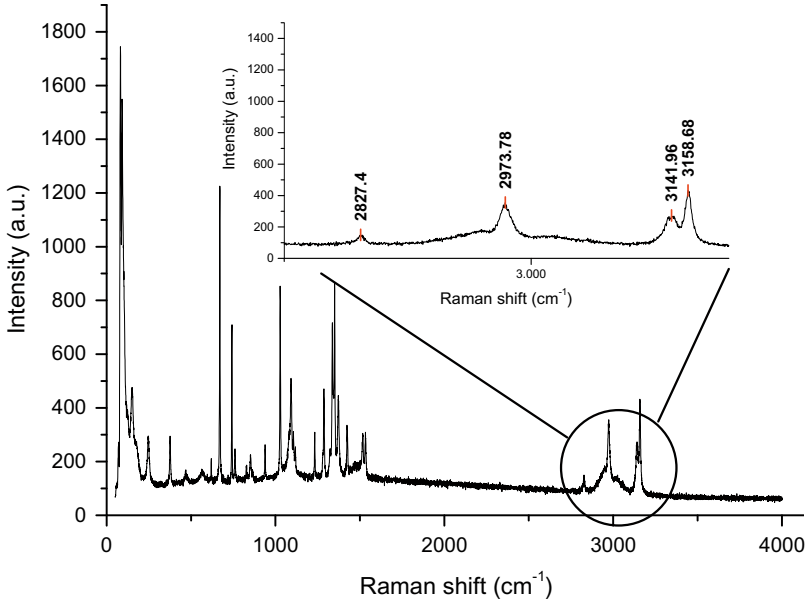

Fig. 3. Raman spectra of the deposited layer of IL/silica on IDE. The inset spectrum shows the peaks of C—H stretching and ring stretching.