CHAPTER 6

NETWORKING OF TITANIA NANOPARTICLES: A TEMPLATE-FREE METHOD FOR THE SYNTHESIS OF MESO-STRUCTURED ANATASE SPHERES FOR CATALYTIC APPLICATIONS

6.1. Introduction

In Chapter 4, we have discussed about how to build networks of gold NPs resulting in the formation of mesoporous sponge. In this chapter, we discuss about how the in-situ networking of nanoscale structures can lead to the formation of mesostructured metal oxide materials. Historically, the mesoporous silica and other metal oxide systems have been synthesized using the template based methods, wherein a sacrificial organic template, generally a self-assembled nanosized bundle (such as a micelle, bilayers, block copolymers, etc.), is used. Many types of mesoporous silica or metal oxide systems having different pore sizes and shapes have been synthesized and reported in the literature. In this chapter, we also present results on the use of this mesoporous titania as support for Au and Au-Ag alloy NPs for application as heterogeneous catalysts.

Titania, being an n-type wide band semiconductor, has several industrial applications and the dye-sensitized, mesoporous anatase is currently being proposed as a potential replacement for silicon as the photoactive material in solar cells, offering tremendous opportunities for harvesting solar energy at low cost. High surface area and crystallinity (anatase) are two factors that are critical in enabling such technologies and thus, inexpensive and environmentally benign methods for the synthesis of meso-structured anatase are important. Ever since the first synthesis of mesoporous titania was reported by Antonelli and Ying, several
researchers have developed diverse techniques to improve its surface area and crystallinity.\textsuperscript{283-287} Majority of these approaches utilize templates. Although a few attempts \textsuperscript{288,289} towards the development of template-free routes have been reported, these methods did not provide meso-structured anatase. 

Self-assembly, often governed by site-specific intermolecular interactions, has been the focus of immense research in material science in the recent years for the controlled organization of nanoscale materials and the synthesis of meso-structured materials. \textsuperscript{290,291} For example, the self-assembly of several organic surfactants and block copolymers has been successfully used as templates and structure-directing agents for the synthesis of meso-structured metal oxides.\textsuperscript{277,282,283,292-296} The use of such auxiliary templates or structure directing agents, some of them ionic liquids,\textsuperscript{297} necessitates techniques for their removal such as calcination or solvent extraction under extreme conditions, raising environmental and economical concerns. Herein we investigate the template-free, room temperature hydrolytic condensation of inorganic-organic hybrid systems such as metal alkoxides in suitable solvents such as ethyl acetate as a “green” approach for the synthesis of meso-structured metal oxides.

The approach presented herein is based on the microphase separation and organization of Ti(IV) \textit{n}-butoxide, TiOB (monomers or polyalkoxides, as many alkoxides exist at room temperature) when dispersed in a medium like ethyl acetate, as a result of their different intermolecular association behaviour resulting from site-specific polar and non-polar interactions. Such microphase separation (or microheterogeneity) is a well-established phenomenon in simple solvent mixtures.\textsuperscript{268} In this Chapter, in addition to the synthesis of mesoporous anatase, we also report
the preparation of mesoporous anatase supported Au and Au-Ag alloy NP catalyst systems and their applications in typical chemical reactions.

6.2. Experimental

6.2.1. Materials used: HAuCl4·3H2O (99.9+, Sigma Aldrich), AgNO3 (99+%, Sigma Aldrich), D(+)Glucose (ACS reagent, Sigma), and NaOH (Extrapure AR, SRL) were used as purchased. Ethyl acetate, EA (99.5%) and titanium(IV)tetrabutoxide, TiOB (97%) for the preparation of mesoporous TiO2 are products from Sigma and Aldrich respectively. Reagent solutions were prepared in deionized water.

6.2.2. Template-free Preparation of Mesoporous Titania (Anatase): In a typical procedure, about 2ml of TiOB was added to 6ml of dehydrated EA with continuous stirring at 25 °C (RT). After stirring the mixture rigorously for about 5 minutes, 3 ml of deionized water was added with stirring to hydrolyze TiOB. A white slurry of TiO2 was formed almost instantaneously and it was kept overnight at RT for drying. The sample was subjected to heat treatments as mentioned in the Results and Discussion section.

