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Editorial

Mesoporous Metal Oxide Films

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Abstract: Great progress has been made in the preparation and application of mesoporous metal oxide films and materials during the last three decades. Numerous preparation methods and applications of these novel and interesting materials have been reported, and it was demonstrated that mesoporosity has a direct impact on the properties and potential applications of such materials. This Special Issue of Coatings contains a series of ten research articles demonstrating emphatically that various metal oxide materials could be prepared using a number of different methods, and focuses on many areas where these mesoporous materials could be used, such as sensors, solar cells, supercapacitors, photoelectrodes, anti-corrosion agents and bioceramics. Our aim is to present important developments in this fast-moving field, from various groups around the world.

Keywords: metal oxide; mesoporous; sol-gel; sensor; supercapacitor; photoelectrode; corrosion; dye sensitized solar cell; PEG; bioceramics; TiO_2; SnO_2; ZnO; NiO; Mn_2O_3

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1. Introduction

Porous materials have been widely investigated and applied in many fields owing to their outstanding structural properties. According to the definition of International Union of Pure and Applied Chemistry (IUPAC), porous materials can be categorized into three types: microporous materials (pore size < 2 nm), mesoporous materials (2–50 nm) and macroporous materials (pore size > 50 nm). In the past two decades, great progress has been made in the aspects of fabrication and application of mesoporous metal oxides [1–3].

Mesoporous metal oxide films exhibit excellent physicochemical properties, such as large band gap, large surface area, controllable pore size and morphology, good thermal and chemical stabilities, unique optical and electrical properties, non-toxicity and low costs. Many methods of generating mesoporous films have been developed since mesoporous TiO_2 films were synthesized by O'Regan et al. in 1991 [4]. Most notably, the methods that have been used for the preparation of such metal oxide films include sol-gel screen printing, dip coating, spin coating, sputtering spray pyrolysis, atomic layer deposition, electrodeposition and anodic oxidation. A great deal of effort has been made to simplify these methods in order to prepare films faster and in a more reproducible way. Over the last 30 years, films have attracted significant attention for various applications, ranging from dye-sensitized solar cells, adsorption and separation, chemical and biochemical sensors, gas sensors, drug delivery, electrochromic windows, photo and/or electrocatalysis and energy storage devices such as rechargeable batteries and electrochemical supercapacitors [1–6]. More recently, these materials have been used as the scaffold for the development of perovskite solar cells and sensors [7].

Compared with non-porous metal oxides, the most prominent feature is their ability to interact with molecules not only on their outer surface but also on the large internal surfaces of the material, providing more accessible active sites for reactants. These film electrodes with open, interconnected structures ensure the accessibility of reactants to the active surface sites of electrodes by increasing the mass transport. However, their preparation could be a lengthy process that is difficult to accurately reproduce (thickness and uniformity), involving sol-gel synthesis and sintering. Great effort has been made by researchers worldwide to prepare films faster, in a more reproducible way and at lower temperatures to a degree that would allow their commercial application. The aim of this Special Issue was to put together research articles showing recent developments in the preparation and use of mesoporous metal oxide materials.

2. This Special Issue

This Special Issue, entitled "Mesoporous Metal Oxide Films" contains a collection of ten research articles covering fundamental studies and applications of different metal oxide films. Going into detail, Samourganidis et al. [8] investigated the use of a Metglas ribbon substrate modified with a hemin SnO_2 coating for the development of a sensitive magneto-electrochemical sensor for the determination of H_2O_2. The mesoporous SnO_2 films were prepared at low temperatures, using a simple hydrothermal method that is compatible with the Metglas surface. The Hemin/SnO_2-Metglas sensor displayed good stability, reproducibility and selectivity towards H_2O_2.

A facile hydrothermal process was also used by Son et al. [9] in order this time to synthesize well-crystalline mesoporous Mn_2O_3 materials for the fabrication of a pseudocapacitor. These materials exhibited a high surface area and uniformity of unique mesoporous particle morphology, generating many active sites, a fast-ionic transport and enhanced capacitive properties. Chaudhary et al. [10] also used a hydrothermal approach for the controlled growth of gadolinium oxide (Gd_2O_3) nanoparticles in the presence of ethylene glycol (EG) as a structure-controlling and hydrophilic coating source. The structural, optical, photoluminescence, and sensing properties of the prepared materials, as well as their thermal stability, resistance toward corrosion, and decreased tendency toward photobleaching made Gd_2O_3 a good candidate for the electrochemical sensing of p-nitrophenol and hydrazine using voltammetric and amperometric techniques. The developed sensor exhibited good sensitivity, selectivity, repeatability and recyclability.

