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Sol-Gel Preparation of Nanoscale TiO_2/SiO_2 Composite for Eliminating of Con Red Azo Dye

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ABSTRACT

A new anatase/SiO_2 nanocomposite was synthesized by sol-gel method at room temperature using titanium tetrachloride and tetraethylorthosilicate as raw materials. Characterization of the product was carried out by means of X-ray diffraction (*XRD*), *X-ray fluorescence spectroscopy* (*XRF*), *transmission electron microscopy* (*TEM*), *Brunauer-Emmett-Teller* (*BET*) *specific surface areas*, *Thermogravimetry analysis* (*TGA*), *Fourier transform infrared* (*FT-IR*), *and UV-vis absorption spectroscopy. Thermal phase transformation studies of composite were carried out up to* 1100˚C *which showed the establishment of anatase TiO_2 phase. The presence of some tetrahedral coordination of TiO_2 species in SiO_2 matrix was confirmed by UV-Vis study. The produced TiO_2/SiO_2 nanocomposite has good photocatalytic properties due to its anatase phase*, *existence of tetrahedral coordination of TiO_2 in the SiO_2 matrix and very large surface area. Furthermore, the synthesized anatase/SiO_2 shows significant adsorption ability towards Congo Red* (*CR*) *azo dye in comparison with the pure commercial TiO_2 which is known as Degussa*, *P*25.

***Keywords*:** *TiO_2/SiO_2*, *Nanocomposites*, *Sol-Gel Preparation*, *Photocatalyst*, *Congo Red*

1. Introduction

In the area of advanced oxidation technology, titanium dioxide semiconductor photocatalysis has been widely studied because of its potential application in air clean-up and water purification. TiO_2 is largely used as photocatalyst due to its beneficial characteristics: high photocatalytic efficiency, physical and chemical stability, low cost and low toxicity [1-9].

TiO_2/SiO_2 composites are very promising in field of heterogeneous photocatalysis, since they could provide simultaneously enhanced photocatalytic and thermal properties compared to pure TiO_2 photocatalyst [10-13]. It has been reported that photocatalytic reactivity of TiO_2/SiO_2 nanocomposites is highly dependent on the Ti/Si ratios [14-17]. The photocatalytic activity and mechanical stability was reported to improve by the addition of about 50% SiO_2 [18].

In the present study, anatase/SiO_2 nanocomposite was synthesized via sol-gel method at room temperature. The effect of calcination temperature on particles size, BET surface area and phase transformation of anatase to rutile TiO_2 were investigated. Moreover, characterization of the coordination sphere of Ti ions incorporated into silica matrix of the composite was studied. These investigations could provide vital information for the design of highly efficient photocatalytic systems in the degradation of toxic compounds diluted in a liquid phase.

2. Experimental

2.1. Chemicals

The chemicals used in this study were titanium tetrachloride ($TiCl_4$, 99.9%), Fluka, as a titanium precursor, tetraethylorthosilicate (TEOS, 98%), as silica source, Congo Red ($C_{32}H_{22}N_6Na_2O_6S_2$), HNO_3 (70 wt%, d = 1.42 g·cm^{-1}), NH_4OH (25 wt%), and anhydrous ethanol (C_2H_5OH) from Merck.

2.2. Preparation of TiO_2/SiO_2 Composite

Titanium tetrachloride was added to distilled water under vigorous stirring in an ice water bath. The produced dispersion was treated by NH_4OH and pH adjusted to 7. The resulting solid was collected by filtration and washed with distilled water. The precipitation was dispersed in 200 mL of 0.3 M HNO_3. The mixture was refluxed under vigorous stirring at 70˚C for 16 h as Titania sol was prepared. 25 mL of tetraethylorthosilicate was added drop

wise to the above sol and stirred at 70˚C. The resulting powder was filtered and washed with distilled water then dried at room temperature. The composite produced was denoted as TSR. In order to study phase transformation of prepared composite, it is calcined for 1 h at 800˚C and 1100˚C and the obtained samples were denoted as TS800 and TS1100, respectively.

