



CHAPTER II

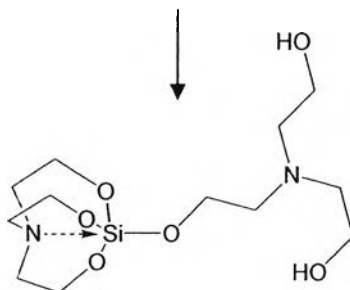
BACKGROUND AND LITERATURE SURVEY

2.1 Synthesis of Metal Alkoxides

The metal alkoxide precursors for catalyst synthesis are of interest in this work. Apparently, the synthesis of new metal alkoxides possessing unique structures and properties is of great significance for the investigation of sol-gel process as well as the evolution of metal alkoxide chemistry. However, there are a few drawbacks of metal alkoxides that make it difficult to study their structures and properties thoroughly, such as, the extreme moisture sensitivity and the tendency to form mixtures of structurally complex species upon hydrolysis. Many scientists thus tried to improve the properties of metal alkoxides (Grainsford *et al.*, 1995; Wang *et al.*, 1999).

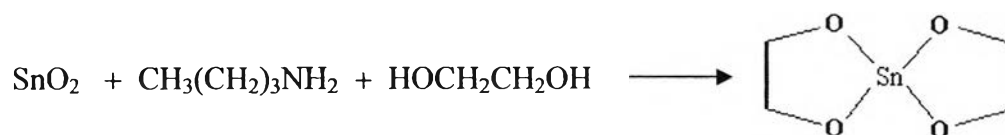
Laine *et al.* (1991) investigated a straightforward and low-cost synthesis of metal alkoxide precursor. The synthetic method used inexpensive metal oxide precursor to react with ethylene glycol in one step called “Oxide One Pot Synthesis Process (OOPS)” to successfully produce a group I metal alkoxide (Laine, 1995; Blohowiak, 1992).

Wongkasemjit *et al.* (2001) also synthesized silatrane using SiO_2 and triethanolamine/triisopropanolamines (Scheme 2.1). The precursor exhibited outstanding high stability not only in alcohol, but also in water.



Scheme 2.1 The preparation of silatrane complexes by Wongkasemjit's method.

Not only atrane complexes, but also many metal glycolates were synthesized, especially, Ti, Zr, Ce, Sn and Mo (Ksapbutr *et al.*, 2001; Phontammachai *et al.*, 2003; Junin *et al.*, 2004; Sadtayanon *et al.*, 2004).



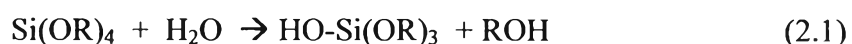
Scheme 2.2 The preparation of Tin Glycolate complex (Junin *et al.*, 2004)

These precursors obtained are highly pure and suitable for studying optimal conditions of the sol-gel process for high surface porous metal oxides suitably used as a catalyst or a catalyst support, such as TiO_2 or TS-1 for being used as photocatalysts.

2.2 Sol–Gel Processing

Sol-gel technique has been extensively used to prepare amorphous and crystalline materials. In general, the sol-gel process of metal oxides/alkoxides is the synthesis of an inorganic network at low temperature. This technique involves the transition characterized by a relatively rapid change from a liquid (solution or colloidal solution) into a solid (gel-like state).

Metal alkoxides are a member of metal organic compounds containing an organic ligand attached to a metal or metalloid atom. Metal alkoxides are popular precursors for the sol-gel process because they react readily with water via hydrolysis reaction to form metal hydroxide, as shown in the following reaction.



where R represents an alkyl ligand (then OR is an alkoxy group), and ROH is an alcohol. Depending on the amounts of water and catalyst in the system, hydrolysis may go to completion, meaning that all of the OR groups are replaced by OH, or partially occur, $\text{Si}(\text{OR})_{4-n}(\text{OH})_n$. Moreover, the molar ratio of $\text{H}_2\text{O}:\text{Si}(\text{OR})_4$ should be

at least 2:1 to approach complete hydrolysis of the alkoxide (Nicolaon and Teichner, 1968).

At its simplest level, sol-gel chemistry with metal alkoxides can be described in terms of two main reactions:



where X can be either H or R (an alkyl group).