Gent et al. [11] prepared multi-layered mesoporous thin TiO_2 films as photoelectrodes using an evaporation-induced self-assembly (EISA) method and layer-by-layer deposition. These films represent suitable host structures for the subsequent electrodeposition of plasmonic gold nanoparticles, exhibiting sufficient UV absorption and electrical conductivity as assured by adjusting film thickness and TiO_2 crystallinity. Enhanced activity was observed with each additional layer of TiO_2. As the surface area was increased, it offered access to more active sites and displayed improved transport properties. These films were tested towards the photoelectrochemical oxidation of water under UV illumination and exhibited good electrochemical and mechanical stability. Katsiaounis et al. [12] prepared mesoporous TiO_2 thin films on fluorine-doped indium tin oxide (FTO) glass substrates using a sol-gel route and the "Dr. Blade" technique, allowing them to directly adsorb Ag plasmonic nanoparticles (AgNPs), capped with polyvinyl pyrrolidone (PVP), on their surface. Voltammetric and spectroelectrochemical techniques were used to characterize the electrochemical behavior of composite films. The electrophotochromism of the Ag-TiO_2 composite is due to oxidation/reduction of the AgNPs that form a thin layer of Ag_2O on the metallic core, forming core/shell nanoparticles. This leads to the fabrication of a simple photonic switch. The phenomenon of the plasmon shift is due to a combination of plasmon shift related to the form and dielectric environment of nanoparticles.

Ammar et al. [13] used ZnO nanoclusters for the detection of chloroform ($CHCl_3$) using density functional theory calculations implemented in a Gaussian 09 program. The results revealed that ZnO nanoclusters with a specific geometry and composition are promising candidates for $CHCl_3$-sensing applications. The adsorption of $CHCl_3$ on the oxygenated ZnO reduces its bandgap, and the deposition of O on a ZnO nanocluster increases its sensitivity to $CHCl_3$ and may facilitate $CHCl_3$ removal or detection. Another facile, low-cost hydrothermal method was used by Umar et al. [14] for the synthesis of Fe-doped TiO_2 nanoparticles. These nanoparticles were used to prepare modified glassy carbon electrodes (GCE) for the development of a hydrazine sensor. The electrochemical sensor based on the metal oxide nanoparticles displayed good sensitivity, linear dynamic range, a low limit of detection and is of low cost. Furthermore, the Fe-doped TiO_2-modified GCE showed a negligible interference behavior towards other analytes that could act as interferents on the hydrazine-sensing performance. Yet again, these metal oxide materials are very promising to be used as coatings for the development of sensors.

One of the most frequent uses of mesoporous metal oxide films is their use as working electrodes for the fabrication of dye-sensitized solar cells (DSSC). In this Special Issue, Tsai et al. [15] added NiO nanoparticles to a TiO_2 paste and used a screen-printing method to make a composite film that could be used for the fabrication of a DSSC. The results showed that the addition of NiO nanoparticles to the TiO_2 working electrode inhibited electron transport and prevented electron recombination with the electrolyte. The electron diffusion coefficient decreased following an increase in the amount of NiO added, confirming that NiO inhibited electron transport. The energy level difference between TiO_2 and NiO generated a potential barrier that prevented the recombination of the electrons in the TiO_2 conduction band with the I_3^- of the electrolyte used. Finally, there was an optimal TiO_2–NiO ratio (99:1) in the electrode for increasing the DSSC device efficiency and electron transport.

Singh et al. [16] synthesized guar gum-grafted 2-acrylamido-2-methylpropanesulfonic acid (GG-AMPS) using guar gum and AMPS as the base ingredients. This material was used as a coating on copper to examine its ability to inhibit copper corrosion. Several heteroatoms present in the GC-AMPS coating promote its good binding to the copper surface, thereby reducing the corrosion rate. The weight loss studies revealed good performance of GG-AMPS at a 600 mg/L concentration. The efficiency decreased with the rise in temperature and at higher concentrations of acidic media. However, the efficiency of the inhibition increased with the additional immersion time. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies suggested the potential corrosion mitigation of GC-AMPS coatings on copper surfaces in 3.5% NaCl solution. Finally, Kumar et al. [17] extensively studied the effect of polyethylene glycol (PEG) on $Ca_5(PO_4)_2SiO_4$ (CPS) bioceramics. Sol-gel technology was used to produce bioactive and more reactive bioceramic materials. The addition of 5% and 10% PEG significantly affected the porosity and bioactivity of sol-gel-derived CPS and improved its morphology and physiology. The porous structure of CPS revealed that an apatite layer could be generated on its surface when immersed in synthetic body fluid (SBF). The bioactive nature of CPS could make it a suitable material for hard-tissue engineering applications and for drug loading.

In summary, this Special Issue of Coatings comprises a series of research articles demonstrating the potential use of mesoporous metal oxide films and coatings with different morphology and structures in many technological applications, particularly sensors, supercapacitors and solar cells.

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