6.2.3. Preparation Au and Au-Ag Alloy NP loaded Titania

Au and Au-Ag (80:20) aqueous NP dispersions of average particle size around 6 nm were prepared as mentioned in Chaper 3. In order to prepare the NP loaded mesoporous titania, a variant of the method described in the previous paragraph was employed as follows. About 2ml of TiOB was added to 6ml of dehydrated EA with continuous stirring at 25 °C (RT). After stirring the mixture vigorously for about 5 minutes, a stochiometrically selected volume of Au or Au-Ag (80:20) alloy dispersion was added with stirring to hydrolyze TiOB in such a manner that about 5
weight percent of the metal/alloy NP is incorporated into the titania system along with the hydrolytic condensation itself. An additional 3 ml of water was added to the system for completion of the hydrolytic condensation process. The slurry formed was kept overnight at RT for drying. The sample was heated for 6 hours at 600°C. The samples thus prepared, TiO$_2$-AuNP (5%, abbreviated as TiOAu) and TiO$_2$-AuAg (80:20) NPs (5%, abbreviated as TiOAuAg) were used for carrying out prototype reactions such as photocatalytic oxidative mineralization of two organic compounds- Methylene Blue and Congo Red- and normal CO oxidation at elevated temperatures. The choice of the dyes as the photocatalytic degradation systems is to ensure easy monitoring of the progress of the reaction by means of UV-Visible absorption spectroscopy.

6.2.4 Photo-reactor Set-up.

PSA W90 Raynonet type photo reactor (Popular Science Apparatus Pvt. Ltd., Haryana) having heavy metal enclosure and eight 8W UV lamps and highly polished stainless steel reflector is used. Two clamping rods are provided for holding the suspended glass reactor. A cooling fan is provided at the base of the reactor. Continuous stirring is ensured using a magnetic stirrer.

6.2.5 Dyes used in the present study

The dyes used for this photocatalytic study are methylene blue and Congo red (Fig.6.1.a&b). Methylene blue is a potent cationic dye with $\lambda_{\text{max}}$ around 670 nm and Congo red is the sodium salt of 3,3'-(1,1'-biphenyl)-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid with $\lambda_{\text{max}}$ around 498 nm. It is a secondary diazo
dye. Congo red is water soluble, yielding a red colloidal solution; its solubility is better in organic solvents such as ethanol.

![Structure of (a) Methylene blue and (b) Congo red](image)

**Figure 6.1.** Structure of (a) Methylene blue and (b) Congo red

### 6.2.6. Photocatalytic Studies

The photocatalytic oxidative mineralization of two organic dyes, Methylene Blue and Congo Red were carried out as follows. 0.0012g of commercially purchased Methylene Blue was taken, dissolved in deionized water and made up to 250 ml in a standard flask to prepare 5mg/L solution. Similarly Congo red solution was prepared by dissolving 0.0018 g dye in 250 ml deionized water in a standard flask to prepare 7mg/L solution.

In a typical procedure, 0.05 g catalyst and 12.5 ml dye solution were taken in a quartz tube and placed in the photo reactor with magnetic stirring. A definite amount
of solution was withdrawn, filtered and absorbance measurements were taken at every half an hour interval.

6.2.7. Absorbance Measurements

The choice of the dyes as the degradation systems is to ensure easy monitoring of the progress of the reaction by means of absorbance measurements using a colorimeter (CL 157 - ELICO). The absorbance measurements were performed by using 620nm filter for Methylene Blue and 480nm for Congo red.

6.3. Results and Discussion

6.3.1. Synthesis and Characterization of mesoporous titania: Transmission electron microscope (TEM) images reveal that the sample consists of TiO$_2$ nanospheres in the sub-micron size range (typically between 100 to 700 nm (Figure 6.2.). In some cases, these nanospheres appear to be associated (Figure 6.2 A). Closer observations using high resolution TEM (HRTEM) reveal that these nanospheres are micro/sub-mesoporous (Figure 6.2 B, C & D).
Figure 6.2. TEM images of the RT-synthesized (A, B, C and D) and heat treated (E& F, 60 °C, 1 week) mesostructured titania nanospheres at various magnifications. Images G and H correspond to the bulk TiO$_2$ (prepared in the absence of EA) in the RT- synthesized form and after heat treatment (60 °C, 1 week), respectively.
These pores correspond to an interparticle, worm-hole type architecture with the pore sizes ranging from 1.2 to 1.6 nm. Small angle XRD (Figure 6.3 A, blue curve) for this sample clearly shows the presence of mesoscale order in this system with a peak around $2\theta = 2^\circ$ ($d$ spacing = 4.8 nm).