The most important characteristic of the sol-gel preparation of catalytic materials is its ease to control the reaction rate, leading to the following advantages:

- (i) The ability to maintain high purity (because of purity of starting materials);
- (ii) The ability to change physical characteristics, such as pore size distribution and pore volume;
- (iii) The ability to vary compositional homogeneity at a molecular level;
- (iv) The ability to prepare samples at low temperatures;
- (v) The ability to introduce several components in a single step;
- (vi) The ability to produce samples in different physical forms.

The M-O-M network product is formed by polycondensation reactions, as shown in Reaction 2.3 in which alcohol and water are produced as by-products. These reactions lead to a degree of gelation regarding to the appropriate amount of water. Other critical parameter usually considered is viscosity of the solutions. Therefore, many applications of controlled hydrolysis to obtain a desired molecular structure and appropriate viscosity of the solution are employed to improve spin and coating abilities.

Further extent of the condensation of the sol results in the formation of gel. There are many parameters affecting gel properties, such as temperature, pH, type of precursor, and solvent. Varying the temperature is the most effective when it can alter the relative rate of competing reactions. Solvent can change the nature of an alkoxide precursor through solvent exchange or directly affect the condensation reaction. It is also possible to prepare gel without solvent as long as another mean,

such as ultrasound irradiation, is used to homogenize. Furthermore, pH of the solution, which can be changed by the addition of either acid or base catalyst, is also the most important parameter in obtaining gel because the rate and content of the hydrolysis reaction are influenced by the change in pH (Aelion *et al.*, 1950).

In general, the sol-gel process gives high surface area, pore structure, homogeneous property of the products, and moreover, it is a low-temperature method for converting metal alkoxide to metal oxide. Many works investigated the sol-gel process using various types of precursors for certain properties.

2.3 Electrospinning Technique

Electrospinning technique is a simple and versatile method for fabricating nanofibers. In the electrospinning process, polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field. Charge is induced to the liquid surface by an electronic field. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone. When the electric field reaches a critical value at which the repulsive electric force overcomes the surface tension force, a charged jet of the solution is ejected from the tip of the Taylor cone. Since this jet is charged, its trajectory can be controlled by the electric field. As the jet travels in air, the solvent evaporates, leaving a charged polymer fiber behind which lays itself randomly on a collecting metal screen. Thus, continuous fibers are laid to form a non-woven fabric (Jayesh and Reneker, 1995).

Electrospinning process involves polymer science, applied physics, fluid mechanics, electrical engineering, mechanical engineering, chemical engineering, material engineering, and rheology. Many parameters, including the electric field, solution viscosity, resistivity, surface tension, charge carried by the jet and relaxation time can affect the process. A comprehensive mathematical model of this process was developed by Reneker *et al.* (Reneker *et al.*, 2000).

The electrospinning process, see Figure 2.1, consists of three stages: (1) jet initiation and the extension of the jet along a straight line; (2) the growth of bending instability and the further elongation of the jet, allowing the jet to become very long

and thin while it follows a looping and spiraling path; (3) solidification of the jet into nanofibers.

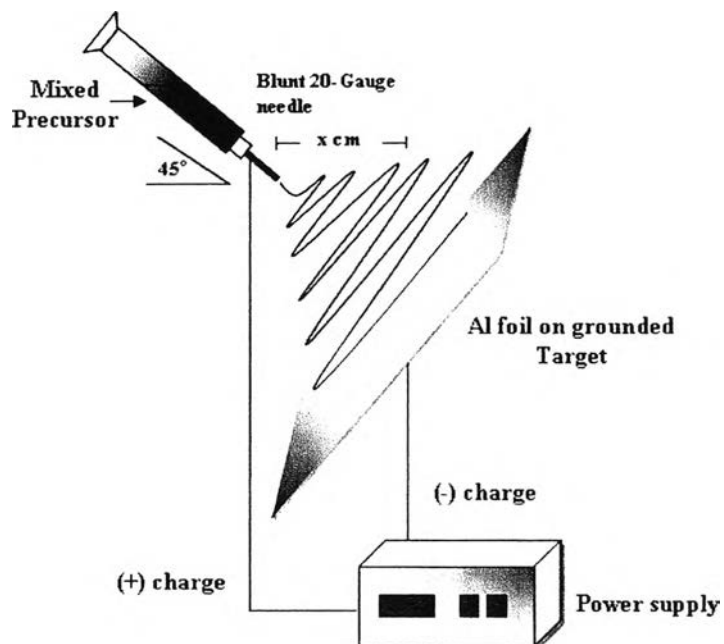


Figure 2.1 Schematic drawing of the electrospinning apparatus utilized in this work

