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ScienceDirect

Sensors and Actuators A 136 (2007) 191–198

SENSORS AND ACTUATORS A PHYSICAL

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Comparison of morphology and electrical conductivity of various thin films containing nano-crystalline praseodymium oxide particles

S. Shrestha [a], C.M.Y. Yeung [a], C. Nunnerley [b], S.C. Tsang [a,*]

[a] *The Surface and Catalysis Research Centre, Department of Chemistry, University of Reading, Reading, RG6 6AD, UK*
[b] *Smiths Detection, 459 Park Avenue, Bushey, Watford, Herts WD23 2BW, UK*

Received 1 September 2006; received in revised form 17 October 2006; accepted 15 November 2006
Available online 14 December 2006

Abstract

It is well known that sensing performances depend critically on nature of sensor material, its structure and morphology. Praseodymium oxide nanoparticle has currently been receiving much attention as a new sensor material. Thus, three methods for the preparations of praseodymium oxide nanoparticles namely (i) direct heat treatment of praseodymium nitrate powder; (ii) precipitation of praseodymium nitrate solution as hydroxide nanoparticles followed by heat treatment; and (iii) synthesis of hydroxide nanoparticles in reverse micromulsion followed by heat treatment are hereby intensively studied. Powder X-ray diffraction and transmission electron microscopy (TEM) are employed to characterise the size and morphology of the praseodymium oxide particles. It is found that the microemulsion method gives the smallest particle size while the direct heat treatment gives the largest oxide particle size. In addition, the prepared oxide nanoparticles are fabricated as thin films on tin-doped indium oxide (ITO) electrode surface for electrochemical AC impedance characterisation. The impedance measurements of the films reveal that their electrical conductivity is inversely proportional to particle size, which is attributed to the decreasing resistance of grain boundaries as the grain size decreases.

Keywords: Praseodymium oxide; Nanoparticle; Direct heat treatment; Precipitation; Microemulsion; Particle size; Impedance; Grain size

1. Introduction

Over the past few years new trends in developing sensors are the integration of sensors with miniaturised (micromachined) analysers, nanoscale design of recognition elements, ultra fast monitoring of dynamic events in microscopic environments, molecular sized electrodes and introduction of advanced sensing materials [1]. Thus, the miniaturization has been the primary driving force by which the semiconductor industry has achieved the unprecedented gains in productivity and performance [2]. As a result, tremendous interest in assembling nanomaterials to produce functional sensors with novel electronic, magnetic and optical properties is denoted [3]. Nanosized materials are attractive because of their small size with corresponding large surface to volume ratio and tunable physico-chemical properties, which are directly related to size, composition and shape of the assembled particles. The tailored size, shape and structure and hence properties of nanomaterials offer excellent prospects for designing novel sensing systems [4,5]. In particular, the possibility of systematically controlling the electronic energy level spacing by adjusting the length scale of the nanomaterial comparable to the electron wavelength as bio-conjugating quantum dots has been attracting significant attention [3]. Some new but diverse applications such as, cell labelling [5], cell tracking [6], *in vivo* imaging [7], DNA detection [8,9] and multiplexed beads have recently appeared in the literature [10].

We have been interested in the synthesis of rare earth oxides, particularly the praseodymium oxide nanoparticles as they are playing an important role in modern catalytic, electronic and sensor materials [11–18]. For example, we and others have reported earlier that Pr_6O_{11} shows exceptionally high electrical conductivity due to electron hopping between the mixed metal ion valence states of the lattice [19]. As a result, superior sensitivity/selectivity using Pr_6O_{11} as a sensor material for the detection of ethanol vapour has been demonstrated [20]. In addition, Pr_6O_{11} displays great promise as a promoter in three-way catalyst [21], as phosphors for organic light emitting diode [22], as a semiconducting oxide for high-κ materials [23] and as

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[*] Corresponding author. Tel.: +44 118931 6346; fax: +44 118931 6632.
E-mail address: s.c.e.tsang@reading.ac.uk (S.C. Tsang).

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doi:10.1016/j.sna.2006.11.019

non-volatile ferroelectric random access memory (Nv-FRAM) devices [24].

As far as we are aware, there are very limited numbers of methods reported in the literature for the preparation of praseodymium oxide nanoparticles. As a result, three preparation methods namely (i) direct heat treatment of praseodymium nitrate powder; (ii) precipitation of praseodymium nitrate solution as hydroxide nanoparticles followed by heat treatment; and (iii) synthesis of hydroxide nanoparticles in reverse micelles followed by heat treatment have therefore been intensively studied and reported. It is noted that sensing performances (selectivity, sensitivity, accuracy, detection limit, response time) depend critically on nature of sensor construction material and its structure and morphology [25,26]. Thus, the size and morphology of the praseodymium oxide nanoparticles prepared by these three methods with respect to their physicochemical properties have been particularly investigated.

