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Effect of Hydroxy Propyl Cellulose, Polyethylene Glycol, Carboxy Methyl Cellulose and Polyvinyl Pyrrolidone on the Microstructure and Photocatalytic Activity of Nd-TiO_2/SiO_2 Films under Visible Light Irradiation

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Nd-TiO_2/SiO_2 films were prepared separately by the sol-gel method with the addition of polyethylene glycol (PEG 2000), hydroxy propyl cellulose, carboxy methyl cellulose and polyvinyl pyrrolidone as dispersions. The porous Nd-TiO_2/SiO_2 was obtained after heat treatment for 2 h at 500 ºC in air, with the surface area up to 331.76 $m^2 g^{-1}$, which measured using the Brunauer- Emmett-Teller method. Scanning electron microscopy showed that the particle size of Nd-TiO_2/SiO_2 with hydroxy propyl cellulose is smaller than the others and the microstructure of the film became loose with the addition of carboxy methyl cellulose. The influence of dispersions on the phase transformation of Nd-TiO_2/SiO_2 from amorphous to anatase was investigated by using X-ray diffraction. The sample structures were characterized by infrared spectroscopy. Subsequently, the photocatalytic activity of Nd-TiO_2/SiO_2 film under visible light irradiation would be enhanced by polyvinyl pyrrolidone, carboxy methyl cellulose and polyethylene glycol as dispersions.

Key Words: Nanocomposite, Photocatalysis, Self-cleaning, Sol-gel, Dispersion

INTRODUCTION

In recent years Titanium dioxide (TiO_2) with an energy band gap of 3.2 eV[1] has received increasing attention as a photocatalyst due partly to large-scale commercialization of self-cleaning glazing products[2]. Titanium dioxide, particularly as thin films, shows much potential for various applications, such as: photocatalytic devices[3,4], electrochromic properties[5], gas sensors[6], interference filters and antireflection coatings[7], dielectrics in optoelectronic and electronic devices[8].

The amorphous form of TiO_2 is known to have no photocatalytic activity while, the anatase form of titanium dioxide is active. Rutile form seems to present a weaker photocatalytic activity due to its smaller band gap width. Though some results, suggests that rutile particles present a larger pore size and a better resistance[9] and that anatase/ rutile interface may be an active site for photocatalytic activity[10,11].

It is generally recognize that anatase films with a lower crystal size display a higher photocatalytic activity, which can usually be achieved by varying thermal treatment or by addition of SiO_2[12-15]. On the other hand, by mastering size and organization of the nanoparticles in colloidal suspensions, titania films with controlled porosity and surface area can be synthesized. These nanoparticles are usually prepared from the hydrolysis and condensation of titanium alkoxides in water[16].

Because the nanoparticles have a strong tendency to agglomerate, due to the van der waals interaction, electrostatic or steric stabilization is usually used to stabilize colloids by creating repulsions between the particles[17]. Electrostatic stabilization consists on the adsorption of ions on the surface of the particles with creation of the electric double layer, whereas steric stabilization can be achieved by the adsorption of large molecules such polymers forming a dense layer around the particles[18]. Coil dimensions of polymers are usually larger than the range over which attractions between colloidal particles are active. Particles coated by a polymer shell are considerably more stable against aggregation, because of a large decrease of their surface energy in comparison with bare particles[19].

Hybrid polymer- inorganic nanocomposite materials are promising for a variety of applications. Because of their unique electronic, optical and mechanical properties, they have attracted the particular attention of researchers and engineers in recent decades[20]. It was also found that the kind of polymer and molecular weight of the polymer used greatly influence the average size of the nano particles, as well as their size distribution and stability against aggregation[21].

In present work, hydroxy propyl cellulose, polyethylene glycol, carboxy methyl cellulose and polyvinyl pyrrolidone were introduced separately to prepare nanosized Nd-TiO_2/SiO_2 composite films by the sol-gel method.

EXPERIMENTAL

Titanium tetra isopropoxide (TTIP) and neodymium nitrate (both AR analytical grade, Merck chemical company) were used as titanium and neodymium sources for the preparation of the Nd-TiO_2 phtocatalysts. Polyethylene glycol, carboxy methyl cellulose, hydroxy propyl cellulose, polyvinyl pyrrolidone, HNO_3, SiO_2 colloid solution and absolute ethanol, were purchased from Merck chemical company and deionized water.

