Investigation of Physico-Chemical Properties of TiO$_2$ Nanorod by Direct Sol Filling and Heating Sol-Gel Template Method

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Abstract: TiO$_2$ nanostructured material has been used in various industrial applications. The characteristics which played vital role to improve the efficiency of the TiO$_2$ nano materials used for the above mentioned applications. In the present work, preparation of TiO$_2$ nanorods by novel direct sol filling and heating sol-gel template method using titanium (IV) isopropoxide as a precursor is presented. After, the obtained TiO$_2$ nanorods are treated by direct current excited oxygen plasma as a function of power level. The structure, morphology and chemical state of the TiO$_2$ nanorods are analyzed by X-ray diffraction (XRD), scanning Electron Microscope (SEM), transmission electron microscopy (TEM) and X-ray photo electron spectroscopy (XPS). It was found that the structure of the both as prepared and plasma treated TiO$_2$ nanorod exhibited the anatase phase and the size was found to be 10 nm. XPS results clearly revealed that the as prepared TiO$_2$ nanorod contained 99% of Ti$^{4+}$ oxidation state which further converted to Ti$^{3+}$ state by oxygen plasma treatment. Hence the phase, size and changes in chemical state induced by the plasma treatment can facilitate to enhance the efficacy of the TiO$_2$ nanorods which suitable for different practical applications.

Introduction

In the recent years, physical and chemical properties of titanium oxide (TiO$_2$) nanostructured materials have great potential for its use in various industrial technology such as solar cells, electrochemical sensing and photocatalysis [1-3]. The functional properties of TiO$_2$ nanorods are strongly influenced by morphology, phase, size, dimensional, structure and heat treatment conditions [4-6]. Recent years, one dimensional (1D) TiO$_2$ structures like nano wires or nano rods, nano flowers, nano tubes [4,5] and other hierarchical structures have played vital role in photocatalysis, dye sensitized solar cells and other applications. Recently, TiO$_2$ nanostructured material have been synthesized by various methods such as chemical vapor deposition (CVD) [7], solvothermal [8-10], vapor-liquid-solid (VLS) [11], hydro thermal [12,13], surface directed and the sol gel filling templates and heating method [14-21]. Among them template assisted synthesis is one of the most effective and promising method to synthesis nanoscale materials in nanotechnology because of its uniform pore size, relatively low cost and mode of preparation has been found as a productive way for the analysis of one dimensional structures of TiO$_2$.

In this present work, TiO$_2$ nanorods are synthesized by direct sol gel filling and heating template method. Consequently the obtained TiO$_2$ nano rods are treated by direct current excited oxygen plasma. The phase, morphology and chemical composition of both as prepared and plasma treated TiO$_2$ nanorods are analyzed by X-ray diffraction (XRD), scanning Electron Microscope (SEM), transmission electron microscopy (TEM) and X-ray photo electron spectroscopy (XPS).

Experimental

Chemicals

The commercial anodic alumina membranes (AAM) purchased from Whatman Company were used as the template materials. Other chemicals titanium tetra-isopropoxide (TTIP $\geq 97 \%$, Alfa Aesar), acetylacetone (AcAc: $\geq 98 \%$, Merck), ethyl alcohol (EtOH: 99.9 % purity), Sodium hydroxide pellets are procured from Merck, India. All the chemicals used are analytical grade.

Synthesis of TiO$_2$ sol and nano rods
The TiO$_2$-sol was prepared by mixing titanium (IV) isopropoxide (TTIP), AcAc, H$_2$O and ethanol in the molar ratio of 1:1:3:20 at ambient temperature. Initially, acetylacetone was added dropwise into ethanol-water mixture, followed with titanium (IV) isopropoxide and ethanol solution into the above mentioned mixture. Further, mixture was allowed to stir for approximately 2 hrs, resulting the TiO$_2$ sol (Fig. 1). Furthermore, the obtained solution was injected several times through syringe into anodic alumina templates (Whatman Anodisc 47) with the average pore radius of 10 nm (Fig. 2). The templates were dried for 24 hrs at room temperature and heated at 100 °C for 8 hrs to remove the residual water and alcohol (Fig. 1).

