Investigation on the Photocatalytic Properties of TiO_2 NTs Powders Prepared via Rapid Breakdown Anodization for Methylene Blue Degradation

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Abstract: In this paper, preparation of titania nanotubes (TiO_2 NTs)through rapid breakdown anodization (RBA) is described. Bundles of TiO_2 NTs were formed as observed in the Scanning Electron Microscope (SEM) at an applied potential of 20 V. Elemental analysis through Electron Diffraction X-ray Analysis (EDAX) confirmed the presence of only Ti and O peaks and revealed the absence of any impurities in the formation process. The anatase phase of TiO_2 NTs was established using X-ray Diffraction (XRD). Characteristic peaks of TiO_2 were noticed in the Fourier Transform Infra-red Spectroscopy (FT-IR). The TiO_2 NTs powder was found to be stable in anatase form till 500 ^{o}C using Thermogravimetry and Differential Thermal Analysis (TGDTA). This TiO_2 NTs powder sample was then subjected to investigate the photocatalytic activity through the photo-degradation of methylene blue (MB). The percentage of photo-degradation was examined using UV-Visible spectrophotometer (UV-Vis).

Keywords: Titanium dioxide, Nanotubes, Rapid breakdown Anodization, Photocatalysis

Introduction

Titanium dioxide (TiO_2) has a wide range of engineering applications with direct relevance to the society. In particular, the nanostructured semiconductor TiO_2 is of special research interest due to its possibility to be used in photocatalysis [1], solar energy conversion [2] and gas sensing applications [3]. There are various forms of TiO_2, such as nanorods [4], nanofilms [5] and nanotubes [6]. Among these, nanotubes are observed to be superior in terms of high-aspect-ratio, large surface area (both internal and external) [7] and excellent 1D charge transport properties [8]. Moreover, the architecture is exceptionally suitable for energy and sensing applications. TiO_2 NTs can be prepared using several techniques like sol-gel [9], hydrothermal [10] and metal-organic chemical vapor deposition [11], electrochemical anodization [12] and rapid breakdown anodization techniques (RBA) [3]. However, of all these methods, RBA stands out due to its easy handling, quality of NTs powder and cost effectiveness. Moreover, it is flexible enough to adapt to harsh conditions like high humidity and can even be used in the presence of several organic contaminants [13]. Therefore, TiO_2 NTs powder is established to possess better physic-chemical properties in the desired architecture.

The present work deals with the preparation of TiO_2 NTs powder through novel RBA method. The experimental condition for the formation of TiO_2 NTs powder with preferred morphology is optimized, analyzed and confirmed using FESEM. Thus prepared TiO_2 NTs were then subjected to elemental and structural analyses employing EDAX and XRD, respectively. Since metal oxides have characteristic infra-red induced electronic vibrations, the NTs powders were tested for their feature peaks. The thermal stability of the TiO_2 NTs was investigated using TG-DTA technique. Finally, the as-prepared TiO_2 NTs powder was tested for its photocatalytic efficiency by photo-degrading methylene blue dye.

Experimental

Titanium foil (1 × 25 × 25 mm^3) was initially degreased and cleaned using isopropanol, acetone and deionized water. Thereafter, it was dried under natural conditions. Ti foil and Platinum mesh (25 × 25 mm^2) were employed as the anode and the cathode, respectively in a two-electrode electrochemical cell in 0.3 M NaCl solution as the electrolyte. A potential of 20 V was applied using Keithley SourceMeter 2400 until the Ti foil completely transformed into TiO_2 NTs powder[14]. Thus obtained powder was centrifuged, collected and annealed at 450 ^{o}C for a period of 5 h to crystallize the NTs. The photocatalytic property of the TiO_2 NTs powder was investigated in a dark room under UV irradiation (365 nm). Different samples at various time intervals were collected to examine the percentage degradation of methylene blue and were studied using UV-Vis spectrometer.