2.3.1 Jet Initiation and Diameter of a Single Jet

In a typical experiment, a pendent droplet of polymer solution is supported by surface tension at the tip of the spinneret. When the electrical potential difference between the spinneret and the grounded collector is increased, the motion of ions through the liquid charges the surface of the liquid. If the electrical forces at the surface overcome the forces associated with surface tension, a liquid jet emerges from a conical protrusion that formed on the surface of pendant droplet. The jet is electrically charged. It carries away the ions that are attracted to the surface when the potential is applied. The potential increases both charge density on the jet and the flow rate of the jet.

The jet diameter decreases with the distance from the orifice. A higher electric fields and a lower surface tension coefficient favor the formation of a thicker jet. Addition of salt (NaCl) to the solution, with other parameters held constant, reduces the diameter of the jet. Both higher and lower viscosity also favors

a thinner jet. The largest jet diameter occurs when the solution viscosity is in a medium range.

2.3.2 Bending Instability and Elongation of the Jet

After initiation, path of the jet is straight for a certain distance. Then, an electrically driven bending instability grows at the bottom end of the straight segment. The bending allows large elongation to occur in small region of space. The electrically driven bending instability occurs in self-similar cycles. Each cycle has three steps and it is smaller in scale than the preceding cycle.

The three steps in each cycle are:

Step 1 A smooth segment that is straight or slightly curved suddenly develops an array of bends.

Step 2 As the segment of the jet in each bend elongates, the linear array of bends becomes a series of spiraling loops with growing diameters.

Step 3 As the perimeter of each loop increases, the cross-sectional diameter of the jet forming the loop gets smaller, and the conditions for Step 1 are established everywhere along the loop.

The continuous elongation of each segment is most strongly influenced by the repulsion between the charges carried by adjacent segment of the jet. The externally applied field, acting on the charged jet, causes the entire jet to drift toward the collector, which is maintained at an attractive potential.

There are several parameters affecting the electrospinning process (Dietzel *et al.*, 2001; Frenot and Chronakis, 2003; Li *et al.*, 2004) i.e. (1) system parameters, such as molecular weight, molecular weight distribution and architecture of the polymer (branched, linear, etc) as well as properties of polymer solution (viscosity, conductivity, dielectric constant, and surface tension); (2) process parameters, such as electrical potential, flow rate, and distance between the capillary and collected screen; and (3) ambient parameters (temperature, humidity, and air velocity in the chamber). For instance, the polymer solution must have concentration high enough to cause polymer entanglements, but not so high to prevent motion of polymer induced by the electric field. The solution must also have surface tension low enough, charge density high enough, and viscosity high enough to prevent the jet from collapsing into droplets (or beads) before the solvent has evaporated.

Morphological changes can occur upon decreasing the distance between the syringe needle and the collector. Increasing or decreasing the electrical field decreases the bead density, regardless of the concentration of the polymer in the solution.

In recent years, electrospinning technique has been adopted for the synthesis of ceramic nanofibers. Shao *et al.* (2003) were the first to prepare silica (SiO₂) fibers (200–300 nm in diameters) from the e-spun silica/poly(vinyl alcohol) (PVA) composite fibers after calcinations at 400°–800°C. The sol suspension was prepared from tetraethylorthosilicate (TEOS), phosphoric acid (H₃PO₄), distilled water in the molar ratio of 1:0.01:11, and the weight ratio between SiO₂ gel and PVA in the spinning SiO₂/PVA suspension was 59 %. Choi *et al.* (2003) prepared e-spun SiO₂ fiber (200–600 nm in diameters) directly from a sol suspension of TEOS/ethanol/ distilled water/hydrochloric acid (HCl) in the molar ratio of 1:2:2:0.01 without the use of any polymeric gelator. Since no polymeric gelator was used, further calcination was not necessary. Zhang *et al.* (2004) also used the direct spinning method to prepare e-spun SiO₂ fibers from a sol suspension of TEOS/water/HCl in ethanol. The concentration of each component in the ethanolic solution was 1/2/0.01 M.