Preparation of samples: The preparation of sample solution is described in details elsewhere[22,23]. Briefly titanium tetra isopropoxide was dissolved in absolute ethanol. Then dispersion (Fig. 1) was added with molar ratio titanium tetra isopropoxide/ ethanol/dispersion = 1/125/4.5 × 10^{-3} gg^{-1}_{sol}. and stirring until complete dissolution (Table-1). Afterward another mixture of absolute ethanol, HNO_3, deionized water, $Nd(NO_3)_3$ and SiO_2 with molar ratio of ethanol/HNO_3/H_2O/$Nd(NO_3)_3$/SiO_2 = 43/0.2/1/0.002/0.30, added under vigorous stirring drop wise in to it. The obtained transparent colloidal suspension was stirred for 45 min and then left for 48 h until would be formed as a gel. The tiles were coated by dip-coating method, after pretreatment with fluoric acid. Finally, the porous nanocomposite films were obtained after heat treatment for 2 h at 500 °C in air.

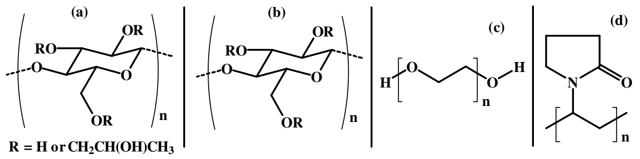


Fig. 1. a) HPC, (b) CMC, (c) PEG, (d) PVP

TABLE-1
FORMULATION OF SAMPLES

Sample	Amount of HPC in solution (gg^{-1}_{Sol})	Amount of CMC in solution (gg^{-1}_{Sol})	Amount of $PEG_{(l)}$ in solution (gg^{-1}_{Sol})	Amount of PVP in solution (gg^{-1}_{Sol})
S	-	-	-	-
HPCS	4.5 × 10^{-3}	-	-	-
CMCS	-	4.5 × 10^{-3}	-	-
PEGS	-	-	4.5 × 10^{-3}	-
PVPS	-	-	-	4.5 × 10^{-3}

Photocatalysis: The solution of methyl orange in deionized water with a concentration of 5 ppm was chosen as a subject for photodegradation. This solution was set in the vicinity of tiles under a 400 W high-pressure mercury vapour lamp (Osram). The spectrum of this lamp was shown in Fig. 2 (by AvaSpec 3648-UA-25-AF). As it shown, large amount of the radiation is located in visible region. The concentration changes of the methyl orange was determined by UV-VIS spectrophotometer. Methyl orange solution was set in the vicinity of tiles for 12 h in the darkness, for elimination of adsorption of the solution to the surface of the catalyst.

Characterizations: The phase composition of the powders was determined by a SCIFERT-3003 PTS X-ray diffractometer with CuK_α radiation. Powder XRD was used for the phase identification. The crystallite size can be determined by Scherrer equation[24-26]:

$$L = k\lambda/\beta \cos\theta$$

where L is the crystallite size, λ is wavelength of the CuK_α = 0.15418 nm, k is usually taken as 0.89, β is the line width at half-maximum height and θ is the angle of diffraction. FT-IR analysis was carried out for the samples by Bruker Tensor 27 FT-IR spectrometer. The microstructure of the film samples was observed with a SEM- XL30 scanning electron microscope. The specific surface area of powder was measured by Beijing JWGB Sci. Model JW-K. The photocatalytic properties of the films were investigated by measuring the optical absorption of a 5 ppm methyl orange solution by Varian UV-Vis spectrophotometer. The photocatalytic activities were studied at the absorption peak (465 nm) before and after the photodegradation.