Results and discussions

The SEM micrographs of TiO_2 NTs powder prepared via RBA are illustrated in Fig. 1. The images reveal that the NTs powder is obtained as bundles and are of almost uniform length. However, the thickness of the bundle varied largely. The length of each TiO_2 NTs bundle is around 15 – 20 µm and the diameter of each tube is observed to be less than 100 nm. In addition, the uniformity of the tubular structures is appreciably substantial over the entire region under consideration. The parameters of the TiO2 NTs prepared in this work are found to be on par with the reported works [15]. The elemental composition investigation indicates that the obtained NTs are pure without any external impurities neither during the anodization process nor while separating the powders from the electrolyte. The EDAX spectrum [Fig 1b inset] specifies the exclusive presence of Ti and O peaks as expected.

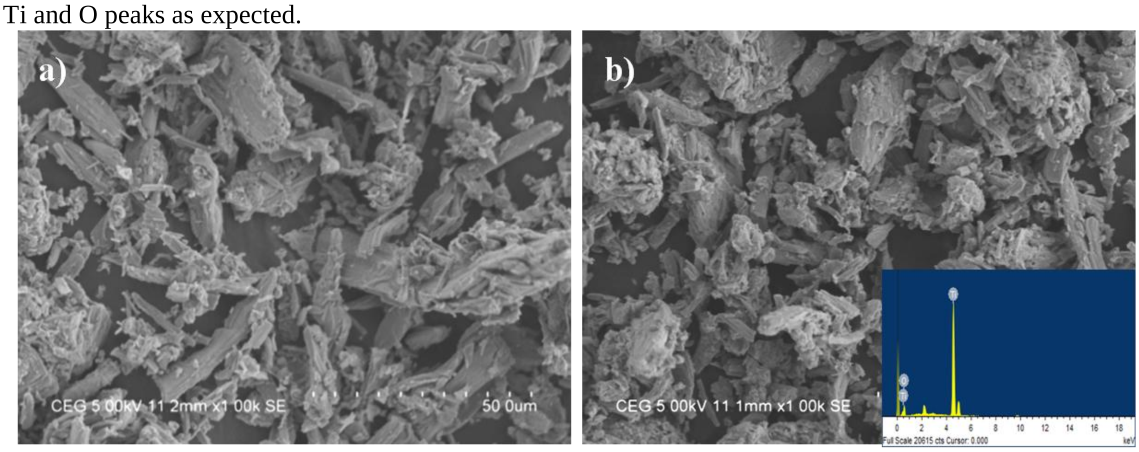

Fig. 1 a,b) SEM images of TiO_2 NTs powder and b inset) EDAX spectrum of TiO_2 NTs

The powder X-ray diffraction of the TiO_2 NTs is shown in Fig. 2a. The XRD patternof all the samples displayed the peaks (101), (004), (200), (105), (211), (204) and (220) at the 2θ values 25.35, 37.84, 48.14, 53.97, 55.18, 62.81 and 70.45, respectively clearly reveals the pure anatase form of the TiO_2 NTs and is confirmed using the JCPDS No: 89-4921. The FT-IR spectrum [Fig. 2b] of the TiO_2 NTs provides information with characteristic dip peak around 600 cm^{-1}. The sharp peak at 1600 cm^{-1} is due to the presence of hydroxyl groups on the surface of the NTs [16]. The information is substantiated with the observation of a shoulder peak at 3500 cm^{-1} further implying the occurrence of a single form hydroxyl group. Fig. 2c, depicts the TG-DTA curve of TiO_2 NTs. The gradual weight loss in the TGA graph indicates the moisture is present in the system and is leisurely drawing out. On the other hand, DTA graph signifies a phase change of TiO_2 from anatase to rutile after 500 ^oC [17]. The information denotes that TiO_2 can be used in anatase phase only till 500 ^oC, after which the phase change will induce rutile phenomenon.

