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Preparation, Characterization and investigation of Photocatalytic Properties of Co, Nd-codoped TiO₂Nanocomposites

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A b s t r a c t

Recently, TiO₂ is one of the most important materials in the field of photocatalytic activity. In the present study, Co-TiO₂, Nd-TiO₂, and Co,Nd-TiO₂nanocomposites powders were prepared via sol-gel method. Moreover, the advantage of metal doping and co-doped effects on photocatalytic activity were investigated. Structure and photocatalytic activity were studied by several methods such as: FT-IR spectra, Scanning Electron Microscopy (SEM), and X-Ray Diffraction (XRD). The results have revealed that Co,Nd-codoped TiO₂ nanocomposite has better photocatalytic activity in comparison with Co-doped TiO₂ and Nd-doped TiO₂nanocopmosites.

Keywords: Codoped TiO₂, Sol–gel method, Photocatalytic activity.

1. Introduction

Titanium dioxide (TiO₂) is an attractive material for researchers in recent years, due to its extensive applications such as white pigment, gas sensor, and as a photocatalyst. Moreover, for environmental applications, TiO₂ is one of the most efficient materials because of its strong oxidizing power, non-toxicity, high photochemical corrosive resistance and cost effectiveness. These distinguished properties, have led to that TiO₂ is very suitable candidate for degradation of toxic organic pollutants in water, soil and air [1–5].Yet, the major disadvantage of using TiO₂ as a photocatalyst is that it is active only under UV irradiation due to its wide band gap (3.2 eV). Thus, the possibility of employing solar light in TiO₂photocatalysis is limited. To shift the optical response from the UV to visible spectral range and in order to improving photocatalytic properties, TiO₂ catalyst can be modified with addition of various impurities. For example, metals or metallic oxides can be added either into the TiO₂ structure by doping, implanting or co-precipitating or onto the TiO₂ surface by coating or photodepositing as metal islands [6-8].

In this work Co,Nd-codoped TiO₂ nano composite was synthesized by the sol-gel method and the influence of two metal doped on the properties, structure and photocatalytic activity under UV-irradiation for removal of organic pollutant were investigated by IR spectra, Scanning Electron Microscopy (SEM), and X-Ray Diffraction (XRD) methods.

2. Experimental

2.1. Materials

Titanium tetra isopropoxide (TTIP) (AR analytical grade, Merck Chemical Company) were used for the preparation of TiO₂ phtocatalysts as Titanium sources. Acetic acid, Co(NO₃)₂. 5H₂O, Nd(NO₃)₃.6 H2O, Diethanol Amine (DEA), absolute ethanol, and deionized water were purchased from Merck Chemical Company.

2.2. Test Equipments

FT-IR spectra were performed as KBr pellets using Shimadzu FT-IR spectrophotometer. XRD measurements were obtained using a Philips x' pert pero MPD diffractometer with CuK$_\alpha$ radiation from 10 to 80 (2θ) at room temperature. Morphology and microanalysis of the samples was observed by a scanning electron microscope (SEM, SEM-4100, Jeol). Ultraviolet-visible (UV-Vis) absorption spectrum was obtained by means of Varian UV-Vis spectrometer.

2.3. Sample preparation

The doped TiO₂ materials were synthesized by standard sol-gel methods with doping levels of 0.1 to

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0.5 at. % but the best results have been reported (doping levels of 0.3).

TiO$_2$/CoO nanocomposite powders (sample 1) were prepared with following procedure.

2.3.1. Preparation TiO$_2$ sol

Yellow color TiO$_2$ sol was made at room temperature in 3 steps:

Step1) solution **I**: TTIP was dissolved in absolute ethanol (with molar ratio 1: 9) under vigorous stirring for 10 min.

Step 2) solution **II**: Acetic acid and deionized water was dissolved in absolute ethanol (with the molar ratio of 6: 1: 10).

Step 3) solution **II** was added slowly into solution **I** by a vigorously stirring for 15 minutes to achieve a yellow transparent sol.

2.3.2. Preparation of CoO sol

CoO sol was also prepared as in 3 steps:

Step1) solution **I**: Co(NO$_3$)$_2$.5H$_2$O was dissolved in absolute ethanol (with the molar ratio of 0.1 : 110).

Step2) solution **II**: Di-ethanol amine and deionized water was dissolved in absolute ethanol (with the molar ratio of 2: 1: 10).

