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Introduction, Historical review and Aim of work
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1.1 Introduction

Many researchers are working on developing new technologies for synthesizing nanostructured materials and one of the recent nanomaterials that have attracted a great deal of attention is Titanium Dioxide (TiO$_2$). TiO$_2$ powder and films possess interesting structural, optical, electrical and catalytical properties, which finds many industrial applications. Due to its semiconducting activity TiO$_2$ is used as photo-catalyst in environmental related problem of pollution control. It is well known that nanostructured materials have high active surface, which make them preferred materials over macro porous materials [1-9].

TiO$_2$ has also been studied and found to be suitable as gas sensors and exhibit good self-cleaning and wettability properties. TiO$_2$ (titania) is a cheap, non-toxic semiconductor and environment friendly material [10-12]. TiO$_2$ is also a promising candidate for opto-electronic, microelectronic devices, corrosion free coating [13-21]. It is known that TiO$_2$ shows three crystalline structure i.e. anatase, rutile, brookite [22].

1.2 Titanium Dioxide (TiO$_2$)

Titanium dioxide, also known as titanium (IV) oxide or titania, is a naturally occurring oxide of titanium and its chemical formula is TiO$_2$. It is noteworthy for its wide range of applications, form paint to sunscreen to food colouring. TiO$_2$ shows three phase: rutile, anatase and brookite. Rutile phase is most stable as compared to anatase and brookite phase. At low temperature it shows anatase phase and after heating treatment it in converted to rutile phase. TiO$_2$ is widely used as a pigment because of its high refractive index. Approximately 4 to 5 million tons of pigmentary TiO$_2$ are consumed annually worldwide. TiO$_2$ thin films also shows high refractive index and different colour with transparency and is used as optical coating for dielectric mirrors and some gemstones. TiO$_2$ is specifically employed as a
pigment, plastics, papers, inks, food, medicines (i.e. pills and tablets), toothpastes, etc. [23-24].

1.2.1 Anatase TiO$_2$

The anatase phase of TiO$_2$ is one of its two metastable phases together with brookite phase. TiO$_2$ anatase convert to rutile generally at the annealing of 600-700 °C. Some researchers have also found it to achieve rutile structure at 500 °C and some have found rutile structure at annealing temperature of more than 800 °C. Thus, anatase and rutile phase strongly depends on thermal treatment conditions. Anatase structure is tetragonal, with two TiO$_2$ formula unit (six atoms) per primitive cell. Lattice parameter are, \( a = b = 3.7710 \text{ Å} \) and \( c = 9.430 \text{ Å} \) with \( c/a \) ratio of 2.5134 as shown in figure (1-1) [25].

\[ \text{Figure 1-1, Anatase Phase of Crystalline TiO}_2 \ (\text{http://cst-www.nrl.navy.mil/users/sullivan/TiO2/tio2.html}) \]

1.2.2 Rutile TiO$_2$

Titanium dioxide (IV) has a stable phase rutile (material structure) and the schematic rutile structure is shown in figure 1-2. Its unit cell contains Ti atoms occupying the center of a surrounding core composed of six oxygen atoms placed approximately at the corners of a
quasi-regular octahedron as shown in the fig (1-2). The lattice parameters are $a = b = 4.5933$ Å and $c = 2.9592$ Å with $c/a$ ratio of 0.6442 [25].

![Figure 1-2, Rutile Phase of Crystalline TiO$_2$](http://cst-www.nrl.navy.mil/users/sullivan/TiO2/tio2.html)

1.2.3 **Brookite TiO$_2$**

The brookite structure is more complicated and has a larger cell volume as compared to anatase and rutile. It is also the least dense of the three forms. The unit cell is composed of eight formula units of TiO$_2$ and is formed by edge sharing TiO$_2$ octahedra, similar to rutile and anatase as shown in the fig (1-3) [23].

![Figure 1-3, Rutile Phase of Crystalline TiO$_2$](http://cst-www.nrl.navy.mil/users/sullivan/TiO2/tio2.html)
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The difference in these three crystal structures can be attributed to various pressures and heats applied from rock formations in the Earth. The rutile phase is more stable at high temperature. Although rutile is the most abundant of the three phases, many quarries and mines contains only the anatase or brookite form. Brookite was first discovered in 1849 in Magnet Cove, a site of large deposits of the mineral. It was originally dubbed ‘arkansite’ for the state it was discovered in Arkansas [26]. The optical properties of each phase are almost similar, but have minor differences. The absorption band gap for the rutile, anatase, and brookite phases were calculated to be 1.78eV, 2.04eV, and 2.20eV, respectively. In the form of addition to the slight increase in the band gap, the anatase form also has a slightly higher Fermi level (0.1eV). In thin films it has been reported that the anatase structure has higher mobility for charge carriers versus the rutile structure [27]. For photocatalytic processes, anatase is the preferred structure, although all three forms have shown to be photocatalytic. The electronic structure of brookite is similar to anatase, based on minor differences in the local crystal environment [28-29].

