CHAPTER 1

INTRODUCTION

On the history time line of zinc oxide (ZnO), it was known since around 4,500 B.C. as in the copper age. It was a by-product of copper smelting. In that process, the zinc proportion of copper ores was reduced to zinc vapor which oxidized and deposited in the furnace flues as an impure powder known as “cadmina”. Later on, the brass was successfully first made by melting of it with copper (copper-zinc alloy). The clever application for using ZnO in medical and other purposes was a special process which was devised and purifying cadmina by designing furnace. Finally, the oxide was lead to ointment and used it stick to the walls and roof until it appeared like skins of wool. It was called “philosopher’s wool”. All of these, they still did not outstanding about the science of materials. Until in 1520, Zn was only recognized as an element by Paracelsus and O_2 was only formally discovered in 1774 by Priestley [1].

However, before that, the Chinese commercially used ZnO for several centuries. The modern history of ZnO started around the middle of the 18th century. German scientist name Cramer who discovered that ZnO could be made by burning metallic Zn in air. In 1840, the manufacture of ZnO started in France. In 1871, ZnO was used in the paint trade due to its whiteness, fine texture and opacity. Moreover, the development of rubber and ceramic industry, which have demanded smaller amount of ZnO, quickly attacked the paint industry due to insufficient quantities of ZnO at that time. The first radio broadcasting stations started transmitting in the

1920's, ZnO crystals also came into popular demand for their materials with semiconductor properties. Using an antenna and a fine copper whisker (cat's whisker), the RF signal was adjusted at the junction of the wire and the crystal [1].

Science research on ZnO started in the 1930s. For the example, lattice parameters of ZnO were investigated for many decades [2−7]. Similarly, optical properties and processes in ZnO as well as its refractive index were extensively studied many decades ago [8−20]. Vibrational properties by techniques such as Raman scattering were also determined early on [21−27]. Following previous many investigations of ZnO properties, it was considered that ZnO samples were available. In terms of devices composing with ZnO, Au Schottky barriers by Mead in 1965 [28], demonstration of light-emitting diodes by Drapak [29] in 1968, in which Cu_2O was used as the p-type material, metal-insulator-semiconductor structures by Minami et al. in 1974 [30], ZnO/ZnSe n-p junctions by Tsurkan et al. in 1975 [31], and Al/Au ohmic contacts by Brillson [32] were achieved [33].

During the last 10 years, the research on ZnO was found more in each year continuously with average 1,400 ZnO significant papers per year. The total number of these papers exceeds 35,000 as indicated e.g. by databases ISI web of knowledge. Figure 1.1 showed the recorded exponential growth, with three-parameter function, of ZnO research since 2001. Therefore, up to now, ZnO is popular and holds a key in many researches since ZnO is a versatile smart material.

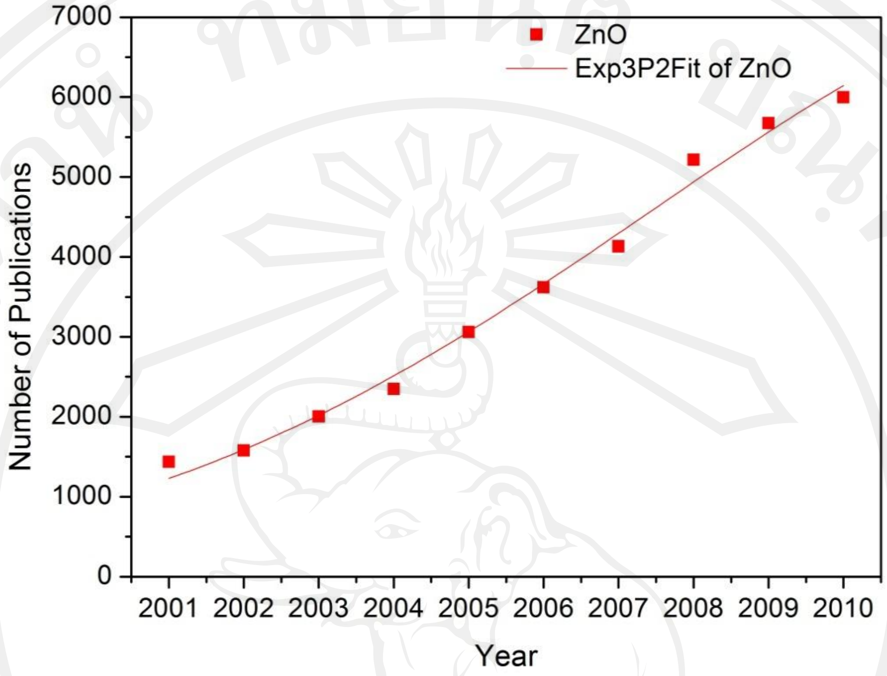

Figure 1.1 Annual number of papers published related to ZnO. Literature search was carried out ISI Web of Knowledge using the keyword "ZnO*" or "Zinc Oxide*".