2.3. Characterization

Phase identification of the products was carried out by X-ray diffraction (XRD) obtained on Philips X-pert diffractometer using Cu Kα line radiation. The crystallite size of the samples was determined by Scherrer equation [19]. Thermogravimetry analysis (TGA) was performed using STA 150 Rhenometric Scientific unit. Measurement was taken with a heating rate of 10˚C/min from 25 to 800˚C in argon atmosphere. For the composition analysis X-ray fluorescence spectroscopy (XRF) using Oxford ED 2000 was employed. Spectroscopic analysis of the nanocomposite was performed using a Fourier transform infrared (FT-IR) spectrometer (Perkin-Elmer 843) and UV-vis spectrophotometer (Shimadzu UV 2100). The morphology of the products was studied by transmission electron microscopy (TEM, Philips-EM208S electron). The specific surface area of the samples was determined through nitrogen adsorption using a surface area analyzer (CHEMBET3000).

2.4. Photoreactor

Photocatalytic activity of the synthesized nanocomposites and commercial TiO_2 were evaluated by the degradation of Congo Red. All of the experiments were conducted in an opened Pyrex vessel of 50 ml capacity and in identical conditions. A 30 W UV-C lamp was used as light source. The distance between the UV source and the vessels containing reaction mixture was fixed at 15 cm. Air was continuously bubbled into the solution in order to provide a constant source of dissolved oxygen. 0.025 g of photocatalyst was placed in a 50 mL aqueous solution of 5 ppm Congo Red. Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min. Then the lamp was switched on to initiate the reaction. During irradiation, the suspension was sampled at regular intervals and immediately centrifuged to remove catalyst particles. The photocatalytic degradation was monitored by measuring the absorbance of the solution samples with UV-vis spectrophotometer.

3. Results and Discussion

3.1. FT-IR Spectroscopy

FT-IR spectrum of the as-synthesized composite (**Figure 1**) has three characteristic bands that appeared at around

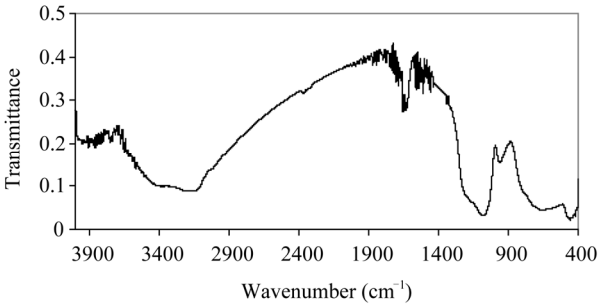

Figure 1. FT-IR spectrum of the as-synthesized TiO_2/SiO_2 nanocomposite (TSR).

1100 950, and 650 cm^{-1}. The bands at around 650 and 1100 cm^{-1} are representative of TiO_2 and SiO_2 matrixes in nanocomposite. The band at around 950 cm^{-1} has been assigned to the stretching of the Si-O$^-$ species of Si-O-Ti or Si-O defect sites which are formed by the inclusion of Ti^{4+} ions into the SiO_2 matrixes. Thus, the appearance of the band at around 950 cm^{-1} indicates that the TiO_2 species are embedded into SiO_2 matrixes within TiO_2/SiO_2 nanocomposite. the broad peak appearing at 3100 - 3600 cm^{-1} is assigned to the fundamental stretching vibration of hydroxyl groups (free or bonded) which is further confirmed by the weak band at about 1620 cm^{-1} [20-23].

3.2. X-Ray Diffraction

Figure 2 shows the XRD patterns for synthesized composite and calcined samples. It reveals that as-synthesized TiO_2/SiO_2 nanocomposite (TSR) has crystalline anatase phase in amorphous silica matrix. Both calcined nanocomposites TS800 and TS1100 have anatase phase TiO_2 but in TS1100, amorphous silica transforms to crystobalite silica phase. Both the interactions Si-O-Ti and high dispersion of TiO_2 in SiO_2 prevent the crystalline transition to rutile [24,25]. The sizes of the anatase crystallites in the prepared TiO_2/SiO_2 nanocomposite samples measured according to the Scherrer equation are 5.0, 7.8, and 26.7 nm for RSR, TS800, and TS1100, respectively. Doping of SiO_2 into TiO_2 could effectively retard the growth of nanoparticles and thus reduce the particle size. This observation may have resulted from the formation of the Ti-O-Si bond and due to the presence of amorphous SiO_2 around TiO_2, which would prevent the growth of TiO_2 particles [26]. The particle size of TSR and TS800 are close together but at 1100˚C a clear jump in the particle size is shown due to transformation of amorphous silica to crystobalite.