In order to obtain anatase phase TiO$_2$ nanorod, samples were consequently calcined up to 400 °C and this temperature is maintained for about 2 hrs and after that it was cooled to room temperature naturally. The alumina templates were further dissolved by NaOH solution to obtain fine TiO$_2$ nanorods. Finally the samples were centrifuged using C-854-4 clinical centrifuge machine and washed by double distilled water several times for the removal of sodium hydroxide present along with TiO$_2$ nano rods.

**Oxygen plasma treatment of TiO$_2$ nanorod**

The obtained TiO$_2$ nanorods was further treated by oxygen plasma treatment using Glow discharge plasma processing reactor. It consists of parallel electrodes and mass flow controllers (MFC) for control the flow of gas into the chamber, substrate holder between the electrodes, prani gauage for measure the pressure inside the vacuum chamber and rotary pump.

![Fig. 2 SEM images of the AAM templates](image)

Intially, prepared TiO$_2$ nanorods was taken in the crucible and placed on the substrate holder. The chamber was air tightened and evacuated at the pressure level of $10^{-3}$ mbar by rotary vacuum pump. After that the oxygen gas is allowed to pass with the flow rate of 20 sccm within the chamber and the pressure inside the chamber was maintained at 0.2 mbar. DC potential was applied between the two electrodes and the same was adjusted until glow discharge is created between the electrodes. Finally, the TiO$_2$ nanorods was further treated by obtained oxygen plasma at a fixed discharge potential and treatment time of 500 V and 10 min.

![Fig. 3 SEM image of the TiO$_2$ nanorod arrays](image)

**3. Results and Discussion**

Fig. 3 shows the cluster of nanorod arrays with uniform diameter of 10 nm and the same was confirmed with the obtained nanorod samples depend on the choosed AAM templates. Hence, size of TiO$_2$ nanorods were dependent on pore size of the AAM templates. Simialrly the TEM images also showed (fig. 4) the average diameter of the nano rod was 10 nm which highly agreed with the results of SEM.
The XRD pattern (Fig. 5) of the synthesized TiO$_2$ nanorods exhibits that the strong 2θ peaks at 25.15°, 37.90° and 54.02°, which may be attribute to the 101, 004, 105 crystal plane of anatase TiO$_2$ nano rods.

Furthermore, chemical states of the components of the TiO$_2$ nanorods were analyzed using XPS. Fig. 6 shows the survey scan spectra of untreated and plasma treated TiO$_2$ nanorods. It is clearly show that the major components of untreated TiO$_2$ nanorod was C1s, O1s and Ti2p. After the plasma treatment the concentrartion of O1s and Ti2p increased significantly whereas the component C1s decreased, which may be due to formation of oxygen containing polar functional groups which are incorporated in the TiO$_2$ nanorods. The above chemical changes in the TiO$_2$ nanorods have greater potential in influencing efficiency of the TiO$_2$ nano materials, which can be utilized in various practical applications.

**Summary**

In the present study, TiO$_2$ nanorods consisting of pure anatase phase have successfully prepared by direct sol filling and heating sol-gel template route using titanium (IV) isopropoxide as a precursor. It was found that the size of nanorods strongly depends on the pore size of the template and XRD analysis confirmed that the prepared TiO$_2$ nanorod exhibits anatase structure. The diameter of the synthesized nanorod was found as 10 nm, as confirmed by SEM and TEM analyses. XPS study reveals that the higher concentration of O1s and Ti2p was incorporated on TiO$_2$ nanorods by oxygen plasma treatment. Finally we concluded that the plasma treatment is not affecting the any morphological change of the TiO$_2$ nanorods. However it produces the significant chemical changes. The chemical changes induced by the plasma treatment highly improve the working efficiency of the TiO$_2$ nanorods.

**References**


