1 Introduction

Semiconductor nanoparticles have attracted a great deal of attention due to their potential applications in solar energy conversion (1), dielectrics (2) and heterogeneous photocatalysis (3). Although, several semiconductor nanoparticles such as ZnO, SnO2, WO3 and Fe2O3 have been used for the above-mentioned applications, TiO2 is believed to be the most promising currently known material, due to its excellent optical properties of a high refractive index leading to a high hiding power and whiteness, high chemical durability, strong oxidizing power, nontoxicity, low cost and availability (4-8). However, it has been found that the process and processing conditions under which the TiO2 nanoparticles are synthesized lead to significant variations in their structure, stoichiometry, particle size, optical and electronic properties, and hence, photoactivity (9).

2 Experimental

TiOSO4. 5H2O (Nacalai tesque Co.Ltd) was dissolved in water at room temperature and then 30% H2O2 was added in to this solution. A yellow colored solution was immediately obtained, indicating the formation of peroxo complex of Titanium solution (11). This new method is simple, inexpensive, environmentally benign and promising to be used for the preparation of large quantity of TiO2 nanoparticles.
after keeping at room temperature for few hours. Then
the gel was separated by centrifugation at a rotation
speed of 10,000 rpm, washed with double distilled
water and then dried over night in the oven. Finally, the
dried titanium-peroxo complex was annealed in air at
different temperatures ranging from 200 to 550°C for 1
hr to obtain TiO₂. The FT-IR spectra of the as-prepared
and heat-treated samples were measured by the KBr
pellet method (Jasco FT/IR 610). The powder was ana-
lyzed by an X-ray diffractometer (RIGAKU RAD-2R)
with Cu Kα radiation. The average sizes of anatase
crystallites were calculated from the full width at half
maximum (FWHM) of diffraction peaks from the (101)
plane of anatase, using scherrer’s equation. The particle
shape was observed by using field emission-SEM (FE-
SEM HITACHI S-4300SE/N).

3 Results and Discussion

Figure 1 shows the FT-IR spectra of the as-prepared
and sintered titanium dioxide powders. The absorption
from 3000 to 3600 cm⁻¹ in Fig. 1a can be assigned to
the stretching vibration of the hydrogen-bonded OH
groups of the adsorbed water and the titanium hydrox-
ide. The absorption peak at around 1620 cm⁻¹ is may be
due to the bending vibration of coordinated H₂O as well
as from the Ti-OH. The absorption peak at around
900cm⁻¹ in Fig. 1a can be assigned to characteristic
stretching vibration of peroxo groups; hence the shoul-
der observed at around 690 cm⁻¹ may have been due to
the vibration of the Ti-O-O bond in the titanium peroxo
gel (13,14). It is believed that Ti⁴⁺ ions and H₂O₂ inter-
act strongly and thereby it forms a Ti-peroxy compound
(15, 16). The above results indicate the presence of Ti-
O bonds, peroxo groups and OH groups in the as-pre-
pared powder. The sample, which is annealed at 200°C,
shows that the shoulder assigned to peroxo groups
became weak and it reveals the decomposition of per-
oxo group by thermal annealing. The peaks attributed
to the adsorbed water almost disappeared but the vibration
of hydroxyl groups still can be seen at about 3400 cm⁻¹,
which was not detected after annealing at 300°C. The
powder samples annealed at more than 300°C do not
show the peaks, which are corresponds to the peroxo
group and adsorbed water. Therefore it is concluded
that the peroxo group was completely decomposed due
to the heat-treatment.

The X-ray diffraction (XRD) of the TiO₂ powder
obtained by annealing the Ti-oxy-hydroxide at various
temperatures is shown in Fig. 2. Pattern (a), (b), (c) and
d (d) in Fig. 2 shows the characteristic peaks of the heat-
treated samples at 200, 300, 450 and 550°C, respective-
ly for 1 hr. The powder annealed at 200°C was amor-
phous, while the powder annealed at 300°C and above
was crystalline. The broad peaks in pattern (b) indicate
the possibility of either the low degree of crystallinity
of TiO₂ or the ultrafine particle size of the powder. Pat-
terns (c) and (d) are almost the same except the more
sharpness of the peaks in pattern (d), which indicates
the increase of particle size due to the effect of sinter-
ing.

Further, in order to investigate the effect of sintering
temperature on the crystallite growth, the crystallite size
was calculated using the Scherrer’s equation. Indeed, it
has been found that there was an increase in crystallite
size with increase of sintering temperature. A crystallite
size of 28, 39 and 50 nm were determined from the FWHM of the (101) peak of the anatase for the heat-treated at 300, 450 and 550°C respectively. The XRD analysis reveals that the heat-treatment at 200 and 300°C lead to the formation of amorphous and nanocrystalline TiO₂ respectively. It is interesting to note that the onset temperature of crystallization in the present study is much lower as compared to the sol-gel method (12). Organic compounds in sol prepared by the sol-gel method decompose during the heat-treatment and hinder aligned grain growth and densification. The low temperature (below 200°C) decomposition of peroxo group (Fig. 1) and the absence of organic compound could be the reasons for the low temperature crystallization of TiO₂ synthesized by this new method. On the other hand, it can be assumed that the low onset temperature of crystallization be due to the synergistic effect between the decomposition of peroxo group and crystallization.

Figure 3 presents the typical photomicrographs of the as-prepared and sintered titanium dioxide powders. SEM Pictures (a), (b), (c) and (d) in Fig. 3 shows the surface morphology of the as-prepared and heat-treated samples at 300, 450 and 550°C, respectively for 1 hr in air. It reveals the morphological homogeneity with the grain size falling mostly in submicron range. Careful examination of SEM pictures clearly evinces that each grain is made up with an aggregation of (nanometer size) very small crystallites. There is a significant differences can be seen when comparing the microphotographs (Fig. 3a-d). The as-prepared and low temperature sintered samples (Fig. 3a and b) consist of non-porous aggregates, which are made of small crystallites. However, when the annealing temperature increases to higher temperature (i.e from 300 to 450°C or higher), the crystallite size and the porosity are increased (Fig. 3c and d). The increase of crystallite size may be due to the effect of heat-treatment. The estimated crystallite sizes of the sintered samples also support the crystallite growth of the samples by thermal annealing.

In order to investigate the composition of the prepared TiO₂ powder, EDX analysis was carried out for the powder samples heated at 200, 300, 450 and 550°C respectively. The EDX analysis shows that all the samples contain only titanium and oxygen elements and there is no impurity in the samples.

TiO₂ nanoparticles prepared by this new method have considerable high surface area, indicates the possibility of using them for solar cell, catalysis, and electronic devices. Further investigations have to be carried out to

![SEM Photographs of the (a) As-prepared Powder and Those after Annealed at Different Temperatures (b) 300 (d) 450 and (d) 550°C for 1 hr in Air.](image_url)
understand in more detail the formation mechanism, thermal stability, catalytic property of the present TiO$_2$ nanostructure, and the interesting interconnectivity among the nanocrystallites.

4 Conclusions

A simple and inexpensive technique has been established to prepare amorphous and nanocrystalline TiO$_2$ powder from aqueous solution in room temperature. The particle size of the TiO$_2$ nanoparticles increased from 28 to 50 nm with an increase in the sintering temperature from 300 to 550°C. It is expected that the present method can be easily extended to the similar nanostructures of other oxide materials, which is underway.

References