3.3. Thermogravimetric Analysis

The inset of **Figure 2** shows thermogravimetric curve of TiO_2/SiO_2 composite (TSR). After the removal of water and organic residue up to 150˚C, no appreciable change

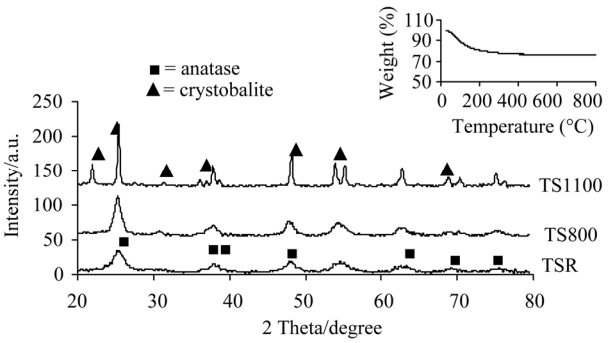

Figure 2. XRD patterns of as prepared nanocomposite (TSR) and calcined composites (TS800 and TS1100), Inset: thermogravimetric curve of (TSR).

of weight is seen in the curve. This reveals that synthesized nanocomposite is thermally stable and no phase transformation occurs, up to 800˚C.

3.4. X-Ray Fluorescence Spectroscopy

The XRF analysis shows that the composite consists of 55% TiO_2 and 45% SiO_2.

3.5. UV-Vis Spectroscopy

Figure 3 shows the absorption spectra of the prepared samples dispersed in ethanol. The band gap of the samples calculated from the straight part of the optical absorption spectra [27,28]. A clear red shift in the absorption edges of composites by increasing of calcination temperature is seen in the **Figure 3**.

The inset shows that the optical band gap of nanocomposite decreases (from 4.25 to 3.82 eV) by heat treatment from room temperature to 1100˚C. The shift can be attributed to the difference in grain size in these samples. Zribi *et al.* obtained similar evolution of optical band gap with the temperature and concluded that the variation of density and the structural modifications may be responsible for changes in the shape of the fundamental absorption edge [29]. According to **Figure 3** a peak corresponding to isolated Ti species which have absorption maxima at about 225 nm is observed in composite spectra. The absorption peak at 200 - 260 nm can be attributed to the charge transfer absorption process involving an electron transfer from O^{2-} to Ti^{4+} ions of the highly dispersed tetrahedral coordinated TiO_4 unit of these catalysts. Anpo *et al.* have reported that titanium oxides having a tetrahedral coordination can be chemically supported onto silica matrix and have shown that such composite materials exhibit significant photocatalytic activities [30].

3.6. Transmission Electron Microscopy (TEM)

Figure 4 shows TEM image of TSR composite. It can be

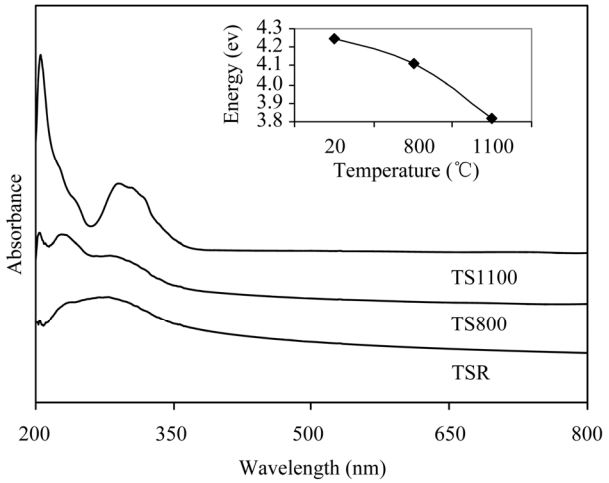

Figure 3. UV-Vis absorption spectra of the nanocomposites dispersed in ethanol. Inset: changes of optical band gap at thermal treatment.