Cristobalite, a polymorph of quartz, is composed of the same chemistry as SiO₂, but has different structures. It forms a stable phase at temperature above ~1470°C, up to the boiling point of SiO₂ (Zhang *et al.*, 2005). The β-cristobalite form of ceramic powder has great potential for fabrication of porous ceramics with high thermal stability, low density and chemically inertness. It has been widely used in several applications, such as, filtration, reinforcing filler in composite materials etc. The formation of cristobalite phase mainly depends on the sintering temperature and time, pressure, composition, and size of sample as well as the properties of the starting materials (Fong *et al.*, 1999; P. Supaphol and S. Chuangchote, 2008).

It has been extensively known that cristobalization of SiO₂ gives unique porous crystal structure that is useful for filler and filter applications (Choi *et al.*, 2003). The cristobalization process typically occurs at high sintering temperature (~1470°C), this paper provides another alternative to produce this structure at much

lower temperature (reduced from 1470° to 700°C), implying an economical route in term of energy.

Along with the development of nanotechnology, one-dimensional (1-D) structural tin oxide (SnO₂, nanowires, nanorods, nanobelts, or nanoribbons) is found wide applications in many fields. Recent study has indicated that the SnO₂ nanostructures are rich in both composition and morphology (Wang and Pan, 2002). Considerable efforts have thus been made to fabricate SnO₂ nanowires, nanobelts, nanorods, or nanoribbons via several routes, such as thermal oxidation, thermal evaporation, molten salt synthesis and self-catalytic growth (Zheng *et al.*, 2001; Liu *et al.*, 2001; Hu *et al.*, 2003; Sun *et al.*, 2003; Wang *et al.*, 2004). Good quality of SnO₂ nano crystalline films was made by several techniques; one of the simplest and economic techniques is the sol-gel process (Diaz-Flores *et al.*, 2003).

In the previous studies, it was demonstrated that the electrospun nanofibers have approximately 1-2 orders magnitude more surface area than those found in continuous thin films (Gibson *et al.*, 2001; Lee *et al.*, 2003). It is expected that this large surface area available in the nanofibers has the potential to unusually provide high sensitivity and fast response that are very essential for nanodevice applications.

2.4 Hybrid Materials

The last two decades have seen the development of some new types of hybrid materials, such as nanocomposites and metal oxide frameworks, and their implementation in various applications, light structural, bioactive, or smart materials (Kickelbick, 2007).

Nanocomposites are multi-phase materials, in which one phase (filler) is dispersed in a second phase (matrix), resulting in a combination of the individual property of the component materials. As an example, the result of the incorporation of inorganic nanoparticles, nanorods, carbon fibers, CNTs and galleries of clay minerals into an organic polymer or a ceramic matrix is considered to be a nanocomposite material. In contrast to some other hybrid materials, nanocomposites simply use the intrinsic properties of their individual component, having discrete and

controllable size, shape, and structure enable a good structure-property relationship. In this respect, the purpose of the filler is often to mechanically reinforce the matrix or to alter its thermal, electrical, or barrier properties, and as such these nanomaterials have already had a considerable impact in applications, such as lightweight structural materials in aerospace, electrically-conducting plastics, and packaging materials with reduced gas permeability.

In general, hybrid materials can be further classified into *Class I* and *Class II* materials. This distinction is based on the strength of interaction between the two components, which also affect the hybrids' properties.

Class I Hybrids typically show weak interactions between the two phases, such as van der Waals, hydrogen bonding, or weak electrostatic interactions. Interpenetrating networks (IPNs) are another example of class I hybrid materials and are formed when an inorganic and an organic compounds form networks that interpenetrate each other without strong chemical interactions.

Class II Hybrid materials are formed via strong chemical interactions between the components, for examples when the discrete inorganic building blocks are covalently bonded to organic polymers, when inorganic sol-gel networks are modified with organic functional groups (e.g. ORCOMER[®]).

