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Instability controlled synthesis of tin oxide nanofibers and their gas sensing properties

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ABSTRACT

Instability dependent electrospinning process has been controlled to obtain tin oxide nanofibers with morphological variation. The effect of spinning parameters such as viscosity, conductivity, flow rate, distance and applied voltage on growth rate of different instabilities was simulated and different deposition conditions were defined from the simulation results. The structural morphology was analyzed using X-Ray Diffraction (XRD) and Scanning Electron microscope (SEM). The sensing behavior of different structures was investigated. The branched structure obtained due to axisymmetric instabilities exhibited best sensing performance owing to high surface to volume ratio.

1. Introduction

One dimensional (1D) nanostructures with well-defined surface morphology and highly reactive surfaces have attracted great interest due to their novel physical and chemical properties. In particular, such structures have shown great potential as chemical gas sensors owing to their high surface to volume ratios. Significant efforts have been made to fabricate these structures via diverse range of approaches such as template-based technique [1], photolithography [2], chemical vapor deposition [3], electrochemical deposition [4] etc. However, these processes are costly, time consuming and often involve complex chemical and mechanical reactions that induces impurities in the grown products [5]. Among these different strategies, electrospinning [6] has emerged as the simplest synthesis route. It is an efficient way to generate ultrafine fibers by accelerating a jet of charged precursor solution in an electric field. The electrospun fibers with its high surface to volume ratio exhibit excellent gas sensing characteristics [7,8]. The gas sensing response of these fibers can be controlled by tailoring the fiber structure.

Growth rate of different instabilities such as Rayleigh, axisymmetric and non-axisymmetric instability during jet transport process play a major role in morphology determination and hence, greatly affect the sensing response [9,10]. Rayleigh instabilities are mainly caused by the surface tension force acting on the jet and may result in disruption of jet into droplets. This phenomenon can be suppressed at high viscosity and electric field strength [11]. In case of other instabilities; electric field and surface charge are the dominant forces. The interaction between tangential stress and surface charge leads to these instabilities. If the surface charge dominates, jet bending takes place. With increase in surface charge density, the jet undergoes a whipping motion which results in jet elongation and thinning. The other instability mode is the axisymmetric instability, in which beads emerge along with straight jet. Thus, the fiber morphology can be well controlled by tuning different electrostatic parameters such as applied voltage, flow rate, nozzle-collector distance and set-up configuration and suppressing the growth of undesired instability.

Several models have been simulated to study different instabilities involved in electrospinning phenomenon [12–14]. Most of the models are either theoretical investigation on the electrospinning phenomenon or empirical observations of effect of

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parameters on fiber diameter [15,16]. But very few studies have combined the two to study the effect of different electrospinning regimes on the physicochemical behavior of metal oxide nanostructures for sensing application.

This work aims to simulate the growth rate of different instabilities during the spinning process at different parametric conditions and study its effect on the morphological structure of tin oxide fibers. In the present work, parameters such as liquid properties, high voltage, nozzle-substrate distance and flow rate have been varied and the effect of different electrospinning regimes on the gas sensing behavior of tin oxide nanofibers has been investigated.

2. Material and methods

2.1. Preparation of precursor solutions

To study the effect of liquid properties on the electrospinning process, model solutions were prepared by blending high molecular weight polyethylene oxide (PEO) (M.W. 13, 00,000) with Tin (II) Chloride Dihydrate ($SnCl_2 \cdot 2H_2O$/PEO) solutions. The precursor solutions were prepared by dissolving $SnCl_2 \cdot 2H_2O$/PEO in ethanol with constant stirring at 80 °C for 2 h. After cooling down to room temperature, a solution of PEO (0.24 g PEO in 5 ml DMF) was slowly added into the $SnCl_2 \cdot 2H_2O$ solution under vigorous stirring. 0.1, 0.3, and 0.5 M $SnCl_2 \cdot 2H_2O$ solutions were prepared in 5 ml ethanol with different concentrations of PEO ranging from 1 to 3wt% to obtain variation in solution properties. The liquid properties of the precursor solutions were measured by different methodologies as described in Table 1.

