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Preparation, Characterization, and Investigation of Photocatalytic Activity of TiO_2/SiO_2/Co Nanocomposite Using Additives

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Abstract

Titanium dioxide has been widely used for photo-catalytic and self-cleaning activities. In this study, TiO_2/SiO_2/Co nanocomposite was prepared by sol-gel method in the presence of Polyvinyl Pyrrolidone (PVP), and Hydroxyl Propyl Cellulose (HPC) as additives, and characterized by IR spectra, Scanning Electron Microscopy (SEM), Energy Dispersive Analytical X-Ray (EDAX), and X-Ray Diffraction (XRD) methods. The influence of metal doping and additives effect onto TiO_2/SiO_2 on the structure and photo-catalytic behavior was evaluated. Moreover, Photo-catalytic activity was investigated in different conditions. The results revealed that the photo-catalytic activity of TiO_2/SiO_2 doped with appropriate content of Cobalt in the presence of additives exceeded, and TiO_2/SiO_2/Co nanocomposite with HPC had the best photo-catalytic activity.

***Keywords**: Photo-catalytic activity, Nanocomposite, TiO_2/SiO_2/Co, Sol-Gel method.*

Introduction

Nowadays, Photo-catalytic and self-cleaning properties can be used for practical applications in environmental purification. Therefore, the focus of the researchers on these properties and Photo-catalytic and self-cleaning applications has become an important subject. Mutual relationship between photo-catalysis and hydrophilicity play an important role in the self-cleaning property. These properties are very useful for decomposition of organic pollutant. On the other hand, the hydrophilicity causes more effective cleaning over the surfaces. Therefore, Titanium dioxide is a good

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candidate for self-cleaning and Photo-catalytic applications because of its relatively large surface area per unit mass and volume [1]. However, it is well known that photo-oxidation retains some typical drawbacks. First, TiO_2 is a high-energy band (Eg = 3.2 eV) material that can only be excited by high-energy ultraviolet irradiation with a wavelength of no longer than 385 nm. This practically rules out the use of sunlight as an energy source for photoreaction. Second, a low rate of electron transfer to oxygen and a high rate of recombination between excited electron-hole pairs result in a low quantum yield rate and a limited photo-oxidation rate [2]. Third, due to the accumulation of stable reaction intermediates on the surface of the TiO_2 during the treatment of volatile aromatic compounds, the Photo-catalytic functions will disappear after treatment [3].

To date, various investigations have been conducted that the use of mixed oxide (TiO_2/SiO_2) is more effective than that of Titanium dioxide [4]. In order to reduce the grain and to improve the efficiency of Photo-catalytic activity, doping of the transition metals and noble elements has been investigated by various methods. Cobalt has been chosen for this process because of its proportional abundance and inexpensive [5-8].

In this study, we have initially prepared TiO_2/SiO_2 nanocomposite, then we have doped with transition metallic Cobalt synthesized by sol-gel method in order to improve the Photo-catalytic activity. Moreover, we have investigated the effects of some organic polymers such as PVP and HPC as modifiers on the size of particles, structures, and Photo-catalytic activities [8-11].

Experimental

Materials

Titanium tetra-isopropoxide (TTIP) (AR analytical grade, Merck Chemical Company) were used as Titanium sources for the preparation of the TiO_2 photo-catalysts. Cobalt (II) Nitrate hexahydrate, Polyvinyl Pyrrolidone (PVP), and Hydroxyl Propyl Cellulose (HPC), Nitric Acid (HNO_3), SiO2 colloid solution, absolute ethanol, deionized water, and Methyl orange were purchased from Merck Chemical Company.

Photo-catalyst samples preparation

All samples were prepared using the Sol-Gel method with following procedure:

Preparation of sample 1 (TiO_2 /SiO_2 nanocomposite)

A: Preparation of solution I: TTIP was dissolved in absolute ethanol (with molar ratio TTIP/ethanol = 1/75).