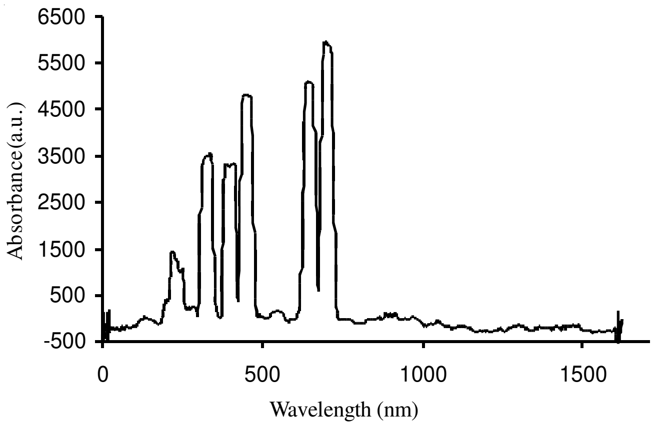


Fig. 2. Spectrum of high-pressure mercury vapour lamp

RESULTS AND DISCUSSION

Effect of hydroxy propyl cellulose, polyethylene glycol, carboxy methyl cellulose and poly vinyl pyrrolidone on the microstructure: FT-IR spectra of the sample films were shown in Fig. 3. The bands in 3700-3000 cm^{-1} region should be assigned to symmetric vibration of surface hydroxyl group[24,25,27,28]. A great amount of propanol appears during the hydrolysis of titanium tetra isopropoxide, which leads to the appearance of hydroxyl bands (3700-3100 cm^{-1}). The absorption bands around 1630 cm^{-1} have been assigned to H-O-H bending physically adsorbed water and hydroxyl group[27]. The band at 608 cm^{-1} corresponds to Ti-O-Ti stretching motion[24-29]. The absorption peak at 1081 cm^{-1} is the asymmetrical vibration of the Si-O-Si bond in the tetrahedral SiO_4 unit of the SiO_2 matrix[30,31]. The peak at 950 cm^{-1} has been ascribed to the vibration involving a SiO_4 tetrahedron bonded to a titanium atom through Si-O-Ti bonds[30,31]. Consequently, the presence of this band confirms the presence of Si-O-Ti linkages in the Nd-TiO_2/SiO_2 nano composite product. The peak at 467 cm^{-1} is due to the vibration modes of anatase. The peak at 467 cm^{-1} is due to the vibration modes of anatase skeletal O-Ti-O-Nd bonds[27,32,33]. The band at 1116 cm^{-1} can be assigned to asymmetric stretching vibration of the Ti-O band[24,25].

The SEM images have been presented in Fig. 4 from sample S to sample PVPS, Nd-TiO_2/SiO_2 particle size decreases and distribution becomes narrow. It was also found that the kind and molecular weight of the polymer used greatly influence the average size of the nanoparticles, as well as their size

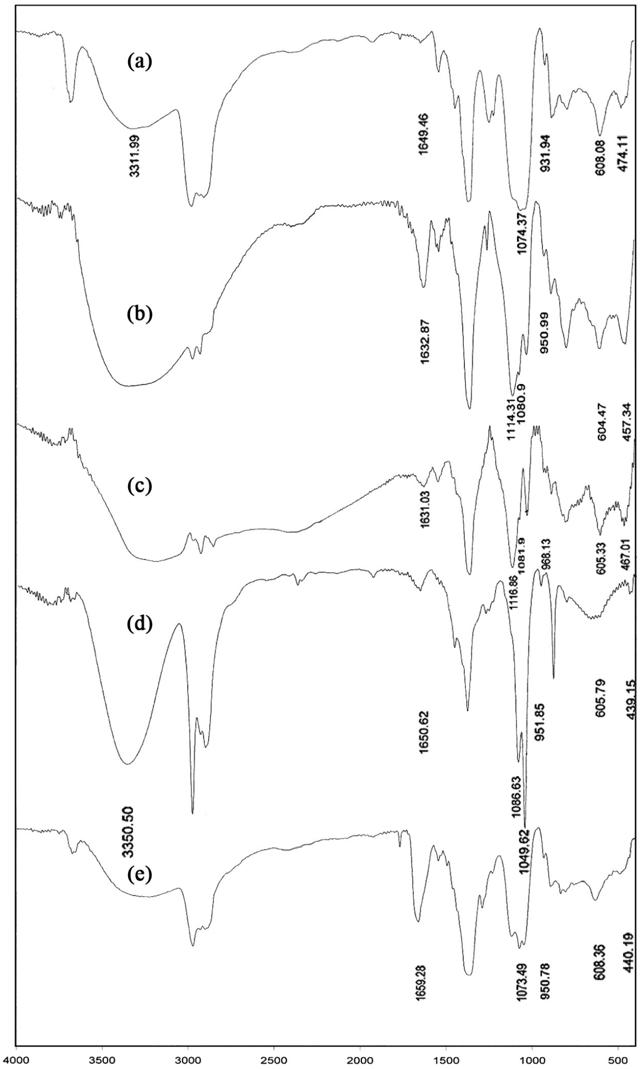


Fig. 3. FT-IR spectra of the samples: a) S, (b) HPCS, (c) CMCS, (d) PEGS, (e) PVPS

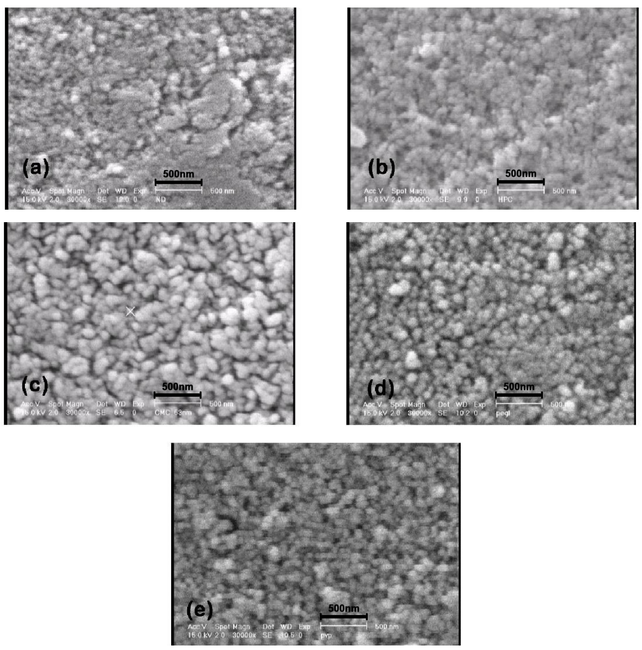
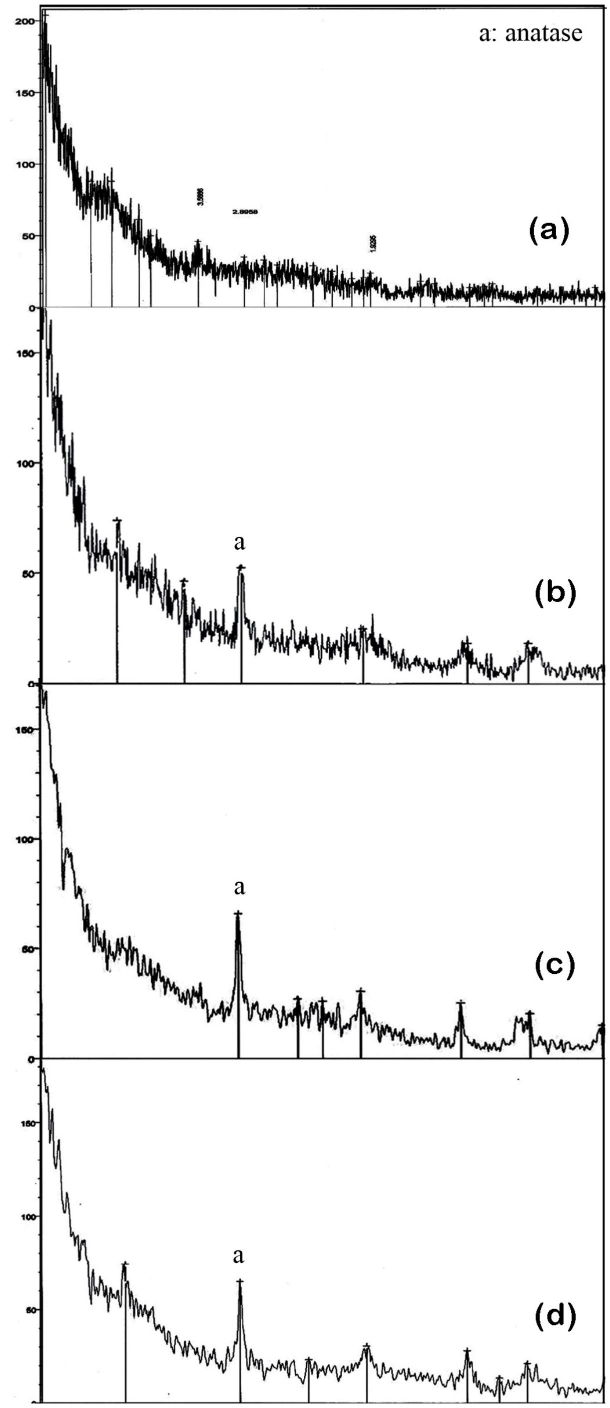


Fig. 4. SEM images for the sample films: a) S, (b) HPCS, (c) CMCS, (d) PEGS, (e) PVPS

distribution and stability against aggregation[25]. Accordingly, sample CMCS had the most uniform particle distribution with low agglomeration and porous microstructure.

Effects of hydroxy propyl cellulose, polyethylene glycol, carboxy methyl cellulose and poly vinyl pyrrolidone on the anatase phase: XRD pattern of five samples were shown in Fig. 5. The XRD measurements have revealed that the samples possess an anatase structure and evidence of rutile and mixed phases have not been observed. The samples have presented different proportions of anatase phase. Sample PVPS is fully crystalline and is only in the anatase form. It is in good shape for self-cleaning ability. It can be deduced that, the addition of dispersions, especially poly vinyl pyrrolidone, have facilitated the formation of anatase phase at a temperature 500 ºC.



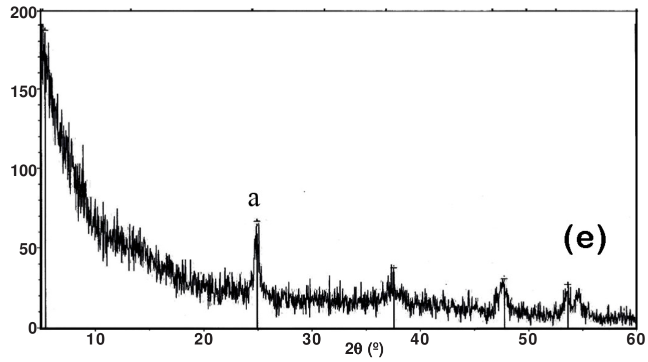


Fig. 5. XRD patterns of samples: a) S, (b) HPCS, (c) CMCS, (d) PEGS, (e) PVPS

According to the Scherre formula, the crystallite size of Nd-TiO_2/SiO_2, was listed in Table-2. The optimum crystallite size for anatase because of getting the highest possible photoactivity is in range 8-10 nm. This range provides the best photoactivity for sample films. Crystalline size for anatase in samples HPCS and CMCS are 11 and 11.6 nm respectively, which is suitable from photoactivity point of view.

TABLE-2
CHARACTERIZATION OF SAMPLES

Sample	Crystallite Size (nm)	Surface area ($m^2 g^{-1}$)	Decomposition time of methyl orange (h)
S	15.0	107.83	5.00
HPCS	11.0	331.76	4.50
CMCS	11.6	229.38	4.00
PEGS	14.1	267.87	4.00
PVPS	11.8	203.62	4.00

Effect of hydroxy propyl cellulose, polyethylene glycol, carboxy methyl cellulose and poly vinyl pyrrolidone on the self-cleaning ability: Table-2 shows the relationship between the kind of dispersion and photocatalytic activity of the samples in visible light region. The decomposition time of methyl orange in samples CMCS, PEGS and PVPS is similar to with each (4 h). But the longest time for decomposition of methyl orange is in sample S (5 h).

The values of surface area for sample films have been listed in the Table-2. As tabulated, the sample HPCS, has the highest amount of surface area, lowest particles sizes of Nd-TiO_2/SiO_2 and presents the long period for the decomposition of methyl orange. It might be inferred, when Nd-TiO_2/SiO_2 particle size decreases, the self-cleaning ability would be increased too, but there is a limitation for the decrease of particle sizes. If particle size decreases under this limited size, self-cleaning ability would be lowered.

Conclusion

The five kinds of Nd-TiO_2/SiO_2 photocatalyst films with and without different dispersions were prepared by using the sol-gel method. The results show that the action between the dispersions decided the distribution of Nd-TiO_2/SiO_2 films. The photocatalytic activity and surface area of the films have been improved by dispersions. It was revealed that carboxy methyl cellulose, polyethylene glycol and poly vinyl pyrrolidone, anchored on the surface of Nd-TiO_2/SiO_2 colloid and increases formation of anatase phase and self- cleaning ability. But Nd-TiO_2/SiO_2 film with carboxy methyl cellulose has the most uniform particle distribution with low agglomeration and porous microstructure.

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