2.2. Control of electrospinning conditions

The main instabilities that affect final film morphology are the Rayleigh, Axisymmetric and Whipping instabilities. The growth rates of these different instabilities on the liquid jet were determined from the already reported dispersion relations by M.M. Hohman et al. [11] and simulated in MATLAB to obtain controlled electrospinning conditions for morphological variation of the tin oxide fibers. The dispersion relations of different instabilities are mentioned in Section 2.3.

2.3. Dispersion relation of different instabilities

During electrospinning as the jet accelerates under the influence of electric field, tiny perturbations exist along the jet stream caused by various interactive forces and are referred as jet instabilities. These are mainly influenced by the liquid properties, electrostatic parameters (voltage, flow rate, nozzle-substrate distance) and ambient conditions. Varying these parameters lead to amplification of perturbations causing transition between various instability modes such as Rayleigh, Axisymmetric and Whipping modes (Fig. 1). The dominant mode of instability depends on the liquid properties and other operating parameters of the electrospinning process and can be predicted by linear stability analysis of the liquid jet.

2.3.1. Rayleigh instability

Surface tension plays the major role in Rayleigh instability resulting in jet break-up. With increase in electric field and viscoelastic force, the effect of surface tension on the jet decreases, preventing the break-up mechanism [17]. Hence, the buildup of the extensional stress stabilizes the jet and suppresses this instability.

There exists a criterion for critical field, above which the Rayleigh instability is suppressed. The critical field strength is denoted in Equation (1).

$$(\in - \overline{\in})E_\infty^2 = \frac{2\pi\gamma}{r_0} \tag{1}$$

where, $\in$ = Dielectric constant of solution, $\overline{\in}$ = Dielectric constant of air, E_∞= Applied Electric Field (V/m), γ = Surface Tension (N/m), r_0 = capillary radius (m).

The above equation has a simple physical interpretation i.e., when the electric field per unit length exceeds the surface tension pressure, the Rayleigh instability is suppressed. Hence, at high field strength the jet break-up does not occur until the jet becomes very thin.

2.3.2. Varicose jet break up

During jet transport, the jet disintegrates into droplets due to decrease in jet radius over a threshold value. So, to determine the morphological structure it is relevant to determine the conditions at which jet break-up occurs.

The radius for a straight and bend jet is determined from the following relations [18,19].

$$h = \frac{\sqrt{(6 \ \mu\rho Q^2)z^{-1/2}}}{\pi IE} : \text{straight jet} \tag{2}$$

$$h = \left(\frac{\rho Q^3}{2\pi^2 IE}\right)^{1/4} z^{-1/4} : \text{bend jet} \tag{3}$$

where; μ = Dynamic Viscosity (Pa.s); ρ = Density (kg/m^3); Q = Flow rate (m^3/s); I = Current (A); E = Electric field (V/m); z = nozzle-substrate distance (m)

Thus, thinning of jet takes place with increase in distance. This results in the jet break up mechanism due to strong mutual forces of repulsion. The characteristic radius (r_j) at which jet break-up occurs is given by Equation (4) [20].

Table 1
Liquid property measurement.

Liquid property	Apparatus	Methodology
Viscosity	Rheometer (BOHLIN INSTRUMENTS, MAL 1034911)	Change in viscosity with shear stress was measured in continuous ramp mode at room temperature using cone and plate geometry
Conductivity	Digital Conductivity meter (EI 611)	Conductivity was measured at room temperature in mS/cm
Surface tension	Capillary method	Thin glass graduated capillary with an inner diameter of 1.2 mm was used to measure the rise in height and contact angle was measured by a high resolution optical camera.
Dielectric constant	LCR meter (Agilent 4284A)	Parallel plate capacitive method was used for indirect measurement of dielectric constant. Prior to the measurement of precursor solution, the technique was calibrated for different known liquids.