Step3) solution **II** was then added drop by drop into solution **I** with stirring for 15 minutes to achieve transparent sol.

2.3.3. Preparation of Co-TiO2 nanocomposite

The prepared CoO sol was added dropwise into TiO$_2$ acidic Sol and vigorously stirred for 30 min at room temperature. After that, to get transparent sol, colloidal suspension was sonicated for 30 min, and aged 72 h to allow forming a gel. The sample was dried in oven at 50°C and ultimately was calcinated at 500°C for 4 h to obtain the final product.

All steps for preparation of sample 1 (Co-TiO$_2$nanocomposite) have been summarized in below Chart. All of steps for synthesis of sample 2 (Nd-TiO$_2$ nanocomposite) is similar to sample 1, but in sample 2 Nd(NO$_3$)$_3$. 6H$_2$O was added instead of Co(NO$_3$)$_2$.5H$_2$O, and in sample 3 Co,Nd-TiO$_2$ nanocomposite with different Co(NO$_3$)$_2$.5H$_2$O and Nd(NO$_3$)$_3$. 6H$_2$O contents were prepared similar to sample 1 but only the best molar ratio (Co/Nd =0.2/0.1) was reported.
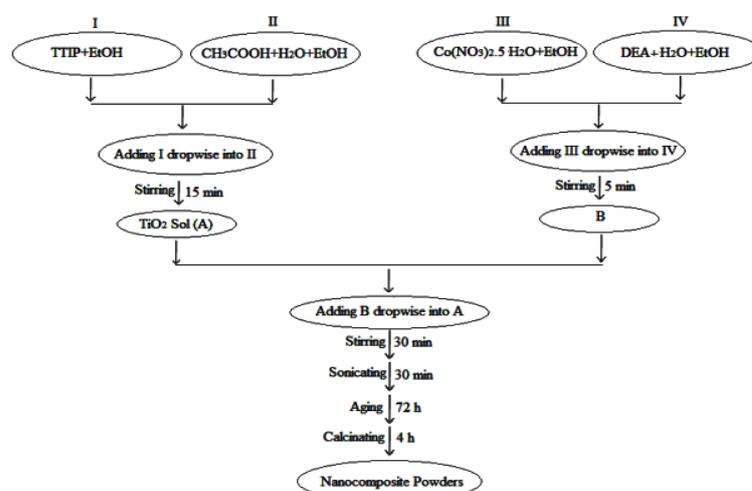

Figure1. Sample preparation chart

3. Results and Discussion

3.1. FT-IR spectroscopy analysis

FT-IR spectra contain peaks corresponding to stretching vibrations of the O–H and bending vibrations of the adsorbed water molecules about 3300–3550 cm^{-1} and 1620– 1635 cm^{-1}, respectively. These results strongly confirm the presence of hydroxyl ions in the structure of the samples. A great amount of propanol appears during the hydrolysis of TTIP, which leads to the appearance of hydroxyl bands (3100-3700 cm^{-1}) [9-15]. In the region below

1000 cm^{-1}, several peaks were ascribed to absorption bands of Ti–O (650–550 cm^{-1}) [16-20]. The bands at 1115 cm^{-1} in samples **1, 2,** and **3** can be assigned to asymmetric stretching vibration of the Ti-O bands [21].The peak at 602 cm^{-1} can be assigned to symmetric stretching vibration of the Ti–O–Ti group and 1037 cm^{-1} which may correspond to Ti–O–C bending [22-24]. Furthermore, the results show that Co and Nd atoms were successfully incorporated into the lattice of TiO$_2$. According to IR spectra, a band at 2366 cm^{-1} in samples 1 and 3 were observed which can be assigned to Co–TiO$_2$ [25-29]. The peaks at

457.34 cm^{-1} in sample 2, 446.41 cm^{-1} in sample 3 and are due to the vibration modes of anatase skeletal O–Ti–O–Nd bands [30].

