สำนักงานวิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER I
INTRODUCTION

In the past decade, much interest has been paid to a fiber-fabrication technique, commonly known as electrospinning (e-spinning), due to its ability to fabricate ultra-fine fibers with diameters in the micrometer to nanometer range (Doshi, 1995; Reneker, 1996). The setup of the e-spinning process is simple, and usually contains three major components: a high-voltage power supply, a container where a polymer liquid (i.e., solution or melt) is placed with a small opening to be used as a nozzle, and a conductive collection device. Under the influence of a high electric field, a partially-spherical droplet of the polymer liquid at the capillary tip is deformed into a conical one. Further increase in the electric field causes an ejection of a charged stream of the polymer liquid (i.e., charged jet), which deposits in a random fashion on the collection device in the form of a non-woven fabric (Doshi, 1995; Reneker, 1996). Due to its high surface area to volume or mass ratio, the electrospun (e-spun) fabric might be suitable for various applications, e.g., filtration, reinforcing materials, wound dressing, tissue scaffolding, releasing carriers of drugs, etc. (Huang *et al.*, 2003; Jayaraman *et al.*, 2004).

The e-spinning process is simple enough to be further developed for the mass production of continuous, ultra-fine fibers from materials of diverse origins, e.g., natural (Sangsanoh and Supaphol, 2006) or synthetic (Mit-uppatham *et al.*, 2004) polymers, and sol-gel-based ceramics (Watthanaarun *et al.*, 2005). The fabrication of e-spun fibers from polymeric materials is straightforward while the sol-gel-based ceramic counterparts can be done in two different methods, viz. the polymer template and the direct spinning methods. Among these two methods, only the first one needs a polymeric gelator to facilitate the e-spinning of a sol solution. Metal oxide ceramics in the form of ultra-fine fibers are finally obtained by further calcination of the obtained e-spun polymer/metal oxide gel composite fibers or the e-spun metal oxide gel fibers.

Among the various metal oxides, silica is the most commonly-found compound in nature as both sand and a major component of the cell walls of diatoms. Silica and mesoporous silica, as nanostructured entities such as nanowires and

nanofibers, have attracted considerable attention because of their unique properties and wide applicability in mesoscopic research, opto- and magneto-electronic devices, sensors, and catalysis (Shao *et al.*, 2002; Zhao *et al.*, 2008).

It is evident that all of these previous reports utilized TEOS as the source of silica. As TEOS is highly sensitive to moisture, handling and controlling the property of the resulting sol suspension over the course of the fabrication process could be problematic. During the last few years, Wongkasemjit and coworkers (2001–2005) synthesized moisture stable metal alkoxides, namely, silatrane, alumatrane, cerium glycolate, zirconium glycolate, titanium glycolate, tin glycolate, and molybdenum glycolate, directly from inexpensively corresponding metal oxides using ethylene glycol solvent via the "Oxide One Pot Synthesis (OOPS)" process. The reaction gives highly pure metal alkoxides. Thus, silatrane, one such structure that possesses a very good moisture stability property, (Phiriyawirut *et al.*, 2005) is another silica source that possesses greater stability towards moisture, alleviating such obstacles.

Transparent conductive oxides (TCO) are very important technological materials because of their multiple applications (Ginley *et at.*, 2000). Nanocrystalline semiconductors have electronic property intermediate between those of macrocrystalline solids and molecular entities. The properties of such materials are fascinating and have formed the subject of intense research in recent years (Weller, 1993; Hagfeldt and Gratzell, 1995). Among them, the most studied TCO are tin oxide (SnO_2), zinc oxide (ZnO) and indium-tin oxide (ITO). SnO_2 is an n-type compound semiconductor with a wide direct energy band gap of 4 eV and an indirect band gap of 2.6 eV (Agnihotri *et al.*, 1983; Summi *et al.*, 1984). Moreover, it is a key functional material that has been extensively used for optoelectronic devices (Aoki *et al.*, 1970; Tatsuyama and Ichimura, 1976), gas sensors detecting leakage (Yamazoe, 1991; Chung *et al.*, 2003), transparent conducting electrodes in devices, such as solar cells, flat panel displays (Agnihotri *et al.*, 1983; Levis *et al.*, 2003; Matsui *et al.*, 2000), and catalyst supports (Wang *et al.*, 1994). There are many reports utilizing $SnCl_2{\cdot}2H_2O$ or $SnCl_4{\cdot}5H_2O$ as the source of tin over last decade. Although their sensing characteristic was good, it still illustrated fairly small surface area-to-volume-ratio. Therefore, our aim is to explore the use of a novel material, inexpensive, and moisture-stable tin glycolate, silatrane as the tin and silica sources,

respectively, for the fabrication of high surface area e-spun silica and tin fibers by using PVA as the polymeric gelator.