B: Preparation of solution II: HNO3, deionized water, TiO_2 and $Co(NO_3)_2.6H_2O$ was dissolved in absolute Ethanol (with molar ratio Ethanol/HNO_3/H_2O/SiO_2 = 43/0.2/1/30).

C: Preparation of TiO_2/SiO_2 nanocomposite:

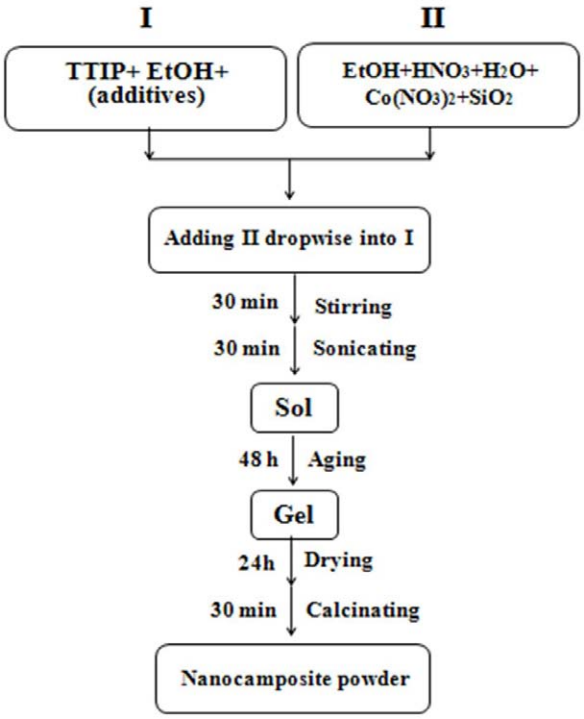
solution II was added dropwise into solution I and was vigorously stirred for 30 min at room temperature. The obtained transparent colloidal suspension was sonicated for 30 min, and aged 48 h to allow it be formed as a gel. The sample was dried in Oven at 50◦C and ultimately was calcinated at 500◦C for 4 hours.

Preparation of samples 2 (TiO_2 /SiO_2 /Co nanocomposite)

Solution **I** was prepared exactly such as sample 1 but $Co(NO_3)_2$ with ratio 0.2% W/W ($Co(NO_3)_2$ / SiO_2), was added to solution II. The other steps are similar to those of the sample 1.

Preparation of samples 3 and 4 (TiO_2 /SiO_2 / Co nanocomposite with additives)

All steps for synthesis of sample 3 and sample 4 are similar to those of the sample 2, but 0.2g additives (HPC for sample 3, and PVP for sample 4) were added to solution I and were stirred until complete dissolution to this solution was achieved. All the above steps have been summarized in bellow chart:



Equipments

FT-IR spectra were obtained as KBr pellets in the range of 4000 to 500 cm^{-1} using Shimadzu FT-IR spectrophotometer. Ultraviolet-visible (UV-vis) absorption spectrum was obtained by means of Varian Carry 300 UV-vis spectrometer. XRD patterns were obtained with a Philips x' pert pero MPD diffractometer with CuKα radiation from 10 to 80 (2θ) at room temperature. The morphology and microanalysis of the samples were observed by a scanning electron microscope (SEM,

SEM-4100, Jeol).

Results and discussion

XRD

The crystalline structure of the samples was analyzed by X-ray diffraction patterns of XRD and results have been shown in Fig. 1. In all samples, all of the detectable peaks can be indexed as the TiO_2 with anatase structure in the standard data (the base peak in range of **20<2θ<30** is an evidence of anatase phase). As it is observed, in XRD pattern of sample 1, anatase structure been has formed less than that of the other samples. But in other samples increasing anatase phase along with increasing Cobalt and additives can be seen.

Sample 2 (TiO_2 /SiO_2 /Co) has shown anatase phase more than sample 1, and this result revealed that metal doping has effect on anatase phase formation. In sample 3, PVP results have confirmed that anatase structure has been formed more than that of the sample 2. According to XRD patterns, anatase phase peak in sample 4 containing Cobalt and HPC additive, is sharper than the same peak in other samples that reveals sample 4 is very good option for Photo-catalytic and self-cleaning ability.

