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The 5th International Symposium on Nanostructured Materials and Nanotechnology was held during the 35th International Conference and Exposition on Advanced Ceramics and Composites, in Daytona Beach, Florida during January 24–29, 2010. This symposium provided, for the fifth consecutive year, an international forum for scientists, engineers, and technologists to discuss new developments in the field of nanotechnology. This year’s symposium had a special focus on the large-scale integration of functional nanostructures and challenges related to the fabrication of nano-devices. The symposium covered a broad perspective including synthesis, processing, modeling and structure-property correlations in nanomaterials and nanocomposites. Over 80 contributions (invited talks, oral presentations, and posters) were presented by participants from universities, research institutions, and industry, which offered interdisciplinary discussions indicating strong scientific and technological interest in the field of nanostructured systems.

This issue contains 17 invited and contributed papers peer-reviewed using The American Ceramic Society review process and covering various aspects and the latest developments related to processing of nanoscaled materials including carbon nanotubes-based nanocomposites, nanowire-based sensors and electrode materials for lithium ion batteries, photocatalysts, self-assembly of nanostructures, functional nanostructures for cell tracking and heterostructures.

The editors wish to extend their gratitude and appreciation to all the authors for their cooperation and contributions, to all the participants and session chairs for their time and efforts, and to all the reviewers for their valuable comments and suggestions. Financial support from the Engineering Ceramic Division of The American Ceramic Society is gratefully acknowledged. The invaluable assistance of the ACerS’s staff of the meetings and publication departments, instrumental in the success of the symposium, is gratefully acknowledged.
We believe that this issue will serve as a useful reference for the researchers and technologists interested in science and technology of nanostructured materials and devices.

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Introduction

This CESP issue represents papers that were submitted and approved for the proceedings of the 35th International Conference on Advanced Ceramics and Composites (ICACC), held January 23-28, 2011 in Daytona Beach, Florida. ICACC is the most prominent international meeting in the area of advanced structural, functional, and nanoscopic ceramics, composites, and other emerging ceramic materials and technologies. This prestigious conference has been organized by The American Ceramic Society’s (ACerS) Engineering Ceramics Division (ECD) since 1977.

The conference was organized into the following symposia and focused sessions:

Symposium 1  Mechanical Behavior and Performance of Ceramics and Composites
Symposium 2  Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications
Symposium 3  8th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4  Armor Ceramics
Symposium 5  Next Generation Bioceramics
Symposium 6  International Symposium on Ceramics for Electric Energy Generation, Storage, and Distribution
Symposium 7  5th International Symposium on Nanostructured Materials and Nanocomposites: Development and Applications
Symposium 8  5th International Symposium on Advanced Processing & Manufacturing Technologies (APMT) for Structural & Multifunctional Materials and Systems
Symposium 9  Porous Ceramics: Novel Developments and Applications
Symposium 10  Thermal Management Materials and Technologies
Symposium 11  Advanced Sensor Technology, Developments and Applications
Symposium 12  Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)
Symposium 13  Advanced Ceramics and Composites for Nuclear and Fusion Applications
Symposium 14  Advanced Materials and Technologies for Rechargeable Batteries
Focused Session 1  Geopolymers and other Inorganic Polymers
Focused Session 2  Computational Design, Modeling, Simulation and Characterization of Ceramics and Composites
Special Session  Pacific Rim Engineering Ceramics Summit

The conference proceedings are published into 9 issues of the 2011 Ceramic Engineering & Science Proceedings (CESP); Volume 32, Issues 2-10, 2011 as outlined below:

- Mechanical Properties and Performance of Engineering Ceramics and Composites VI, CESP Volume 32, Issue 2 (includes papers from Symposium 1)
- Advanced Ceramic Coatings and Materials for Extreme Environments, Volume 32, Issue 3 (includes papers from Symposium 2 and 12)
- Advances in Solid Oxide Fuel Cells VI, CESP Volume 32, Issue 4 (includes papers from Symposium 3)
- Advances in Ceramic Armor VII, CESP Volume 32, Issue 5 (includes papers from Symposium 4)
- Advances in Bioceramics and Porous Ceramics IV, CESP Volume 32, Issue 6 (includes papers from Symposium 5 and 9)
- Nanostructured Materials and Nanotechnology V, CESP Volume 32, Issue 7 (includes papers from Symposium 7)
- Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials V, CESP Volume 32, Issue 8 (includes papers from Symposium 8)
- Ceramic Materials for Energy Applications, CESP Volume 32, Issue 9 (includes papers from Symposiums 6, 13, and 14)
- Developments in Strategic Materials and Computational Design II, CESP Volume 32, Issue 10 (includes papers from Symposiums 10 and 11 and from Focused Sessions 1, and 2)