![Figure 6.3](image)

**Figure 6.3.** Small angle (A) and higher angle (B) XRD of the samples: (blue) as synthesized; (dark red) after heating at 60 °C for 48 hours; (black) after heating at 60 °C for 1 week; (red) after heat treatment at 400 °C for 5 hours.

The broad nature of this peak and the absence of higher order reflections indicate that the mesoscale order is short ranged. The absence of any typical crystalline peaks in the higher angle XRD reveals that the sample is amorphous. To study the effects of heat treatment, about 2 ml of water was added to the sample, stirred well, and left for drying at 60 °C. After about 48 hours, the small angle XRD (Figure 6.3. A, dark red) of the sample showed some degree of sharpening and a slight shift to higher $d$-values (5.3 nm), indicating an increase in the mesoscale order. In fact, since no
templates are employed, we anticipated that the meso-scale order at RT may collapse on heating. The observed increase in ordering may be due to a coupling between the drying induced self-assembly and the Ostwald ripening within the localized, nanoparticulate TiO$_2$ spheres. Higher angle XRD (Figure 6.3 B, dark red) showed that the sample is in the anatase phase. Continued heating of the sample at 60°C for 7 days resulted in significant increase in intensity with increase in d-spacing and sharpening of the low angle XRD peak (Figure 6.3 A, black curve), showing a further increase in the meso-scale order. This may be explained as due to the sharpening of an initially broader particle size distribution at higher temperature, with increase in particle sizes. The particle size from the Scherrer formula and the observed d-spacing agree rather well, supporting this notion.

Also, the small angle peak shifted to relatively larger d-values (11.3 nm), indicating a notable reorganization within the nanospheres as a result of the crystallization. This observation is in contrast to the previous reports$^{296}$ of a decrease in the d-value on heat treatment as a result of wall condensations, suggesting significant differences from the previously reported cases. In the present case, the pores are of interparticle nature and are lesser defined as compared to the structured pores resulting from the template-based strategies. This also provides an explanation for an observed d-value of 11.9 nm for the calcined material with an associated particle size of around 10 nm. However, there is no notable change in the full width at half maximum (FWHM) of the higher angle anatase peaks (Figure 2B, black curve, particle size from Scherrer formula is ~4 nm) for the sample heated for 1 week in comparison with that of the 48 hour sample.

The micro-structures of the TEM images of the heat-treated samples are quite distinct from the as-synthesized samples. The spherical TiO$_2$ assemblies in the heat-
treated samples (Figures 6.2. E and F) appear to be constituted by a stone-wall type packing (where the pores are the interparticle voids) of anatase nanocrystals. Just as the nanosphere association is observed, there appears to be connectivity between the individual anatase nanocrystals. This, and the random misalignment of the crystallographic axes along which these crystals are grown may provide high thermal stability for these mesoscale assemblies, by preventing particle aggregation.

Since one key aspect for the utilization of these materials is their thermal stability, we followed the heating effects on these samples up to 400°C. Small angle XRD (Figure 6.3 A, red curve) shows that while the heat treatment at 400 °C increases the mesoscale order (as evidenced from the significant sharpening of the peak), there is no pronounced shift in the d-spacing (11.9 nm). Also, the higher angle XRD (Figure 6.3 B, red curve) peaks reveal an increase in the crystallite sizes (~ 10 nm, using the Scherer formula). The TEM images also reveal that the spherical assemblies of the TiO$_2$ NPs are intact even after heating at 400°C. We also studied the effects of hydrothermal treatment at different temperatures on these systems. Typically, about 4 ml of deionized water was added to about 1 gm each of the as-synthesized samples taken in three 20 ml, Teflon-lined autoclaves, sealed, and was heated at 60, 80 and 100 °C, respectively, for about 24 hours. Small angle XRD patterns of these samples suggest a dependence of the d-spacing with the temperature. The absence of any structural collapse on hydrothermal treatment also suggests that there is an inherent degree of order in the directed self-assembly of the TiO$_2$ NPs. High resolution TEM images and the electron diffraction patterns of these samples are shown in Figures 6.4.(A) and 6.4(B), respectively, supporting a stone-wall type packing of highly crystalline anatase NPs.
Figure 6.4. Crystallinity of the hydrothermally treated nanospheres. (A) HRTEM image of the hydrothermally treated samples showing the lattice fringes corresponding to the anatase phase, (B) the corresponding electron diffraction pattern, and (C) small angle XRD of the samples corresponding to different treatment temperatures: (black) RT; (red) 60°C; (dark red) 80°C; (blue) 100°C.