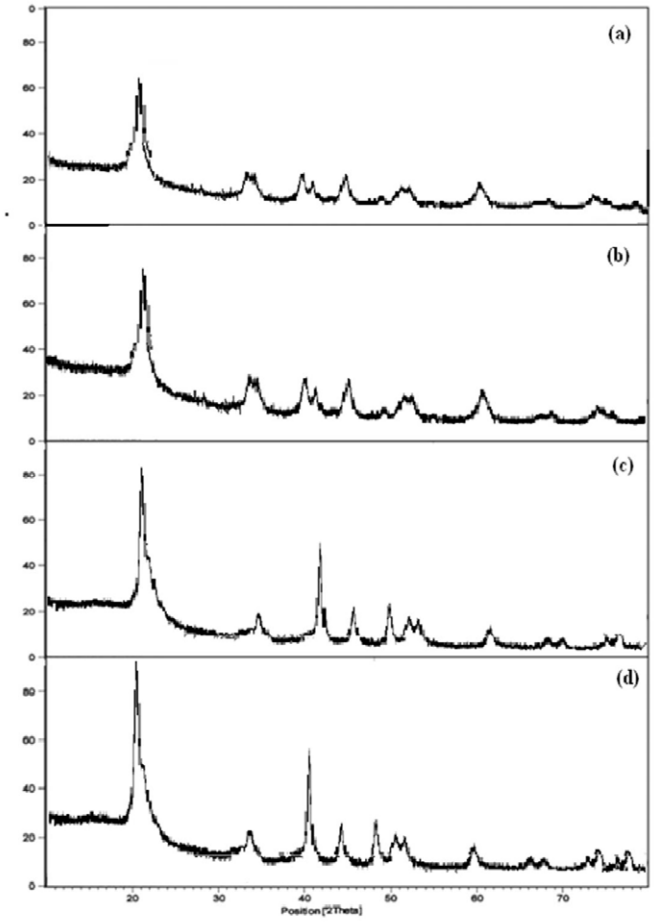


Figure 1. XRD patterns of sol-gel synthesized TiO_2/SiO_2. (a)Sample 1, (b)Sample 2, (c)Sample 3, (d)Sample 4.

Scanning Electron Microscopy (SEM) and EDAX

Figure 2 shows the SEM morphologies of the samples. SEM pictures show the effect of metal doping and organic compound on particle size and morphology. Images revealed that, Sample1 (TiO2/SiO2 nanocomposite) shows high agglomeration and it has the most range particle distribution and the largest size. Co+2 as a doping element was added to sample 2 that its particle size and uniformly are better than those of the sample 1. After adding PVP and HPC, particle size decreases and images show less agglomeration and distribution becomes narrow. Sample 4 with HPC is very uniform with smaller particle size as compared to the others. EDAX analysis has revealed that TiO2, SiO2 and Co is present in all samples. All components and their weight percentages are shown in Table 1.