1.3 Brief Historical Review

Many techniques and process are now available to synthesize TiO$_2$ nanoparticle with different crystalline structure and phases. The properties of TiO$_2$ strongly depend on the synthesis method and condition. TiO$_2$ nanoparticle shows high dielectric constant and it changes with doping of transition and rare earth materials [30-38]. TiO$_2$ also shows high gas sensitivity on doping with a noble metal [39-40].

TiO$_2$ nanoparticles powder and thin films with specific crystal structure, orientation or morphology exhibit specific characteristics, which makes it important to control the phase of TiO$_2$ nano powder and films during the synthesis process. Many synthesis processes are available to make TiO$_2$ nano powders and thin films. e.g., precipitations, solid state reaction,
sol gel are generally used to produced TiO₂ nano powder and sol gel spin coating, thermal evaporation, e-beam evaporation, Chemical Vapour deposition (CVD), Pulse Laser Deposition (PLD), sputtering are used to fabricated TiO₂ films. Among these methods, the e-beam method is generally used for growing oxide films because it allows for stoichiometry of the synthesized materials.

In recent years, application to environmental cleanup have been one of the most active areas in heterogeneous photocatalysis. This is inspired by the potential application of TiO₂ based photocatalysts for the destruction of organic compounds in polluted air and wastewater [41].

The synthesis of nanoparticles of titanium dioxide (TiO₂) with varying percentages of anatase and rutile phases is also reported by Banerjee et. al.. This was achieved by controlling the operating pressure in a transferred-arc, direct current thermal plasma reactor in which titanium vapors are evaporated, and then exposed to ambient oxygen. The average particle size remained around 15 nm in each case. The crystalline structure of the as-synthesized nanoparticles of TiO₂ was studied with X-ray diffraction analysis; whereas the particle morphology was investigated with the help of transmission electron microscopy. The precursor species responsible for the growth of these nanoparticles was studied with the help of optical emission spectroscopy. As inferred from the X-ray diffraction analysis, the relative abundance of anatase TiO₂ was found to be dominant when synthesized at a pressure of 760 torr, and the same showed a decreasing trend with decreasing chamber pressure. The study also reveals that anatase TiO₂ is a more effective photocatalytic agent in degrading methylene blue as compared to its rutile phase [42].

S. R. Dhage et. al., has reported on a gel formed when a mixture of TiOCl₂ and tartaric acid was heated on a water bath. Ultrafine powders of TiO₂ in the anatase phase were formed,
when the gel was decomposed at 623 K and the mole ratio of tartaric acid to titanium. The anatase phase was converted into rutile phase on annealing at higher temperatures, 773 K. When initial ratio of titanium to tartaric acid, the decomposition of gel leads to the formation of mixed phases of rutile and anatase. However, pure rutile phase was not formed by the decomposition of gel for any ratio of tartaric acid and titanium. These powders were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and surface area measurements. The average particle size obtained for anatase phase was 3 nm whereas it was 30 nm for rutile phase. Raman scattering experiments were also performed to confirm both anatase and rutile phases [43].

L. Kumaresan et. al., has reported on strontium doped titania (TiO$_2$) nanoplates and titania nanoparticles were synthesized by sol gel method. The characterization of the materials revealed the mesoporous nanoplate-like structure for Sr$^{2+}$ doped TiO$_2$. The thickness and edge length of Sr$^{2+}$ doped TiO$_2$ nanoplates were found to be 12 nm and 25-75 nm, respectively. TiO$_2$ nanoparticles and Sr$^{2+}$ doped TiO$_2$ nanoplates showed higher surface area due to the presence of mesopores. The photocatalytic activity of TiO$_2$ nanoparticles and Sr$^{2+}$ doped TiO$_2$ nanoplates was evaluated using 2,4-dinitrophenol (DNP) as a model pollutant. The photocatalytic activity of Sr$^{2+}$ doped TiO$_2$ nanoplates was higher than both TiO$_2$ nanoparticles and commercial TiO$_2$. Sr$^{2+}$ doped TiO$_2$ nanoplates exhibited enhanced photocatalytic activity due to increases in the band gap energy and surface area [44].

M. Okutan et. al., had investigated alternating current (AC) conductivity and dielectric properties of the Co-doped TiO$_2$ were investigated. The temperature dependence of AC conductivity and the parameters, is reasonably well interpreted by the correlated barrier hopping (CBH) model. The activation energy (E), and the density of states at Fermi level, N(E_F) were determined. The dielectric constant decreases with frequency at low frequencies and increases at high frequencies [45].
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Y. Zhang et. al., had prepared four different sols of pure TiO$_2$, F doped TiO$_2$, Fe doped TiO$_2$, and F–Fe co-doped TiO$_2$ sols, by peroxidation at low temperature. The crystal structure, morphology, light adsorption, and photocatalytic properties of the pure and doped TiO$_2$ were examined by X-ray diffraction, transmission electron microscopy, and ultraviolet–visible spectrophotometry. The relationship between the average size, crystal type, range of visible light absorption, and photocatalytic activity and content and type of doped ions were investigated. The results showed that the average size of the F–Fe co-doped TiO$_2$ composed of both the anatase and rutile phases was the same as that of pure TiO$_2$. Furthermore, the visible light photocatalytic activity of the F–Fe co-doped TiO$_2$ was significantly improved over pure TiO$_2$, F-doped TiO$_2$, and Fe-doped TiO$_2$ due to the large red shift in the light adsorption edge [46].