Carbon-inorganic hybrid materials are a new class of functional materials that gained tremendous interest in recent year (Kickelbick, 2007). The combination of two materials can show properties superior to those of their individual constituents. These researches are focused on a new class of hybrid materials made from carbon nanotubes (CNTs) and inorganic glasses or ceramics, CNT-inorganic hybrids. Many advantages of CNTs in hybrid materials include their high aspect ratio (>1000) and tubular geometry, which provides ready gas access to a large specific surface area, and percolation at very low volume fractions. Their excellent mechanical, electrical, and optical properties support CNTs as an ideal building block in hybrid materials, thus enabling the widely use in photochemical, catalytic, and electrochemical technologies.

Scaling down the particle size to nanometer dimensions also increases the specific surface area of the material; thus, applications with reactions at the gas-solid or liquid-solid interface will also benefit from this "striving to the smaller". Typical applications include catalysis, energy conversion, electrochemistry, and environmental chemistry, where the use of nanomaterials increases response time, efficiency and sensitivity (On, 2001). One of the major challenges in nanoscale science is the synthesis of nanomaterials with monodisperse sizes, uniform morphologies, and functionalised surfaces.

As we mentioned above, mesoporous silica and silica have attracted great attention because of their unique properties and wide applicability in mesoscopic research, opto- and magnetoelectronic devices, sensors, and catalysis (Shao *et al.*, 2002; Zhao *et al.*, 2008). In this work, we do not present only a new way to synthesize ultra fine SiO_2 fiber using moisture stable silatrane as precursor, but also a new and simple process to produce high surface area SiO_2 nanotube using CNT as template.

Nowadays water pollution has become a global concern threatening the survival of human beings. Effluents discharged from textile industries which often contain harmful dyes, such as rhodamine B (Rh-B) (Venkatachalam *et al.*, 2007; Li *et al.*, 2008) as well as toxic aromatic compounds, such as 4-nitrophenol (4-NP) —

one of the most common pollutants present in industry's waste water (Carriazo *et al.*, 2009). Photocatalysis is a novel method for the treatment of air and water pollutants. Many researchers have done a lot of works in this field (Evans *et al.*, 2007; El-Sharkawy *et al.*, 2007; Orlov *et al.*, 2007; Bejarano-Perez *et al.*, 2007; Patil *et al.*, 2005). One of the catalysts in this application is TS-1 zeolite. It is of interest because of its outstanding catalytic activity and selectivity in the oxidation of various organic compounds using H_2O_2 as an oxidant (Phonthammachai *et al.*, 2006; Ramkrishna *et al.*, 2002). It was used as a photocatalyst for decomposition of 4-nitrophenol, toxic and carcinogenic compounds in waste water, with H_2O_2 (Lee *et al.*, 2003). The enhancement of the photocatalytic activity of TS-1 can be attributed to the efficient formation of hydroxyl radical ($^{\cdot}OH$) from H_2O_2 and the close proximity of $^{\cdot}OH$ radicals to the reactant molecules.

Carbon nanotubes are also the best candidates for the preparation of photocatalytic composites (Iijima, 1991; Jitianu *et al.*, 2004). Although various applications of TS-1 and many types of metal and semiconductor nanoparticles coated on CNTs have been reported (Han and Zettl, 2003; Li, 2003; Li *et al.*, 2002; Zhu *et al.*, 2009), the photocatalytic properties of TS-1/CNTs composite photocatalysts remain largely unexplored. Taking advantage of the unique electronic and physical properties of the CNTs, we study the combination of CNTs with TS-1 for hopefully inducing interesting charge transfer and thus enhancing the photocatalytic activity of TS-1.

In this thesis, not only the preparations and characterizations of SiO_2 and SnO_2 fibers were studied, but also a route enabling TS-1 to be uniformly coated on CNTs using benzyl alcohol (BA), which is inexpensive and can be attached equally on both tips and sidewalls of CNTs to provide complete uniform inorganic coating (Eder, 2010), as surfactant; and a way providing crystal within very short time around 30-90 min by the application of microwave irradiation were investigated. Moreover, the effects of TS-1-CNTs hybrid material on photocatalytic activities were studied by destructing the Rhodamine B Dye and 4-nitropenol in both UV and visible regions. CNTs, TS-1, and TS-1 doped with CNTs by mechanical mixing were also studied for comparison. To the best of our knowledge, this work may be the first

report about the synthesis of TS-1-coated on CNT under microwave irradiation and its application as novel photoactive material.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย