



Surface modification of titania aerogel films by oxygen plasma treatment for enhanced dye adsorption



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ABSTRACT

Titania aerogels were synthesized by sol–gel route followed by ambient pressure subcritical drying technique. The aerogels synthesized in the present work possess a maximum surface area of 252 m²/g. The pore size distribution is between 2 and 30 nm which confirms their mesoporosity. The oxygen plasma treatment on titania aerogel thin films improved the surface area up to 273 m²/g and produced additional hydrophilic groups on the surface. It is confirmed by BET surface area, XPS and thermal analysis in conjunction with dye adsorption studies. After plasma treatment the dye adsorption capacity was increased 2.5 times higher than that of untreated aerogel film. The increased surface area and the hydrophilic groups generated on the titania aerogel surface during plasma treatment are responsible for enhanced dye adsorption. The overall nanoporous morphology of titania aerogel is preserved after plasma treatment.

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1. Introduction

Mesoporous titanium dioxide has attracted much attention because of their interesting properties such as high surface area, tunable pore sizes, large pore volumes as well as their promising applications in photo catalysis and energy conversion [1,2]. The presence of mesopores greatly extends their potential application for adsorption, separation, sensing and biomedical fields [3,4]. The high surface area facilitates the attachment of bulky dye molecules and large pore volume assists the diffusion of electrolyte and reactants. Ordered mesoporous titania spheres with high surface area were synthesized using pluronic 123 as template and reported for photo catalysis and energy conversion [5]. Mesoporous titania is widely used as photoanode material in dye sensitized solar cell (DSSC) due to the fact that the mesopores (2–50 nm) are capable of encapsulating bulky dye molecules and permeation of electrolyte that cannot be accomplished using micropores (<2 nm) [6]. Mesoporous titania nanocrystals prepared by sol–gel method were employed as photoanodes in DSSC and high performance was attained [7,8].

Aerogels are one such fascinating mesoporous structure offering large internal surface area, wide pore size distribution, high optical transparency and low density [9]. These properties of aerogel compared to other nanostructures like nanospheres, nanorods and nanotubes

make them as potential candidates for photovoltaic applications [10]. Generally, titania aerogels are synthesized through sol–gel method followed by supercritical drying [11,12]. However, supercritical drying requires high temperature and pressure and also it creates hydrophobic surface which is redundant for catalytic and photovoltaic applications. In addition to supercritical drying, freeze drying and ambient pressure drying can be employed for drying of wet gels to preserve the aerogel network. Among the three drying techniques ambient pressure drying is technically simple and economically interesting for large scale synthesis of aerogels [13]. Therefore, we adopted ambient pressure subcritical drying technique in our process. In this technique, the pore liquid was effectively exchanged with another liquid having low surface tension without affecting the walls of the pores present in aerogel network. It is also reported that the surface area and pore size of the aerogels prepared with subcritical drying are comparable to that of supercritically dried aerogels [14]. Pradip et al. also reported that the aerogels prepared using ambient pressure drying exhibit high surface area and large pore volume [15].

The surface properties of mesoporous titania determines its specific application and strongly rely on the surface modification and also on the interactions with the environment [16]. The surface modification not only affects the interfacial energy but also has significant impact on the charge separation, transport, and recombination processes. For instance, TiCl₄ pretreatment enhances the adhesion of nanocrystalline layer and retards charge recombination processes [17,18]. Also, the surface hydroxyl groups and defects validate its potential use in DSSC.

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Because, the hydroxyl groups available on titania surface are responsible for chemisorption of photosensitizing dyes and the surface defects are responsible for recombination reactions at the electrode/electrolyte interface [19]. It is reported that structural modifications of titania with lanthanum oxide increase the surface acidity, surface area and anatase to rutile transformation temperature [20]. However, metal modification of titania nanopowder creates edge dislocations in the anatase crystal [21]. Various surface modification methods like chemical treatment, ozone treatment and plasma treatment have been attempted to alter the surface properties of materials [22]. Among the reported methods, oxygen plasma treatment is attractive for mesoporous titania surfaces as it can change only the surface without affecting the bulk properties. Moreover, it improves the Ti^{4+} states by reducing the sub-oxides along with the grafting of hydrophilic groups on the surface of titania [23]. Oxygen plasma treatment of ordered mesoporous titania nanotubes demonstrated that an increase in surface hydroxyl groups and thereby improved the amount of dye adsorption [24,25].

As far as titania aerogels are concerned, their synthesis and physical/chemical modification for specific applications are scanty in the literature. High surface area TiO_2 -Pt aerogel composite was prepared and used for photo catalytic hydrogen production [26]. SiO_2 - TiO_2 hybrid aerogel was employed as photoanode in DSSC and 9.4% conversion efficiency was achieved [27]. The effect of annealing temperature and pore size control on high surface area titania aerogel was studied and reported [28,29]. It is also reported that the surface acidic sites were uniformly distributed in titania-carbon composite aerogels [30]. Recently, chemical modification of titania aerogel surface was reported [31]. However, there are no reports available on the effect of plasma treatment on titania aerogel nanostructure. In this article, we report the synthesis of titania aerogel by sol-gel method followed by sub-critical drying and the effect of plasma treatment with excellent dye adsorption capacity. The present work demonstrates the effectiveness of plasma treatment on high surface area titania aerogel for increasing the dye adsorption capacity.

2. Experimental details

2.1. Materials

Titanium(IV) isopropoxide (TIP) was purchased from Sigma Aldrich. Glacial acetic acid, ammonia solution (25%), 2-propanol, and absolute ethanol (EtOH) were obtained from Merck chemicals. Deionized water obtained from Millipore filtration system was used in experiments.

2.2. Synthesis of titania aerogel

The titania aerogel was synthesized by sol-gel method followed by subcritical drying. The molar ratios of titanium isopropoxide, glacial acetic acid and deionized water was 1:10:350. The titania sol was prepared by adding titanium isopropoxide to glacial acetic acid and subjected to controlled hydrolysis with deionized water. The above solution was stirred vigorously for 1 h and the pH was adjusted to 5 using ammonia solution for gelation. The gels were transferred into deionized water and aged for 24 h at 50 °C. The aged gels were then solvent exchanged with 2-propanol at 50 °C to remove water from the aerogel network. The aerogel powder was then dried at room temperature and designated as $AG(H_2O)$. Another titania aerogel $AG(H_2O:EtOH)$ was prepared with the similar procedure using 1:1 mixture of H_2O and EtOH as solvent.

About 1 g of $AG(H_2O)$ was dispersed in 10 mL of ethanol and coated on glass slides using single vessel dip coater. The speed of the upward and downward movement was 2.5 mm/s and kept constant for all dipping. After 1 min dipping the aerogel layer was dried at room temperature for 5 min. After coating 5 layers the thin films were calcined at 350 °C for 1 h.

2.3. Plasma treatment

The titania aerogel thin films were placed inside the plasma chamber and oxygen gas was purged with a pressure of 1.5×10^{-2} mbar. The inductively coupled oxygen plasma was generated by passing a radio-frequency power of 50 W. Three titania aerogel thin films were exposed to oxygen plasma separately for 5, 10 and 15 min.

2.4. Characterization

The powder XRD pattern of the titania aerogels were recorded in a PANalytical X'Pert-PRO diffractometer between 10 and 80° region of 2θ using $CuK\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). BET surface area measurements were performed by nitrogen adsorption at 77 K using a Micromeritics Tri-Star II 3020 analyzer. Before the measurement, the samples were pretreated under the flow of N_2 gas for 3 h at 200 °C. The pore size distribution was obtained from the desorption branches of isotherms using the Barrett-Joyner-Halenda (BJH) method. The morphology of titania aerogel powder and coated samples was analyzed using a field emission scanning electron microscope (FESEM-SUPRA55, CARL ZEISS). The effect of plasma treatment on titania aerogel surface was determined by thermogravimetric analysis (TGA) and dye adsorption studies. For TGA, plasma treated and untreated titania aerogel thin films were kept in humidified chamber for 48 h and the weight loss due to water desorption was calculated. X-ray photo electron Spectroscopy (XPS) analysis of plasma treated and untreated aerogel films were carried out by SPECS-GmbH spectrometer with Phoibos-100 MCD energy analyzer at pass energy of 40 eV under ultra-high vacuum (5×10^{-10} mbar). To study dye adsorption behavior, the samples were dipped in to a 0.3 mM Eosin-Y dye solution for 24 h. Amount of dye adsorption on the coated sample was quantified by desorbing the adsorbed dye in to 0.1 M, 1:1 ethanol water solution of NaOH. The absorbance spectrum of the desorbed dye solution was recorded using a Shimadzu-2600 UV-Vis spectrophotometer. The ATR-FTIR spectrum was recorded using JASCO FTIR spectrometer with a resolution of 4 cm^{-1} .

3. Results and discussion

X-ray diffraction was employed to investigate the crystalline phase of the titania aerogels. The observed XRD patterns of $AG(H_2O)$ and $AG(H_2O:EtOH)$ are presented in Fig. 1. The diffraction peaks observed at 2θ values of 25.3, 38, 48 and 54° in both aerogels indicate that titania preferentially crystallizes in anatase phase (JCPDS No: 21-1272). The

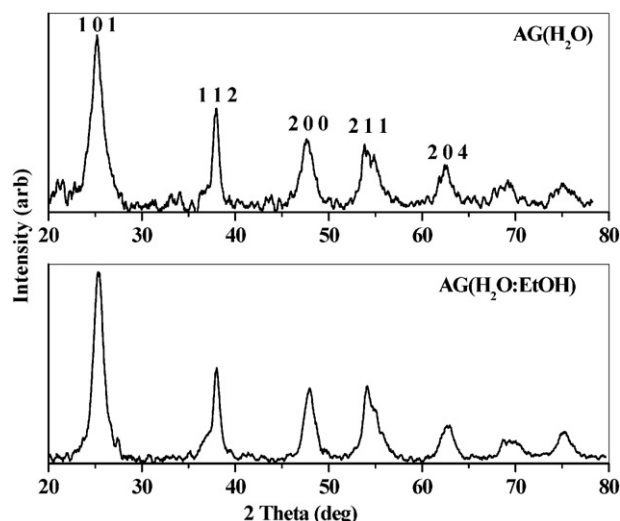


Fig. 1. XRD patterns of titania aerogels $AG(H_2O)$ and $AG(H_2O:EtOH)$.

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