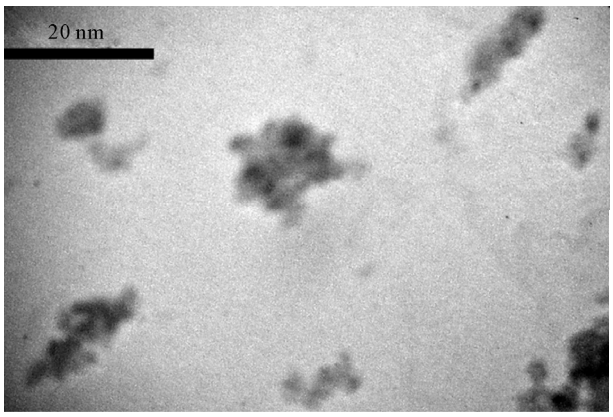

Figure 4. TEM image of the as-synthesized TiO_2/SiO_2 nanocomposite (TSR).

seen from TEM image that the composite sample consists of the nanoparticles with sizes of 5 - 9 nm which is approximately in conformity to XRD result.

3.7. Specific Surface Area Analysis

The specific surface area of the TiO_2/SiO_2 composite (TSR) calculated from BET is 707.59 $m^2 \cdot g^{-1}$. The specific surface area of TiO_2/SiO_2 composite decreases when calcination temperature increases and reaches 142.38 and 13.72 $m^2 \cdot g^{-1}$ for TS800 and TS1100, respectively.

3.8. Photocatalytic Activity Measurements

Figure 5 shows changes of the UV-Vis absorption spectrum of CR after adsorption of dye on TSR at dark and during photocatalysis. The inset also shows adsorption ability and photocatalytic activity of the composites and pure TiO_2 (Degussa P25, BET: 50 $m^2 \cdot g^{-1}$) for removal of CR from aqueous solution as a function of time at λ =

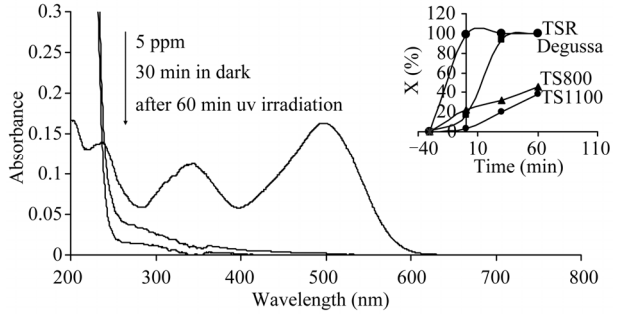

Figure 5. UV-Vis spectrum of CR (5 ppm) using TSR photocatalyst. Inset: Degree of decolorization by various photocatalysts.

497 nm. The efficiency or degree of photodegradation (X) is given by: $X = (C_0 - C)/C_0$, where C_0 is the initial concentration of dye, and C the concentration of dye at time T.

CR dye is strongly adsorbed on the surface of TSR so that more than 98% of dye decolorization performed after 30 min adsorption in dark. Percent of decolorization due to sorption on the surface of Degussa, TS800 and TS1100 are obtained to be 16.7%, 22.3% and 3.5%, respectively. These results are in a good conformity to the BET surface area of the samples.

It reveals that the as-prepared composite is the most effective sorbent and photocatalyst. The samples calcined at 800˚C and 1100˚C are weaker photocatalyst than the commercial P25. Finally, it can be deduced from the results obtained that the well crystallized mixed crystalline structure (75% anatase and 25% rutile) of P25 would be responsible for the photocatalysis superiority in comparison with the calcined nanocomposites, although the sample calcined at 800˚C has larger surface area.

4. Conclusion

TiO_2/SiO_2 nanocomposite was synthesized via sol-gel process at room temperature. Formation of the Ti-O-Si bond and amorphous SiO_2 in TiO_2/SiO_2 could effectively increase the stability of anatase TiO_2, limit the growth of crystallites, and increase the surface area. Significantly, such an increase in the surface area and the existence of tetrahedrally coordinated TiO_2, improves the photocatalytic activities of the TiO_2/SiO_2 ceramic.

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