A. P. Caricato et. al., had reported titanium dioxide (TiO$_2$) nanorods in the brookite phase, with average dimensions of 3–4 nm × 20–50 nm, were synthesized by a wet-chemical aminolysis route and used as precursors for thin films that were deposited by the matrix-assisted pulsed laser evaporation (MAPLE) technique. A nanorod solution in toluene (0.016 wt% TiO$_2$) was frozen at the liquid-nitrogen temperature and irradiated with a KrF excimer laser at a fluence of 350 mJ/cm$^2$ and repetition rate of 10 Hz. Single-crystal Si wafers, silica slides, carbon-coated Cu grids and alumina inter-digitated slabs were used as substrates to allow performing different characterizations. Films fabricated with 6000 laser pulses had an average thickness of ∼150 nm, and a complete coverage of the selected substrate as achieved. High-resolution scanning and transmission electron microscopy investigations evidenced the formation of quite rough films incorporating individually distinguishable TiO$_2$ nanorods and crystalline spherical nanoparticles with an average diameter of ∼13 nm. Spectrophotometric analysis showed high transparency through the UV-Vis spectral range. Promising resistive sensing responses to 1 ppm of NO$_2$ mixed in dry air were obtained [47].
D. Dubal et. al., had prepared nanocrystalline TiO$_2$ thin films have been successfully synthesized by controlled precipitation route. These films are further annealed at 623 K for 2 h. The change in structural, morphological, optical and wettability properties are studied by means of X-ray diffraction (XRD), Fourier transform infrared spectrum (FTIR), scanning electron microscopy (SEM), optical absorption, and contact angle measurement. From the XRD pattern it is clear that the as-grown TiO$_2$ films are amorphous in nature which becomes polycrystalline after annealing. The FTIR study reveals the formation of TiO$_2$ compound. Scanning electron micrographs shows that the as-grown TiO$_2$ film consists of agglomerated nanograins well covered to the substrate surface which gets converted into vertical nano-rods after annealing. As-deposited and annealed TiO$_2$ films showed hydrophilic behaviour as water contact angles were 24$^0$ and 32$^0$, respectively. The optical absorption study reveals the small red shift due to annealing and attributed to grain size. The annealed TiO$_2$ film showed conversion efficiency of 0.037% in photo electrochemical cell with 1 M NaOH electrolyte [48].

E. Gyorgy et. al., has studied the characterization and CO gas sensing properties of pure and doped TiO$_2$ with Pt thin films deposited on glass substrates by (PLD) technique, at laser energy densities of (1 J/cm$^2$). Pure TiO$_2$ thin film were reported to be less sensitive to CO gas as compared to the TiO$_2$ thin film doped with 4% Pt [49].

S. Yoshiakiand et. al., had prepared TiO$_2$ films on different substrate at different temperatures (100-400ºC) by using KrF Excimer laser (Å =532nm, t=3.5ns) at about 1 J/cm$^2$ laser density. They found that all films showed (101) anatase phase at the optimized conditions. Photoluminescence (PL) results indicated that the thin films fabricated at the optimized conditions showed the intense near band PL emissions [50].
T. Nambara had studied the crystalline rutile type titanium dioxide (TiO$_2$) thin films which were prepared by (PLD) at substrate temperature 850 °C. The optical properties of the present rutile films were different from that of single crystal TiO$_2$. UV-Vis spectra of PLD films showed a blue shift. The value of the gap was 3.30 eV, which was shifted from 3.02 eV as the bulk value. They considered quantum size and strain effects of PLD-TiO$_2$ crystalline. [51].

1.4 Importance of the work

In the present work, TiO$_2$ nanocrystalline powder prepared by sol-gel and solid state reaction method were studied for their structural, optical and electrical properties. The prepared nanoparticles were annealed at different temperature. We also report on thin films of TiO$_2$ prepared by sol-gel spin coating and e-beam evaporation method and the structural, optical and electrical behaviour of the prepared films annealed at different temperature. Gas sensitivity, wettability and self-cleaning activity of the prepared films are also reported. Some reports are available of this type work with doping of noble metal but no one has reported on with doping of rare earth and transition metal particular for strontium and cobalt. The work is going on DSSC behaviour of the TiO$_2$ with different doping concentration of Cobalt.

1.5 Specific aims of this dissertation

The aim of the present work is to:

(1) Reveal specific properties of pure TiO$_2$ nanostructured powder and thin film prepared by different synthesis method.


(3) Study the structural, optical and electrical properties of the pure TiO$_2$, Strontium doped TiO$_2$ and Cobalt doped TiO$_2$ nanocrystalline material.
(4) Study the gas sensitivity, wettability and self-cleaning properties of the thin films of pure and Sr-doped TiO$_2$. 
References