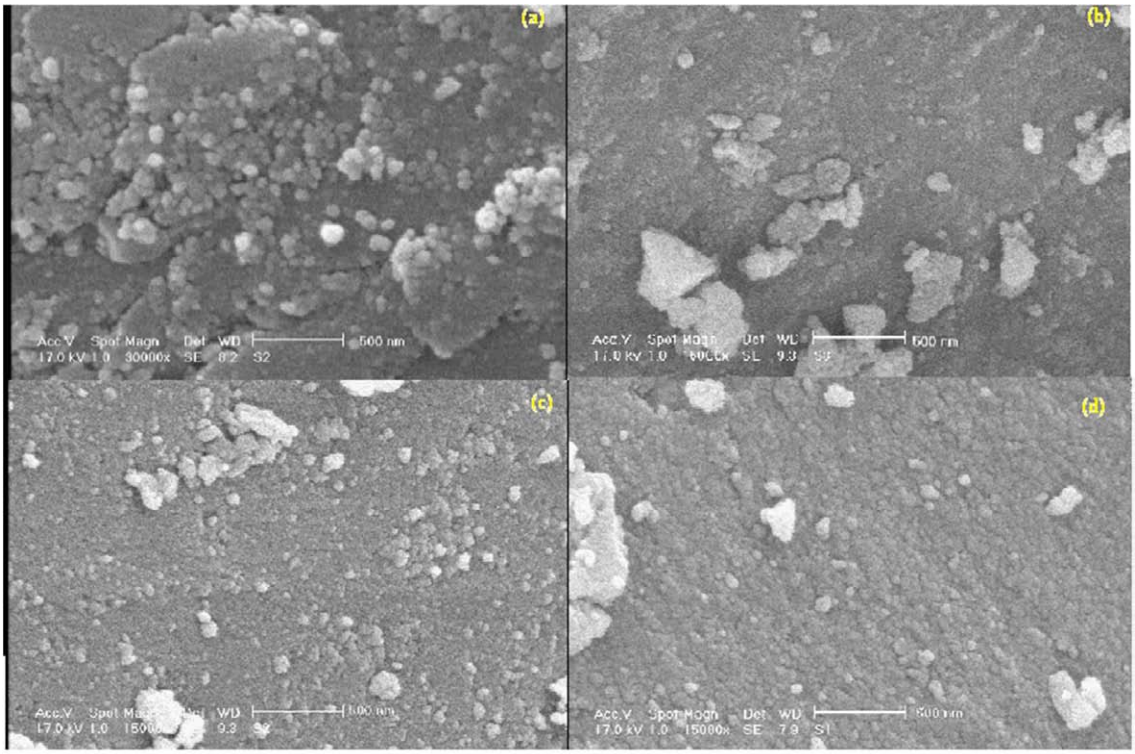


Figure 2. SEM images for the sample powders. (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4.

T able 1. Component and weight percentages of the samples according to EDAX analysis.

Component	Wt%(sample1)	Wt%(sample2)	Wt%(sample3)	Wt%(sample4)
TiO_2	76.78	75.38	77.01	76.05
SiO_2	23.22	22.71	21.62	22.18
Co	0.00	1.91	1.37	1.77

FT-IR spectroscopy

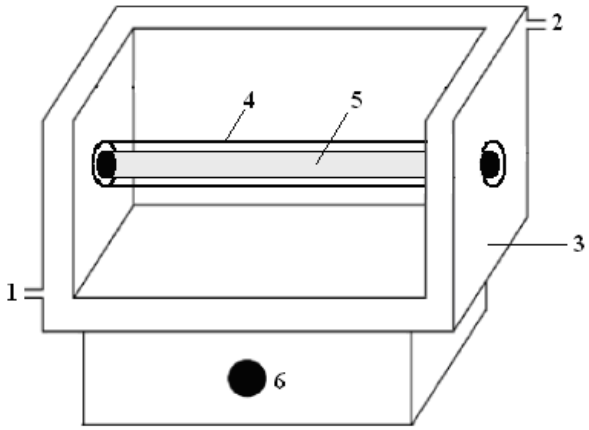
FT-IR spectra of the TiO_2-SiO_2/Co nanocomposite samples are shows the bands at 3400 and 1630 cm^{-1} can be attributed to the stretching vibration of the OH group and molecular H_2O, respectively. A great amount of propanol has been produced during the hydrolysis of TTIP, which leads to the appearance of hydroxyl bands (3100-3700) [12].