At the present worldwide research activities on ZnO, its alloys $Zn_{1-x}A_xO$ (with A=Cd, Mg or Be) and its nano- or quantum structures are driven by various hopes. The predominant one is possibly the hope to obtain a material for optoelectronics covering the spectral range from the green (A=Cd) over the blue to the near UV (A=Mg or Be), especially to obtain light emitting diodes (LED) or laser diodes (LD) in these spectral ranges. ZnO had also been a hope for using substitutable GaN based devices, although the main problem is still a high, stable and reproducible p-type doping. Moreover, Morkoç et al. [34] showed in their cover photo likely the optically pumped blue/UV emission from a ZnO sample in the upper half and a LED in the lower which is still in dark color. Hopefully, it will emit bright blue/UV light in the future.

Another interesting trend of ZnO research is self-organized growth in the form of nanorods [33, 35−39]. This is an aspect to develop it into various applications. There are other self-organized nanostructures, like nanocabbages, corals etc., which gave from unsuccessful attempts to grow a good epitaxial layer or nanorods. However, such nanostructures could help to develop other fields such as nanolasers etc.

Another driving force for new ZnO generating is the fact that diluted magnetic or even ferromagnetic samples can be grown by doping ZnO with ‘magnetic’ ions like Mn, Fe, Co, Ni and V or even with nonmagnetic ones like Ag, Cu and N or with intrinsic defects (ZnO:X) [40]. The ferromagnetic observation was suitably considered that ZnO:X can use in spintronics or in quantum computing. The facts that the para- or ferromagnetic magnetization is tiny apart from the sign frequently of the same order of magnitude as diamagnetism [41]. Moreover, the resulting magnetic flux densities (B) can only be measured with high sensitive SQUID arrangements and their orders of magnitude smaller than the magnetic field of the earth, so this is no doubt on this field of applications [42].

Other future expectancies of applications which are partly already in use or more or less of it are:

- transparent electronics, based on the large bandgap of ZnO, e.g. in the form of field effect transistors (FET) or (transparent) thin film transitions (TFT or TTFT), which do not necessarily require a p-n junction [43−45],

- the use of ZnO:Y (with Y=Al but also In or Ga) as a highly conductive transparent oxide (TCO), expected for substituting the more expensive and poisonous material like indium tin oxide (ITO) [43−44, 46−47],
- the use of ZnO as a gas sensor, due to the strong sensitivity of its surface-conductivity on the surrounding gas atmosphere [48− 49],
- the use of ZnO as photocatalysts for water treatment [50−51],
- the use of pointed nanorods as field emitters [52−56],
- the use as material for random lasers [57−59],
- the application in solar cells [36−37].

Nowadays, actually ZnO is used already by 100,000 tons per year as additive to concrete or to the rubber tires and in smaller quantities as additive to human and animal food, as UV blocker in sun crèmes, as anti-inflammatory component in crèmes and ointments, as white pigment in paints and glazes etc. [34, 60−62]. Moreover, in the twenty-first century, the incontrovertible major problem topics arising from extremely growing of industrial and city age are the problem of environment in air and water pollution. Water [63] and air [64] pollutants have many facets including the resultant health risks on diseases in almost all organ systems. The people deaths around 355,000 were killed per year globally with unintentional poisonings. Two thirds of these deaths occurring in the developing countries, these poisons are extremely associated with excessive exposure to, and inappropriate use of, toxic chemicals. To offer toxic chemicals for various utilizations, they may be released directly into soil, air and water from industrial processes, pulp and paper plants, tanning operations, mining and unsustainable forms of agriculture at levels or rates of those more enough to risk safety to human. Furthermore, The Organisation for Economic Co-operation and Development (OECD) has estimated in upcoming year 2020 that nearly one third of the world's chemical production will take place in non-OECD countries and that global output will be 85% higher than it was in 1995. The chemical production has shifted to poor counties, so this may results in higher risks of health and environment [65]. Thus, it is essential for doing worthy researches for helping to decrease or eliminate these problems.