For the removal of the organic residues (the n-butanol formed as the hydrolysis product and the residual EA) and water from the sample, we employed extrusion using supercritical CO$_2$, which is widely regarded as an environmentally benign and efficient medium due to its non-toxicity, non-flammability, abundance, low cost, and high diffusivity$^{299}$. Also, supercritical fluid (SCF) extrusion is an inherently “dry” process and there is no need for any post-extrusion drying. The BET surface area for the RT sample after CO$_2$ extrusion is 554m$^2$/g. The N$_2$ adsorption-desorption isotherm (Figure 6.5 A) falls on the borderline between the type I and type IV with no hysteresis.
Figure 6.5. $N_2$ adsorption-desorption isotherms for the RT synthesized (A) and the heat treated (60 °C, 48 hours, B) samples. The pore size distributions using HK and DH methods are shown in the insets.
The Dollimore-Heal (DH) pore size distribution shows that the pores are mostly below 1.7 nm and the Horvath-Kawazoe (HK) analysis for the microporous region shows a discrete pore size distribution in the range from 0.5 to 1.4 nm (Figure 6.2 A, inset). These are in agreement with the results obtained from the HRTEM images. The SCF extrusion did not affect the spherical morphology or the d-spacings as evidenced from the TEM and small angle XRD profiles. It is observed that even conventional heating under vacuum at 100 °C can be used for the removal of these residues, which could be of importance in the commercialization of this approach. The anatase sample after heat treatment for 48 hours shows a type IV \( \text{N}_2 \) adsorption-desorption isotherm with a surface area of 388 m\(^2\)/g and a DH pore size of 2 nm, while continued heat treatment for one week causes a decrease in the surface area (260 m\(^2\)/g) and an increase in the DH pore size (4 nm). The samples subjected to heat treatment at 400°C also presents a surface area of 230 m\(^2\)/g, but with an increased DH pore size (8.4 nm). These observations may be explained based on the continued crystal growth process and structural reorganizations within the nanospheres. The hydrothermally treated samples also show surface areas around 250 m\(^2\)/g and DH pore sizes in the range of 5-6 nm.

The mechanistic details regarding the formation of the solution phase nanostructures of TiOB in EA, their size control, and the thermodynamic control are of importance. Compositions with higher amounts of TiOB resulted in porous, but non-structured titania, while lower concentrations show small aggregates with lesser morphological preferences. In order to examine the role of EA in the self-assembly process, we also carried out blank experiments and observed that the mesoscale order exists even in the absence of EA although the spherical morphology is absent. The TEM images for the bulk (synthesized in the absence of EA) sample in the as-synthesized form
and after heat treatment (60°C; 1 week) are given in Figures 6.2. G and H, respectively. These data are in general consistent with those observed for the samples with spherical morphology. This indicates that the observed meso-scale order arises from the self-assembly of TiOB molecules themselves and the role of EA is only in dispersing the bulk associations into thermodynamically stable spherical assemblies. A tentative mechanism is presented in Figure 6.6.

Figure 6.6. Mechanism: The hierarchical organizations of TiOB on hydrolysis forms mesostructured TiO₂ with amorphous walls, which on heating transforms into anatase phase. EA helps in the dispersion of such clusters into spherical assemblies.

It is plausible that the charge separations in the TiOB molecule (with partial positive and negative charges on the Ti and the O atoms, respectively, and the essentially non-polar alkyl chains) may guide the self-assembly of these systems. Although there is no long range meso-scale order in the systems (as evidenced from the absence of higher order reflections in the small angle XRD) present in these systems, these results are significant, not only from an industrial stand-point but also from the understanding of nanoscale organizations.
The spherical morphology of the aggregates formed is also of importance. This may be explained based on the energetics of cluster speciation between the highly charge polarized TiOB and the less polarized EA. In the dispersion concentrations studied, there will be a competition between self-interactions Vs cross-interactions amongst EA and TiOB systems (as well as their partially hydrolysed derivatives) and it is natural that the more interacting (in terms of electrostatics) TiOB molecules will maximize the self-interaction (and minimizes the surface area); thereby causing the observed spherical morphology. The situation is best described by microheterogeneity. While such effects will be less prominent on the morphology of very small clusters, it is bound to be significant in the case of larger clusters. The solvent molecules, thus, may play a significant role in guiding the self-assembly of TiO$_2$ into spherical clusters, although in a passive way. The possibility of the direct participation of EA in the formation of the solution phase nanostructures also cannot be ruled out completely.