The peaks around 1080 cm^{-1} (with a shoulder around 1210 cm^{-1}) and 804 cm^{-1} belong to asymmetric and symmetric Si-O-Si stretching modes, respectively [13]. The band around 457 cm^{-1}, is assigned to the Si-O-Si bending mode [14,15]. The peak at 950 cm^{-1} can be attributed to the Si-O-Ti vibration band [16,17]. This is the evidence of titanium incorporated into the framework of silica. Moreover, the bands at 1117 cm-1 in samples can be led to asymmetric stretching vibration of the Ti-O bands [18-22]. The peak at 602 cm^{-1} can be attributed to symmetric stretching vibration of the Ti–O–Ti group [22-24].

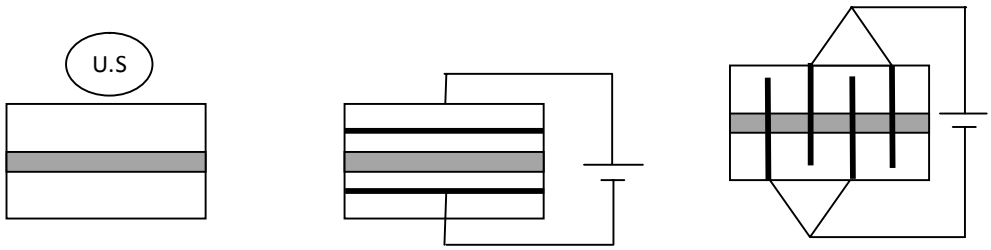
Furthermore, a band at 2366 cm^{-1} was observed which can be assigned to Co–TiO_2–SiO_2. Exhibited broad peaks in the range of 400–1000 cm^{-1} have contribution from anatase phase [21-24].

Photo-catalytic activity tests

In order to investigate the Photo-catalytic activity of the samples and the effect of metal doping and additives on Photo-catalytic activity, the solution of Methyl Orange (with a concentration of 5 ppm) in deionized water was selected as a pollutant solution for photo-degradation. This solution was set in the vicinity of nano photo-catalyst powder (0.5g powder in 1L solution) and then was rested for 24 h in the darkness in order to eliminate the absorptive effect of the solution in the catalyst. Finally it was placed in the photo-reactor system which is shown in Figure 3. Methyl Orange concentration changing under a 15W UV lamp (Osram) was recorded by an UV spectrometer model Varian.



(a) 1-Water inlet, 2-Water outlet, 3-Glass jacket, 4-quartz cover, 5-UV lamp, 6-Stirrer.



(b) Under Ultrasonic Source **(c)** Under Electrophotochemistry

(**d)** Under Electrophoto dialysis

Figure 3. Schematic diagram of the photoreactor systems.

Photo-catalytic activity of the sample with the best Photo-catalytic activity (sample 4) was examined in different conditions such as UV irradiation (photochemistry), Electro photo chemistry, Electro photo dialysis, and in the presence of ultrasonic bath.

Results have been shown in Figures 4 and 5. According to these results, Photo-catalytic activity has increased with the application of metal doping and additives, and sample 4 containing HPC has the best Photo-catalytic activity as compared with the other samples. Therefore, a good Photo-catalytic ability of samples with additives can be attributed to the smaller size of the particle, porous and the less agglomerated nanostructure. Furthermore, results revealed that the application of ultrasonic bath, Electro photo chemistry, and Electro photo dialysis conditions were affective on the decolourization of pollutant and decolourization under the electro photo chemistry and ultrasonic bath condition is higher than that of the other conditions.