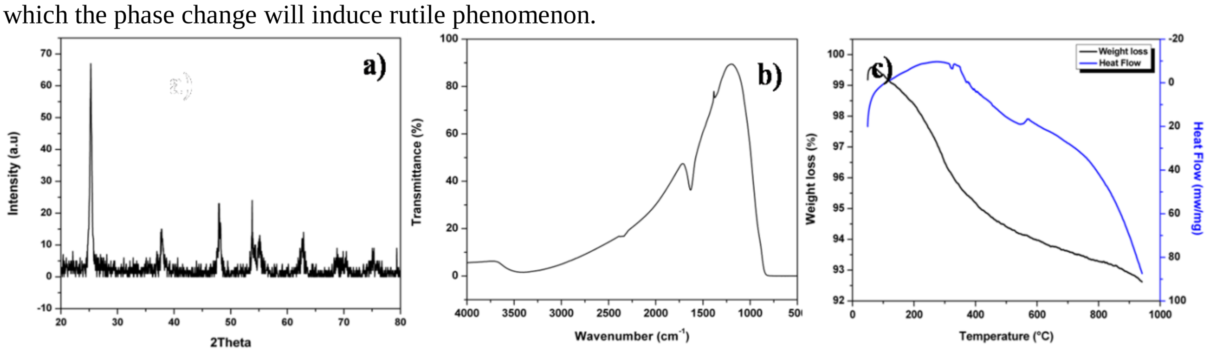

Fig. 2 a) XRD pattern,b) FT-IR spectrum and c) TG-DTA plot of TiO_2 NTs powder

The photocatalytic activity of TiO_2 NTs powder, a wide band gap semiconductor was explored by examining the MB degradation under UV light [18] as depicted in Fig. 3. The MB characteristic peak is observed around 663 nm [19], which upon UV irradiation with TiO_2 NTs photocatalyst gradually weakened. The degradation was observed to be slower with only 11% degradation after first 30 min. However, at the end of 210 min, the degradation was up to 70%. Notably, the photo-degradation is considered to be better as it is carried without the addition of any dopants or any external agents.

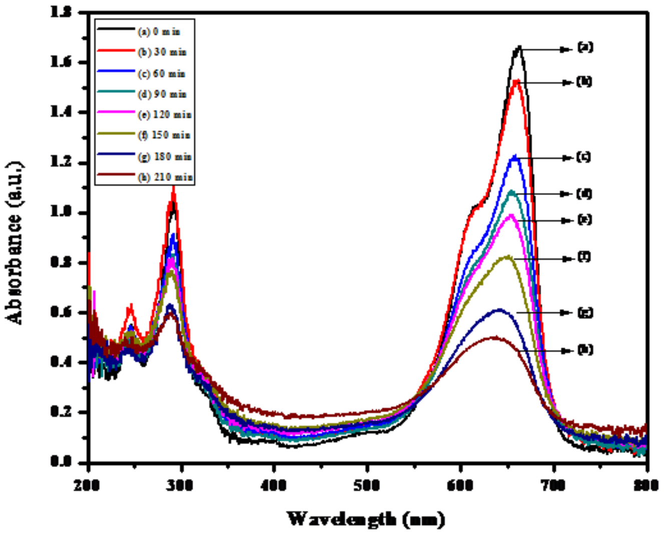

Fig. 4. Time dependent UV-Vis absorption spectra of methylene blue solution during UV light irradiation

Conclusion

In summary, TiO_2 NTs powder was prepared using novel RBA technique. FESEM and EDAX analyses showed that the TiO_2 NTs powder has been obtain as bundles and in pure form. XRD pattern confirmed the anatase phase, FT-IR indicated the presence of surface moisture and TG-DTA designated the usable temperature of the TiO_2 NTs. The photo-degradation studies using TiO_2 NTs powders as photocatalyst substantiated that the MB solution has degraded up to 70% degradation under UV light.

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