An important advantage of hybrid materials is the diversity in suitable synthesis routes. In contrast with pure solid-state inorganic materials that often require a high temperature treatment for their processing, hybrid materials may benefit from the convenience of traditional polymer processing techniques (e.g. extrusion, compression, moulding etc). This is either because of their large organic content or because of the formation of cross-linked inorganic networks from small molecular precursors, as in polymerization reactions. Hence, these materials can be produced at low temperatures (often using sol-gel and hydrothermal reactions) in various morphologies, such as 3D networks, thin films, or nanoparticles.

2.5 Carbon Nanotubes in Hybrid Materials

2.5.1 Why Carbon Nanotubes?

Many textbooks describe CNTs in simple terms as tubular structures made entirely of rolled-up layers of interconnected carbon atoms (Iijima, 1991; Iijima, 1993), with diameters ranging from about one to tens nanometers and lengths up to centimeters.

They are classified as either (a) “single-walled” tubes (SWCNTs, $0.7 < d < 2$ nm), consisting of a single layer of graphene sheet seamlessly rolled into a cylindrical tube or (b) multiwalled CNTs (MWCNT, $1.4 < d < 150$ nm), comprising multiple concentric tubes separated by about 0.34 nm. In general, CNTs possess large specific surface areas due to their hollow geometry, while their structural integrity and chemical inertness support relatively high oxidation stability.

Other advantages including their exceptional physical properties, which have been extensively discussed in several books (Harris, 2003; Dresselhaus *et al.*, 2000; Saito *et al.*, 1998) and reviews (Ajayan, 1999; Terrones, 2003; Dresselhaus *et al.*, 2004), are

Electrical properties: The electrical resistivity of CNTs is determined by the unique structure of graphite and the quantum mechanical properties associated with their 1D character and small size, which results in the near-total elimination of electron collisions (scattering). Hence, CNTs are ballistic conductors, whose resistance is independent of the nanotube length. Furthermore, they can carry the highest current density of any known material, with reported measurements as high as 10^9 A/cm² (For comparison, copper wires burn out at 10^6 A/cm²) (Wei, 2001). Depending on their helicity and diameter, CNTs can be either metallic or semi-conducting. This is of importance as semi-conducting SWCNTs may perform better in charge transfer processes in sensors, field emission devices, and photocatalytic applications, while metallic CNTs are preferred as interconnects in electronic devices or as conductive filler in CNT-composites.

Mechanical properties: The mechanical properties of CNTs originate from the strong C=C double bonds, which yield a very large Young’s modulus in their axial direction (1.4 TPa for single-walled CNTs) (Robertson, 1992). CNTs have an expected elongation-to-failure of 20–30%, which, combined with their stiffness, projecting to a tensile strength well above 100 GPa (e.g. steel: 1–2 GPa) — by far the highest known one (Yu, 2000).

Thermal properties: Theoretical works predicted room-temperature thermal conductivities of individual single-walled CNTs of up to 6600 W/m K (Berber *et al.*, 2000). CNTs would, therefore, transmit nearly twice as much heat as isotopically pure diamond. Experimental studies gave somewhat lower values. Hone *et al.* (2003) reported room-temperature thermal conductivities of 300 W/m K for bulk single-walled CNTs and of 3000 W/m K for individual multi-walled CNTs.

In summary, due to their remarkable mechanical, electrical, biological, optical, and thermal properties, CNTs promise enormous potential for various technological areas in the energy, information, aerospace, medicine, and chemical industries, where they can be used as gas adsorbents, templates, actuators, composite reinforcements, catalyst supports, or chemical sensors, among other things. For the same reasons, they are promising building blocks for hybrid materials.

2.5.2 Preparation of CNTs for Use in Hybrid

Functionalization of CNTs remains one of the most studied areas in the CNT research field, and many review articles have been dedicated to this topic (Tasis *et al.*, 2006; Prato *et al.*, 2004; Kuzmany *et al.*, 2004; Hirsch *et al.*, 2005; Klein *et al.*, 2008; Hirsch *et al.*, 2002). In general, CNTs can be functionalized by (a) covalent attachment of chemical groups through bonding to the π -conjugated skeleton of the CNT or (b) noncovalent adsorption or wrapping of various functional molecules.