This research has been interested in apply ZnO for detecting and degrading organics molecules, relating in air and water pollutants, respectively. Improvement of the basic researches, in many ways, is essential for solving problems or on going to reach a better target. Doping in ZnO with the optimal selective elements can offer an effective method to improve its properties for using in those applications. The dopant content directly influences the rate of e^- / h^+ recombination in ZnO, which is reflected in [66]: $W = 2\varepsilon\varepsilon_0 V_s / eN_d$ where W is the thickness of the space-charge layer, ε is the static dielectric constant of the semiconductor, ε_0 is the static dielectric constant in vacuum, V_s is the surface potential, N_d is the number of dopant donor atoms, and e is the electron charge. When W approximates the penetration depth of the light into the solid $l = 1/A$, where A is the light absorption coefficient at a given wavelength), e^- / h^+ pairs in semiconductor, generated from the absorbed photons, can be separated efficiently.

In this case, shallow doping is in fact the surface modification that it may play in catalytically active sites at the surface of the base material. Ideally, the doping process improves sensor performance by increasing the sensitivity, favoring the selective interaction with the target analyze, decreasing the response and recovery time and reducing the working temperature. Furthermore, surface doping may enhance the thermal and long-term stability. The control parameters are composition, size, habit and redox state of the surface modifiers, as well as their dispersion on and/or into the metal oxide surface. To explain the influence of surface additives, two different mechanisms, that is, electronic and chemical sensitization, have repeatedly been applied [67−68].

Mostly, adding with noble metals, Pt, Pd, Ag and Au, demonstrated good adsorption, stability, selectivity and gas response activity [69−71], and photocatalytic activity [72−74]. On the other hand, some researchers have selected other metals for researching, by hoping that it will enhance the sensitivity and stability of sensor, and the photocatalytic activity. This may be because the reason that the fundamental to apply them in the industries is still depend on the cost, time and findable ability and amount of dopant. For examples, the sensing properties of spray pyrolysis made-ZnO-doped films (ZnO:X films doped with different elements, X=Al, In, Cu, Fe and Sn), to ethanol vapor were reported by Paraguay et al. [75]. The results showed that Sn dopants gave the highest sensitivity in the working temperature of 675 K. Moreover, some researches confirmed the effect of the Sn dopants for enhancing ZnO electrical conductivity, optical transmission [76−82], and the sensing properties of ZnO-based sensor to gases, such as NO_2 [83−84] and ethanol [85] successfully. Together with the photocatalytic properties of Sn-doped ZnO have been rarely reported [86−87], so it is the key point interest to investigate this further. The literature search reviewed relating Sn-doped ZnO about its interesting properties and applications were summarized and categorized in appendix A.

The emphasis of ZnO research is essentially on the same track but more focuses in nanostructures, new growth and doping techniques and applications relating its properties. The interest in nanoparticles especially those of less than 100 nm with functional properties, has increased greatly in the past decade. Nanoparticles in such size range are made up from small clusters of atoms, so they have a large fraction of surface atoms to bulk, and exhibit special intrinsic properties governed by basic materials characteristics such as surface energetic, quantum mechanical or even simple physio-mechanical effects.

The approaches for nanoparticles synthesizing have two ways consisting top-down and bottom-up approaches. Bottom-up synthesis of nanoparticles can be further divided into wet-chemical routes [88−89] or gas-phase processes [90−91]. The drawback of conventional wet synthesis such as precipitation, sol-gel and incipient wetness impregnation are weighty preparation consisting high liquid volumes and a lot of steps involve on post treatment such as drying and calcinations. Moreover, it is difficult to apply this method into industries for the large scale production because it needs a large and high energy equipment. Likewise, the essential thing is low yield production and with a long processing time. If they are possible in the industry, the reflective effect is the high price of final products.

On the contrary, a “dry” alternative, gas-phase process is a capable alternative of synthesizing fine particles in a single-step with large scale easy probability, particularly the flame aerosol technique. At present, large scale synthesis of simple nanoparticles are routinely synthesized in a single-step technique using FSP up to 1.1 kg/h [92]. Flame aerosol technique can be subdivided into vapor-fed flame synthesis

(VFS), flame-assisted spray pyrolysis (FASP) and more recently the flame spray pyrolysis (FSP).

The major advantages of FSP are on the ground of the ability to utilize a broad range of liquid precursors including some inexpensive and non-volatile ones. FSP typical appearance is a necessary self-sustaining flame by continuously injecting highly exothermic precursor selected properly. In a FSP flame, temperature of around 2,600 K has been reported [93]. The FSP process is a transportation of liquid precursors to a high temperature and then they vaporize, oxidize, and finally form metal oxide clusters that coagulate toward nanometer-scale particles [94].