The organization of the Daytona Beach meeting and the publication of these proceedings were possible thanks to the professional staff of ACerS and the tireless dedication of many ECD members. We would especially like to express our sincere
thanks to the symposia organizers, session chairs, presenters and conference attendees, for their efforts and enthusiastic participation in the vibrant and cutting-edge conference.

ACerS and the ECD invite you to attend the 36th International Conference on Advanced Ceramics and Composites (http://www.ceramics.org/daytona2012) January 22-27, 2012 in Daytona Beach, Florida.

SUIJANTO WIDJAJA AND DILEEP SINGH
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Nanomaterials for Photocatalysis, Solar, Hydrogen, and Thermoelectrics
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MORPHOLOGY CONTROLLED ELECTROSPINNING OF V₂O₅ NANOFIBERS AND THEIR GAS SENSING BEHAVIOR

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ABSTRACT

Electrospinning of vanadyl acetylacetonate/polyvinylpyrrolidone hybrid nanofibers and calcination procedures design led to V₂O₅ nanofibers with control over their morphology. The fibers either consisted of densely joint nanorods or anisotropic nanocrystals forming porous nanofibers. They have been analyzed by thermogravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction and scanning electron microscopy. Their dispersions in water/ethylene glycol could be used for inkjet printing of V₂O₅ gas sensors and the particle and film morphology influence on gas sensitivity was investigated.

Keywords: Electrospinning, V₂O₅, Nanorods, Gas-sensing

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INTRODUCTION

Electrospinning is a versatile method for the production of 1D nanofibers. Originally designed for the production of simple polymeric fibers out of polymer solutions, the process was reinvented in the late 1990s for the production of functional nanofibers by addition of specific compounds (metal salts, nanoparticles, drugs) into the polymeric precursor solution. The fiber materials range from biocompatible fibers for tissue-design to ceramic fibers for various applications such as energy storage and gas sensing. The method allows an easy control over fiber morphology and alignment and offers great perspective for fabrication of 1D nanomaterials and possible device integration. V₂O₅ is an intrinsic n-type wide optical band gap semiconductor with an electrical conductivity of around 0.5 S cm⁻¹ at room temperature. The electrical conductivity is increased when part of the V⁵⁺ species is reduced to V⁴⁺ - accompanied by the simultaneous formation of oxygen vacancies - as the electron transport takes place in a hopping mechanism between V⁴⁺ impurities and V⁵⁺ centers. Due to the unique redox behavior, the ability to form a wide spectra of homogeneously mixed-valent phases and the resulting electronic properties, V₂O₅ is of great interest for micro-, optoelectronic and gas-sensing devices. Several published reports suggest a good sensitivity and selectivity of V₂O₅ against reducing gases such as amines. Furthermore its good chemical and thermal stability, the ability of multiple valency and the high redox-potential against Li/Li⁺ makes it a promising cathode
material for Li-ion batteries with high capacity. However, only a few examples of V$_2$O$_5$ nanofiber production by electrospinning can be found in literature. Differences in precursors, polymers or calcination procedures reportedly have a large influence on the V$_2$O$_5$ nanofiber morphologies, meaning that the method is able to produce defined nanocrystal morphologies like in wet chemical methods (e.g., solvothermal) with the advantage of no need of any workup steps.

In this study we present the synthesis of V$_2$O$_5$ nanofibers by electrospinning using the low-cost vanadyl acetylacetonate (VO(acac)$_2$) precursor. By the design of calcination procedures we were able to design the V$_2$O$_5$ crystal morphology. The obtained nanofibers either consisted of dense joint nanorods or porously joint nanocrystals. The gas sensing properties of V$_2$O$_5$ nanoparticle films was comparatively analyzed by testing the sensitivity of inkjet printed gas sensors towards ethanol.