Covalent functionalization of CNTs has been shown to be an efficient method for increasing their solubility and chemical reactivity (Fu and Sun, 2005; Tasis *et al.*, 2003). However, it also introduces additional structural defects and disrupts the delocalized electron system in the CNT sidewalls, and consequently alters the electronic and mechanical properties to a degree that would significantly affect the performance in hybrid materials (Salzmann *et al.*, 2007).

In contrast, non-covalent functionalization utilizes Van-der-Waals interactions and hydrogen bonding. Various surfactants and polymers have been applied to enhance the CNTs' solubility in hydrophilic solvents and to increase their dispersion in polymer or ceramic matrices (Xie *et al.*, 2005). Currently, there is much interest in functionalizing CNTs with biomolecules, such as peptides or DNA (Prato *et al.*, 2007; Cui, 2007; Katz and Willner, 2004). Another approach uses the well-

known π - π interactions between aromatic compound (e.g. porphyrins, pyrens) and the delocalized electron system in CNTs (Giordani *et al.*, 2006, Cambre *et al.*, 2008).

2.5.3 Synthesis of CNT-Inorganic Hybrids

The inorganic component can be attached to the outer surface of CNTs to produce novel hybrid materials. The various synthesis strategies for CNT-inorganic hybrids can be categorized as *ex-situ* and *in-situ* techniques. The *ex-situ* (attaching nanoparticles to CNTs or building block) approach first produces the inorganic component in the desired dimensions and morphology (typically spherical nano-particles), then modifies and attaches this component to the surface of CNTs via covalent, non-covalent, π - π stacking, and electrostatic interactions, as shown in Figures 2.2 and 2.3.

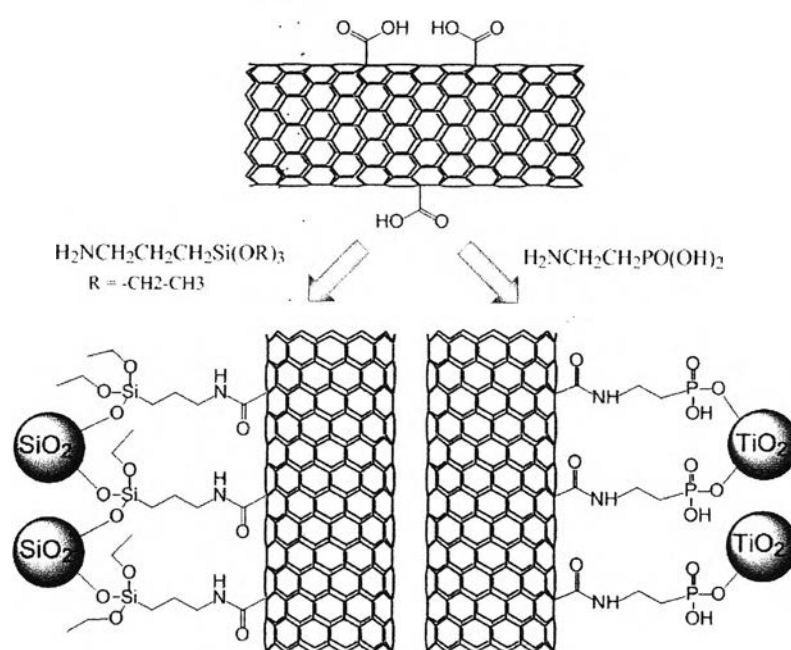


Figure 2.2 Common *ex-situ* process for the covalent attachment of Au nanoparticles to amino- or mercapto-terminated CNTs (Chen *et al.*, 1998).