Much effort is currently being devoted to designing functional nanoparticles for target applications and devices [72, 95−98]. Understanding of materials physiochemical and electronic properties and how to alter them (in a residence time-restrained process) is critical in designing nanoparticles with high-performance functionalities. FSP technique is such an answer that it can design and produce high-performance functional nanoparticles perfectly [99]. For the example, the basic mechanism for formation of supported metals in a flame by Strobel et al. [96]. They synthesized platinum group metals (pgms) by flame aerosol technology and showed that the pgms form finely dispersed clusters on top of nanostructured ceramic supports, which can consist of most metal oxides or their mixtures. In addition, the current researchers look continuously strength to FSP for designing and synthesizing modified metal oxide nanoparticles.

Therefore, in this work, Sn-doped ZnO nanostructures are synthesized by FSP, a combustion-based process whereby a liquid solvent containing appropriate precursors is injected and atomized into a flame. In the FSP synthesis process, undoped ZnO and 0.25, 0.5, 1, 2, 3 and 5 at% Sn-doped ZnO nanostructures were synthesized by using zinc naphthenate and tin (II) 2-ethylhexanoate as the precursors dissolved in xylene under 5/5 (precursor/oxygen) flame condition, previously explored by the researchers in Pratsinis group of Zurich, Switzerland [72, 100−101] that it was the best condition for applying to sensor and photocatalyst applications. The physical characteristics of undoped ZnO and Sn-doped ZnO nanostructures are investigated by X-ray diffraction (XRD), Brunauer Emmett and Teller (BET), transmission electron microscopy (TEM), UV-vis absorption spectroscopy and field emission scanning electron microscopy-energy dispersive spectroscopy (FESEM-EDS) for understanding and relating with physiochemical characteristics in their applications. The samples are tested accordingly to their applications (as photocatalysts and gas sensors).

In sensor application, the ZnO film sensors were fabricated by mixing the nanostructures with an organic binder composed of ethyl cellulose and terpineol. The resulting paste was spin-coated on Al_2O_3 substrates interdigitated with Au electrodes. Undoped ZnO and Sn-doped ZnO gas sensing characteristics were investigated towards acetone ($(CH_3)_2CO$; 100−400 ppm), ethanol (C_2H_5OH; 300−1,000 ppm), hydrogen (H_2; 5,000−20,000 ppm) and methane (CH_4; 10,000−50,000 ppm) gases in the operating temperature range of 200−400°C using a voltamperometric technique at constant bias.

In photocatalyst application, the influence of Sn doping in flame-made ZnO nanostructures on the photocatalytic degradation of phenol (C_6H_5OH) and methanol (CH_3OH) in aqueous solution was also studied in this work. The photocatalytic studies were conducted in a closed-system slurry-type spiral reactor and then detected the amount of CO_2, being the final product of the organic degradation, in water with a conductivity meter. In addition, C_6H_5OH and CH_3OH photodegradation kinetics over as-prepared catalysts were also investigated.

In the thesis, the writing style was planned look like a big article and given more details. It is easy to realize the relationship in each part linked together to the conclusion of this research. The first view was the origin of problem and interest follow with the specific final view until into the research aims which including in Chapter 1. It was intended to show the objectives and what thing is essential and should be studied in this research. In Chapter 2, the significant basic background and relating theory in this research for earlier understanding before move to the result and discussion part. Explaining in experimental details, the usage of the new materials and machines/techniques and steps of the experiments was written in Chapter 3. Chapter 4 showed the results and discussions in consisting with the physical characteristics of Sn-doped ZnO nanostructures which was synthesized by FSP, and their gas sensor and photocatalyst applications. Each part was linked together and revealed the conclusion in Chapter 5. All raw data were inserted at the end of this thesis as shown in the appendix A−C.

1.1 Objectives of this research

This research concentrates on the synthesis of flame-made undoped and Sn-doped ZnO nanostructures and their characterization for using as gas sensors and photocatalysts. The aims of this research consist of:

1) To synthesize and understand the physiochemical characteristics of FSP-made undoped ZnO and Sn-doped ZnO nanostructures.

2) To relate to their overall photocatalytic and gas sensing behaviors for continued applications.
3) To study the effect of dopant (Sn) concentrations on gas sensing and photocatalytic properties of undoped ZnO nanostructures.