**EXPERIMENTAL**

The V$_2$O$_5$ precursor solution consisted of 0.375 mM ml$^{-1}$ VO(acac)$_2$ and 37.5 mg ml$^{-1}$ polyvinylpyrrolidone (PVP, 1.300.000 g mol$^{-1}$) in a mixture of dichloromethane/pyridine (8:2). After 3h of vigorously stirring the dark greenish homogeneous solution was transferred into a syringe and electrospun on a custom-built system consisting of a syringe pump (kdScientific, USA), motorized z-positioning (isel Germany AG, Germany), a high voltage source (HCN 35 – 35000 POS, F.u.G. Elektronik GmbH, Germany) and a grounded metallic collector. The syringe was connected to a needle (0.8 mm inner diameter) via a PTFE tube and set to a potential of 20 kV, the feeding rate was 20 μl min$^{-1}$ and the needle-collector distance was 8 cm. After the spinning process the fibers were dried in vacuum over night and the following calcination procedure was done in two different ways. In the following the two different samples are named V$_2$O$_5$-1 and V$_2$O$_5$-2, respectively. V$_2$O$_5$-1 was calcined at 600 °C in air for 5 h and V$_2$O$_5$-2 was calcined for 5 h under Nitrogen at 500 °C and then postcalcined for 5 h at 600 °C in air. X-ray powder diffraction (XRD) patterns of the samples were measured on a STOE STADI MP diffractometer with Cu-Kα radiation ($\lambda$ = 1.5418 Å). Fourier transform infrared (FT-IR) measurements were carried out on a Perkin Elmer Spectrum 400. The samples morphologies were observed with a FEI Nova NanoSEM 430 scanning electron microscope (SEM). Thermo gravimetric analysis was carried out on a METTLER Toledo TGA/DSC 1 STAR$^\text{®}$ System. Ink-jet printing was done using a Microdrop MD-P-802 printer equipped with a nozzle of 50 μm inner diameter and a heatable stage which was set to 120 °C. The ink consisted of 4 mg V$_2$O$_5$-1 and V$_2$O$_5$-2, respectively, dispersed in a mixture of 4 ml H$_2$O/ethylene glycol (50:50 vol%), which could be printed at a voltage of 119 V and a pulse-length of 42 μs. The gas sensing property of the printed V$_2$O$_5$ nanocrystals was determined using a self designed measurement system operated at 220 °C using a Keithley 2400 source meter for resistivity measurement and controlled by LabView software.

**RESULTS AND DISCUSSION**

A thermo gravimetric analysis (TGA) of as-spun VO(acac)$_2$/PVP composite nanofibers was done in air to define the calcination temperatures for the V$_2$O$_5$ formation. The heating rate was set to 10 °C min$^{-1}$ and the starting weight 4.3 mg. The TGA (Fig. 1) showed
two steps of large mass losses. The first weight loss (180 - 220 °C) step could be attributed to the thermal decomposition of organic ligands from VO(acac)₂ and condensation reactions. The second step (400 - 450 °C) possibly indicated the combustion/oxidation of residual organics and incipient crystallization of V₂O₅. The total weight loss was found to be 70 wt%.

Figure 1: a) Thermo gravimetric analysis of the as-prepared VO(acac)₂/PVP composite fibers carried out in air at a rate of 10 °C min⁻¹. b) SEM micrograph of the as-prepared fibers.

The SEM micrograph of the as-prepared nanofibers (Fig. 1 b) showed homogeneous fibers with a diameter of around 150 nm and bead formation at some spots, which is related to the viscosity of the solution. It has been shown that the rheological properties of the spinning solution are strongly influencing the fibers morphology and higher polymer concentrations by overall constant spinning parameters can suppress bead formation. The control over the V₂O₅ nanofiber morphology could be gained by two distinct calcination processes. The pyrolysis of green fibers for 5 h at 600 °C in air led to the formation of nanofibers consisting of fused V₂O₅ nanorods (V₂O₅-I) with an average diameter of 250 nm and an average length of 600 nm (Fig. 2).

Figure 2: a) SEM image of the fibers calcined at 600 °C for 5 h in air. The fibers consisted of interconnected V₂O₅ nanorods. b) SEM image of the V₂O₅ nanofibers after calcination for 5 h at 500 °C in nitrogen followed by post calcination step at 600 °C for 5 h in air.