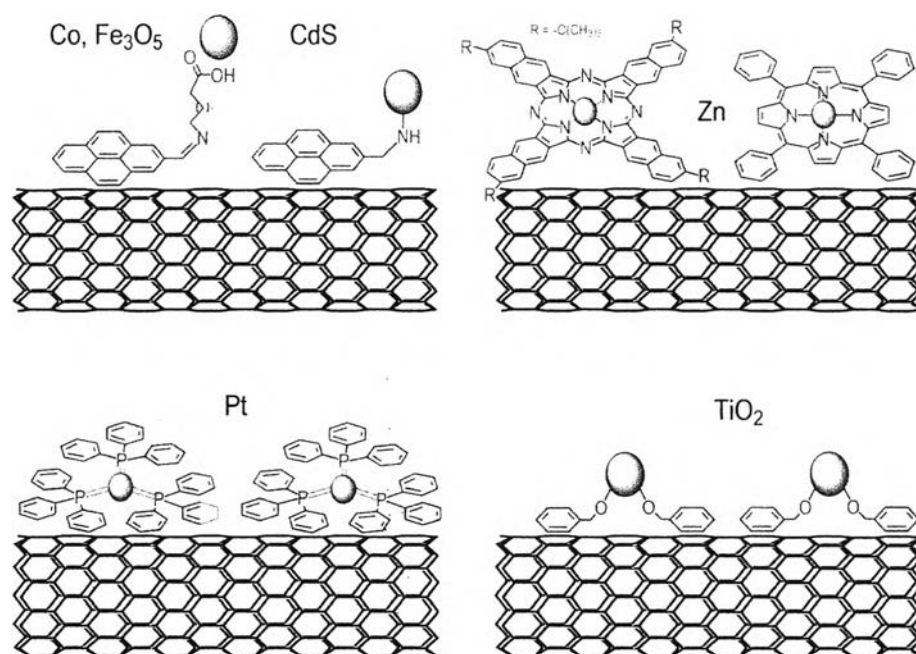


Figure 2.3 Examples of linking agents and ligands used to attach inorganic nanoparticles to pristine CNTs via π - π interactions: (a) pyrene derivatives, (b) porphyrins and phthalocyanines, (c) triphenyl phosphines, and (d) benzyl alcohol (Mu *et al.*, 2005).

In contrast, the *in-situ* approach; direct synthesis on the CNT surface, carries out the synthesis of the inorganic component in the presence of pristine or functionalized CNTs, onto which the inorganic material grows as particles, nanowires or thin films. The main advantage of this route is that the inorganic compound can be deposited as a continuous amorphous or single-crystalline film with controlled thickness, or as discrete units in form of nanoparticles, nanorods, or nanobeads. Furthermore, the CNTs may act as a support to stabilize uncommon or even novel crystal phases or prevent crystal growth during crystallization and phase transformation processes. Finally, a variety of chemical and physical synthesis techniques can be applied. The deposition can be carried out either in solution via electrochemical reduction of metal salts, electro- or electroless deposition, sol-gel processing, and hydrothermal treatment with super-critical solvents, or from the gas phase using chemical deposition (CVD or ALD) or physical deposition (laser

ablation, electron beam deposition, thermal evaporation, or sputtering), as shown in Figure 2.4.