### 6.3.2. Photocatalytic Remediation of Organic Compounds Using Titania

Remediation of organic waste using photo catalysis on semiconductor systems such as Titania is one of the fast growing areas in term of academic research and commercial activity. Titanium dioxide is considered to be an ideal photocatalyst in several respects.$^{300}$ It is relatively inexpensive, possess high chemical stability, and the photo generated holes are highly oxidizing. In addition, photo generated electrons are reducing enough to produce superoxide from dioxygen. Even at room temperature, TiO$_2$ is active enough to completely oxidize organic contaminants in water, air and soil into harmless carbon dioxide, water, or simple mineral acids. For example, if catalytically active TiO$_2$ powder is dispersed in polluted water and illuminated with sunlight, the water will gradually become purified, free of organic
contaminants. This is different from the traditional catalytic oxidation, requiring a high temperature of at least hundreds of degrees. TiO$_2$ has been proved to be effective for remediating various kinds of organic compounds varying from hydrocarbons to carboxylic acids. The 114 kinds of pollutants published by the US Environmental Protection Agency were found to be treatable by TiO$_2$. The oxidative ability of TiO$_2$ is far stronger than that of ozone, hypochlorous acid, and potassium permanganate. TiO$_2$ is not consumed in photocatalytic reactions and it can deoxidize itself under UV irradiation which resumes its high oxidation efficiency.\textsuperscript{301-310}

6.3.3. TiO$_2$ Photocatalysis

Upon irradiation with ultraviolet light having energy higher than its band gap energy (<385nm, usually UVA and UVC are applied), TiO$_2$ absorbs photons causing the excitation of a valence electron into the conduction band. These photo excited charge carriers can initiate the degradation of the adsorbed chemical species by one or more forms of electron transfer reactions. The energy band diagram for TiO$_2$ in pH 7 solution is shown in Fig. 6.7. The redox potential for photo-generated holes is $\approx 2.53$ V. The bulk photoelectrons and holes can recombine to produce thermal energy, or rapidly migrate to the surface and react with adsorbed species at the surface. In a steady state photocatalytic reaction, the rate of oxidation by the holes has to be balanced by the rate of reduction by the electrons. Either of these reactions can be rate determining. Although the above physical events are generally accepted as the initial step for the photo oxidation process, the subsequent chemical events at the liquid-solid interface remain an ambiguous and controversial issue. The trapped holes have been proposed to directly oxidize adsorbed molecules, or to react with surface hydroxyl groups to produce hydroxyl radicals which are strong oxidizing agents. The chemical identification of hydroxylated
oxidation intermediates and the ESR detection of hydroxyl radicals appear to support the hydroxyl radical mechanism. However, these data do not permit the unambiguous delineation of the OH-driven mechanism versus the direct hole oxidation mechanism since similar reaction intermediates are expected from these two schemes in an aqueous system. A recent diffuse reflectance flash photolysis experiment in nonaqueous solution presented evidence in favor of the direct hole oxidation route. The trapped electrons are believed to react with pre-adsorbed molecular oxygen to produce $O_2^-$ and $O_2^{2-}$ anions. However, the ultimate fate of the activated oxygen species was not determined. Depending upon the exact conditions, the holes, OH radicals, $O_2^-$, $H_2O_2$ and $O_2$ itself can all play important roles in the photocatalytic reaction mechanisms. They may directly oxidize organic species, protonate to generate hydroperoxide radicals and hydroxyl radicals, or further react with more trapped electrons to eventually form water. On an electrically isolated TiO$_2$ particle, the anodic and cathodic currents must balance each other precisely. From the band-edge positions of the valence band and conduction band, the redox capability of a photo excited semiconductor particle in the aqueous solution can be estimated.
It is important to note that TiO$_2$ photocatalysis, like the photoelectric effect, depends upon the energy of the incident photons, but, to a first approximation, not on their intensity. Thus, even if there are just a few photons of the required energy, they can induce photocatalysis. This means that even ordinary room light may be sufficient to help to purify the air or to keep the walls clean in the indoor environment, because the amounts of pollutants are typically small. Thus, in a reasonably well-lit room, with a total light intensity of about 10 mWcm$^{-2}$, the intensity of UV light with energy exceeding that of the TiO$_2$ band gap would be approximately 1 mWcm$^{-2}$. As shown later, assuming a quantum efficiency of 25%, this would be sufficient intensity to decompose a hydrocarbon layer of approximately 1 mm thickness every hour.