Perhaps, the first method of study is the most simple and straightforward one *via* a direct heat treatment of volatile precursor compounds such as nitrate, chloride, acetate, oxalate, hydroxide etc. at elevated temperatures in the presence of oxygen. It has been reported [27] that rare earth oxide nanoparticles obtained from direct heat treatment of the volatile nitrate or acetate precursor powders can give small particles associated with higher surface areas [28]. According to Eyring [29] the composition and surface structure of the rare earth oxide depends upon the temperature, oxygen fugacity, physical state and history of preparation. A thermal genesis study of oxide from nitrate showed that a heat treatment of 465 °C for an hour in static air is required [30].

Similarly, metal oxide nanoparticles can be prepared by precipitation of the water soluble metal salt to hydroxide nanoparticles on addition of an alkali in solution followed by heat treatment of the obtained solid particles. Bondioli et al. [31] noticed that the general precipitation method has little control over the shape and size of the precipitate, because of the rapid change in solution concentration and the localised, discontinuous nature of a strong alkali introduction and reaction. On the other hand, Rojas and Ocana [32] have recently reported a controlled precipitation of praseodymium nitrate as hydroxide nanoparticles with uniform particle size by using a weak base, the hexamethylenetetramine (HMTA) that is gradually hydrolysed giving ammonia in controlled manner. This is selected as our second method of preparation.

Finally, the third selected method involves the use of microemulsion. Micelles are single-phase thermodynamically stable, low viscosity dispersions of water/oil in a continuous medium of water/oil stabilised by a suitable surfactant co-surfactant mixture. The preparation of praseodymium oxide nanoparticles by the reverse micelle process involves two steps. One is first to prepare hydroxide nanoparticles in the revised micelle water droplets, which are stabilised by surfactant molecules at the water/oil interface in oil phase. These surfactant stabilised water pools offer an appropriate microenvironment for micro-reaction processing and inhibit the excess aggregation of particles. The other step is to collect the hydroxide nanoparticles and convert them into oxide by subsequent heat treatment. It has been reported that accurate control of the particle size can be achieved by the microemulsion method *via* surfactant molecule stabilization without leading to particle coalescence [33], which governs the physicochemical properties of the synthesised nanoparticles such as crystallite size, shape, distribution, strain and defects [34].

As a result, this short paper is concerned with the preliminary comparative study of morphology and electrical properties of various praseodymium oxide nanoparticles prepared by the above three preparation methods.

2. Experimental

2.1. Materials

Analytical grade praseodymium oxide, Pr_6O_{11}; praseodymium nitrate hexahydrate, $Pr(NO_3)_3{\cdot}6H_2O$ (99.9% pure); hexamethylenetetramine, HMTA; chitosan (low molecular weight); sodium hydroxide, NaOH; cetyltrimethyl ammonium bromide, CTAB; polyvinyledene fluoride, PVdF and glassy carbon (2–12 μm) were obtained from Aldrich and were used without further purification. Sodium chloride and Repelcote (2% solution of dimethyldichlorosiloxane in octamethyl cyclotetrasiloxane) were obtained from Sigma biochemicals and VWR International Ltd., UK respectively. *N*-methyl-2 pyrrolidone (NMP) was obtained from Acros organics. Toluene obtained from Fisher, was dried with molecular sieves. ITO-electrode (tin-doped indium oxide on glass, Image Optics Components Ltd., UK) used for hosting praseodymium oxide nanoparticles, were cut into 1 cm wide and 5 cm long rectangular plates, rinsed with ethanol and distilled water and subjected to heat treatment at 500 °C for 1 h in static air prior use. Deionised water was obtained from a Milli-Q purification system with the measured resistance of 18 MΩ cm. The heating of nanoparticles was conducted using a Eurotherm controlled Carbolite furnace, type SF12/7, Bamford, Sheffield. Slurry in NMP was prepared using a mixture of praseodymium oxide particles, conductive additive (glassy carbon) and the binder (PVdF).

2.2. Preparation methods

(i) Direct heat treatment of $Pr(NO_3)_3{\cdot}6H_2O$.

$Pr(NO_3)_3$ was carefully crushed in an agate mill. About 3.5 g of the crushed precursor was taken in a clean dried crucible and heated in a muffle furnace at 300 °C, 400 °C, 465 °C, 500 °C and 600 °C for 1, 2, 6, 8, 24 and 48 h in static air.

(ii) Precipitation of praseodymium nitrate solution as hydroxide nanoparticles followed by heat treatment.

A mixture of 2 mM $Pr(NO_3)_3$ and 10 mM HMTA in aqueous solution was boiled at 100 °C for 2 h. The solution was allowed to cool to room temperature, centrifuged and the precipitate was exhaustively washed with deionised water and air dried in order to obtain the $Pr(OH)_3$ nanoparticles. The properly dried $Pr(OH)_3$ precipitate was crushed in an agate mill and heated at 500 °C for an hour in static air.