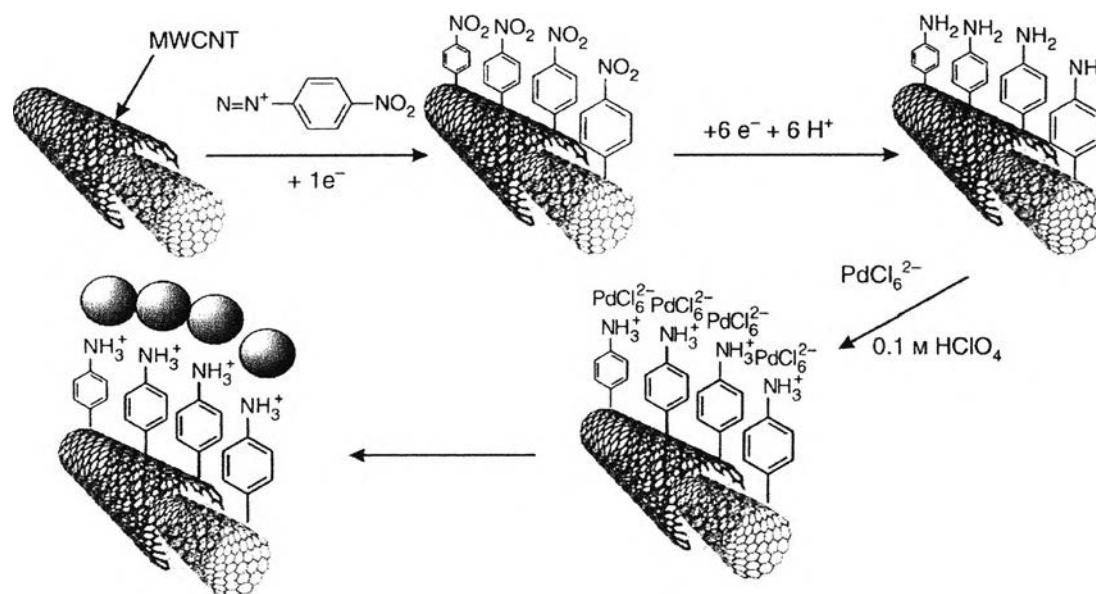


Figure 2.4 Electrodeposition of Pd nanoparticles on MWCNTs, via (1) covalent functionalization of CNTs with aminobenzyl groups via electrochemical reduction, (2) potentiostatic reduction of PdCl_6^{2-} ions to Pd nanoparticles (Guo and Li, 2004).

2.5.4 Applications of CNT Inorganic Hybrids

There are many applications of CNT-inorganic hybrids, such as photo-, electro-, and environmental catalysis, gas sensors, supercapacitors, and field emission devices. This section will be focused on photocatalysis.

There have been quite a few studies concerning the photocatalytic activity of CNT- TiO_2 hybrids, including the oxidation of acetone (Yu *et al.*, 2005), propene (Bouazza *et al.*, 2009), and phenol (Wang *et al.*, 2005; Wang *et al.*, 2005; Bouazza *et al.*, 2009). CNT-ZnO has been investigated for the decomposition of methylene blue (Loiseau *et al.*, 2004), while the decomposition of indigo carmine using both CNT-ZnO and CNT- TiO_2 has also been tested (Byrappa *et al.*, 2008). All of these studies showed superior photocatalytic performance by the hybrid over the individual component.

For instance, Wang *et al.* coated acid-treated MWCNTs with TiO_2 via sol-gel and investigated the degradation of phenol under UV and visible light (Wang

et al., 2005). In both cases they observed a considerable acceleration of the oxidation reaction, with most of the phenol being transformed after 4 h (6 h in visible), while pure TiO₂ needed 6 h (9 h in visible) and pure MWCNTs only converted up to 5 %. The maximum activity was observed with a CNT concentration of 20 wt% and was considerably higher than the simple mechanical mixture of the same composition and surface area. A similar behavior was shown by Yu *et al.* (2005) for the oxidation of acetone (maximum activity at 5 wt% CNTs), as well as by Lee *et al.* for the decomposition of methylene blue, who observed a superior performance of CNT-ZnO hybrids over the mechanically mixed composite. All these works clearly demonstrated a synergistic effect of CNTs in enhancing the performance of TiO₂ or ZnO.

Titanium silicalite-1 (TS-1) zeolite is another interest because of its outstanding catalytic activity and selectivity in the oxidation of various organic compounds using H₂O₂ as an oxidant and because it has been used for many photocatalytic reactions (Phonthammachai *et al.*, 2006; Ramkrishna *et al.*, 2002; Klaewkla *et al.*, 2006; Juan *et al.*, 2009). Yamagata *et al.* (1995) reported that TS-1 also has a unique photocatalytic activity for CO₂ reduction. Moreover, Yamashita *et al.* (1998) found that TS-1 exhibited much higher photocatalytic activity than TiO₂ for CO₂ reduction to CH₄ and CH₃OH. Lee *et al.* (2003) used TS-1 as a photocatalyst for decomposition of 4-nitrophenol, toxic and carcinogenic compound in waste water, with H₂O₂. They reported that the enhancement of photocatalytic activity of TS-1 can be attributed to the efficient formation of hydroxyl radical (\cdot OH) from H₂O₂ and the close proximity of \cdot OH radicals to the reactant molecules.

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 *et al.*, 2003; Li *et al.*, 2003; Zhu *et al.*, 2009), the photocatalytic properties of TS-1/CNTs composite photo catalysts remain largely unexplored. Thus, one of the objectives is to investigate the photocatalytic activity of CNT/TS-1 hybrid as next-generation photocatalysts.