However, the need of an ultraviolet (UV) excitation source restricts its technological utility. For widespread applications, TiO$_2$ photocatalyst effective in visible radiation or solar light needs to be developed as future generation photo-catalytic material. TiO$_2$ absorbs only 3–5% energy of the solar spectrum hence numerous studies have been performed to extend the photoresponse and to enhance the photocatalytic activity by various methods such as modifying its surface structure, surface properties and composition. There are plenty of research works going with an objective to enhance the visible light activity of TiO$_2$ by modifying the band gap. The doping with metal ions and organic polymers has been proven to be an efficient route to improve the photocatalytic activity of TiO$_2$.

6.3.4. Photocatalytic Degradation of Dyes using TiOAu and TiOAuAg
Gold NPs supported on Titania, the synthesis of which is detailed in the experimental section, is used for the photocatalytic degradation of the dyes – Congo Red and Methylene blue. These dyes are chosen since their degradation is easy to follow by observing the reduction in the characteristic optical absorption.

All the three titania samples used for this photocatalytic study were found to be active for the degradation of the sample dye pollutants selected. The results obtained for the photocatalytic study are presented below. Figure 6.8. is the graph plotted between the observed absorbance and the exposure time in the case of Methylene Blue.

![Graph showing absorbance vs. time for different catalysts](image)

Figure 6.8. Plots of the observed absorbance against the exposure time of Methylene Blue for mesoporous titania, Au nanoparticle doped mesoporous titania, and Au-Ag alloy nanoparticle doped mesoporous titania photo catalysts.
From the graph it is clear that, when compared to the undoped mesoporous titania catalyst, the gold nanoparticle loaded TiO$_2$ catalyst as well as the Au-Ag alloy NP doped TiO$_2$ have superior photocatalytic activity as far as the remediation of Methylene Blue is concerned. Among the metal loaded catalysts, the TiOAuAg system was found to be a better catalyst than the TiOAu system. Therefore, we can say that the alloy NP is acting as a better electron scavenger in this particular reaction.

In the case of Congo red also, the photocatalytic remediation of the dye molecule followed the same trend for the three catalyst except that after the initial 30 minutes the degradation rate decreased slightly in the case of Au-Ag alloy NP doped mesoporous TiO$_2$ (Figure 6.9). The reason for this retardation is unclear. One probability is that even though the electron-hole recombinations are less in the alloy NP doped sample, the number of active sites may be lesser in number causing the saturation of active sites after sometime. For conclusive evidences, further studies are required.
6.3.5. CO Oxidation

One important industrially relevant reaction using TiO$_2$ is the heterogeneous catalytic oxidation of Carbon Monoxide to Carbon Dioxide. Catalytic efficiency of the synthesized catalysts were tested for their activity against thermally activated reaction is investigated using both the TiOAu and TiOAuAg. The reaction was carried out in a continuous flow reactor packed with 50 mg of the catalyst. 10 ml of CO (1.02%, He balance) and 10 ml of O$_2$ (100 %) was passed through the reactor maintained at the desired temperature. Product formed was analyzed by injecting into the GC with following standardized parameters (Column Type : MolSeive, Column Temperature : 120°C, Column Pressure : 25 psi/ 1/72 bar, Detector : TCD). The results are shown in Figure 6.10. The results clearly reveal that the TiOAuAg Catalyst is more efficient than the TiOAu system.
6.4. Conclusions

In this chapter, we have presented two important aspects. The first is the synthesis and characterization of the mesoporous titania (anatase) by the template-free, nanoscale self-assembly of NPs. In a simple strategy, we have shown that by the room temperature, hydrolytic condensation of TiOB dispersed in ethyl acetate, we can synthesize mesostructured titania spheres, which can by heat treatment be converted to highly crystalline mesoporous anatase for applications. The spherical morphology of the titania produced can be hypothesized as due to molecular speciation and energetic of molecular self-assembly. By adopting a variant of this method, using aqueous gold sol instead of water for hydrolytic condensation process, we also synthesized titania-supported gold NP systems. It is shown that

Figure 6.10: Plot of Temperature against the % Conversion of CO to CO$_2$. 

![Graph showing Temperature vs. % Conversion of CO to CO$_2$.]
these systems could be used as heterogeneous catalysts in photocatalysis (for remediation of organics) and CO oxidation.