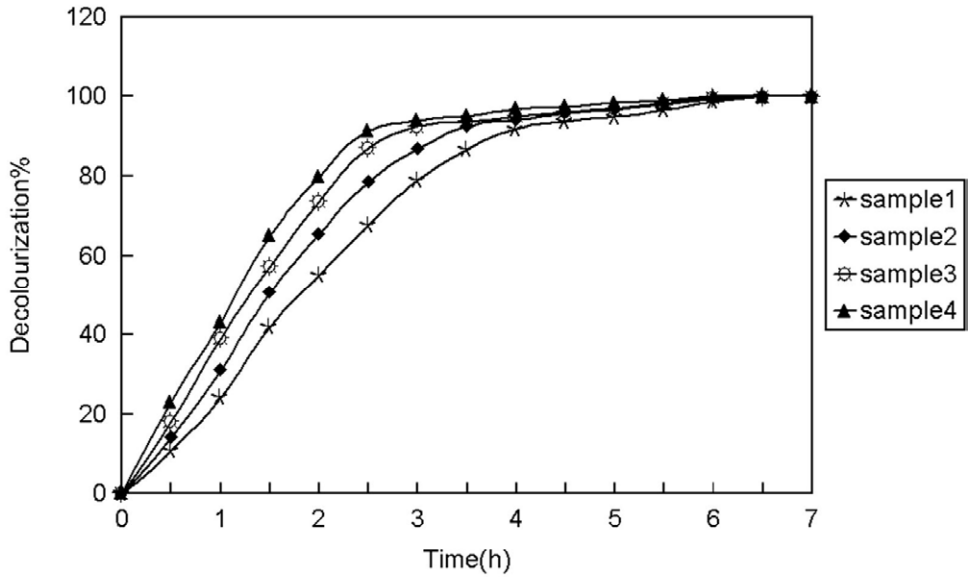


Figure 4. Decolourization percent of Methyl Orange solution under UV radiation.

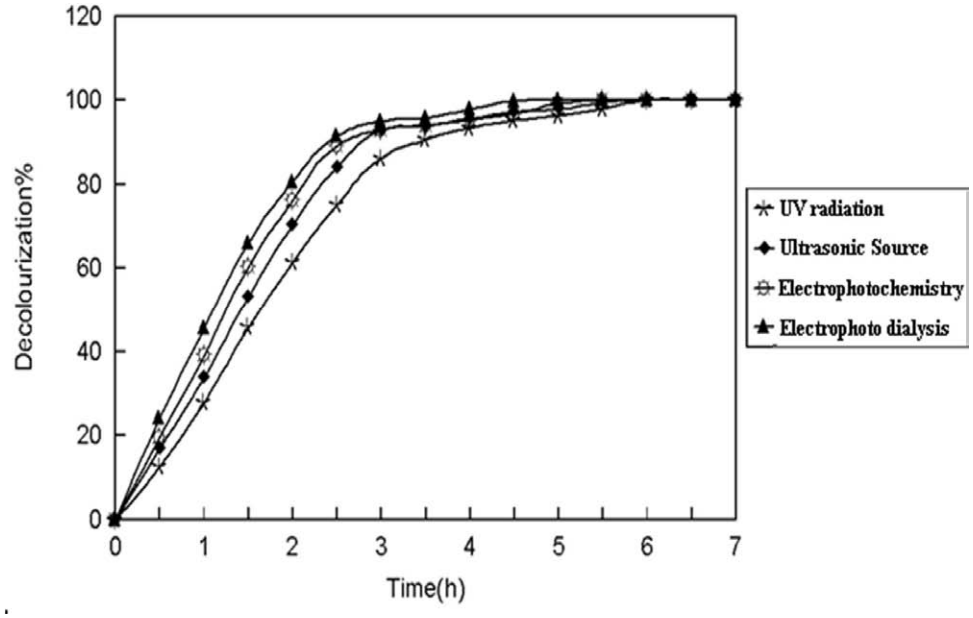


Figure 5. Decolourization percent of Methyl Orange solution of sample 4 under different counditions.

Conclusion

In summary, in this paper, preparation and characterization of TiO_2/SiO_2/Co nanocomposite with and without additives via sol-gel method were investigated. The photo catalytic activity of the samples, were examined for degradation of Methyl Orange in water under different conditions in a batch reactor. Results revealed that, decolourization under the electro photo chemistry and ultrasonic bath condition is higher than that of the other conditions.

This study has confirmed that the Photo-catalytic activity of TiO_2/SiO_2 nanocompsite

powder has been modified by using metal doping and additives. Moreover, the particle size of TiO_2/SiO_2/Co nanocomposite with HPC was smaller than that of the other samples

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