3.2. XRD analysis

For XRD analysis, firstly, the prepared Co-TiO$_2$nanocomposite (sample 1), and Nd-TiO$_2$nanocomposite (sample 2) powders were examined by XRD measurements as shown in Fig. **3.** The XRD patterns results have shown that in samples **1** and **2** anatase structure has formed less than Co, Nd-TiO$_2$nanocomposite powder (sample 3). The base peak in the range of **20<2θ<30** is an evidence of anatase phase [31].In the meantime, XRD patterns for all of samples showed both anatase and rutile phases, but anatase phase was dominating. It has been reported that during improper heat treatment, sol-gel samples of TiO$_2$ undergo a phase transformation from anatase to rutile phase which in this situation have not any self-cleaning ability [31].
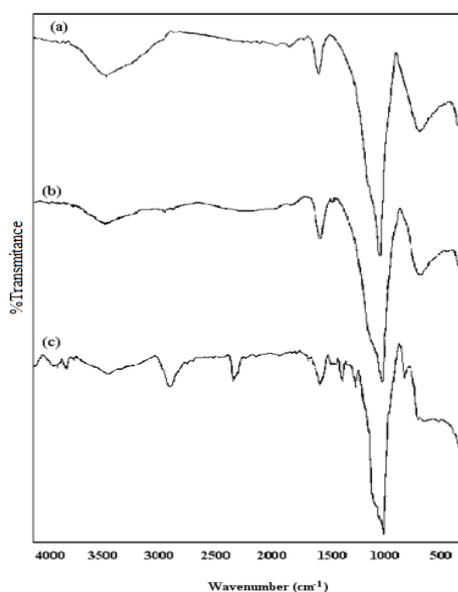

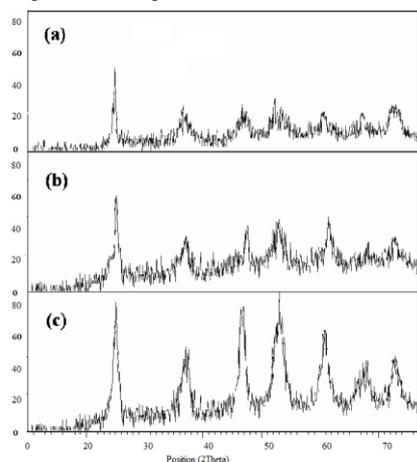Figure 2. Effect FT-IR spectra of the samples: (a) Sample 1, (b) Sample 2, (c) Sample 3.

Figure 3. XRD patterns of samples: (a) Sample 1, (b) Sample 2, (c) Sample 3.

3.3. SEM analysis

The nanocomposite powders were examined by SEM and their images are presented in Fig. **4**. SEM pictures showed that in sample 3 (Co, Nd-TiO$_2$nanocomposite powder) are less agglomerated and very uniform in comparison with other samples.
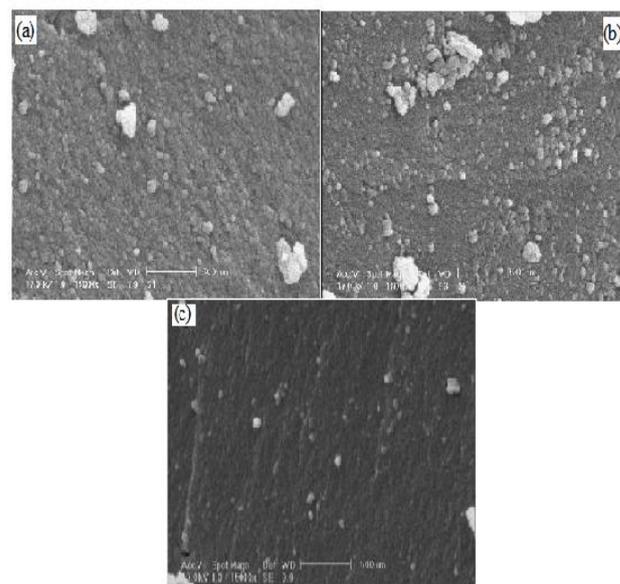

Figure 4.SEM pictures of nanocomposite powders: a) Sample 1, (b) Sample 2, (c) Sample 3

3.4. Photocatalytic activity analysis

By analyzing the photocatalytic activities of the Co-doped and/or Nd-doped TiO$_2$ under ultraviolet irradiation, the probable mechanism of co-doped nanocomposite was investigated. The photocatalytic activities were evaluated by methylorange (with a concentration of 5 mgL^{-1}) in deionized water as a pollutant source for photodegradation.This solution was set in the vicinity of nanophotocatalist powder (0.2g powder in 1L solution). Finally it was placed in the photoreactor system.This system consisted of a cubic borosilicate glass reactor vessel with an effective volume of 1000 mL, a cooling water jacket and a 15W UV lamp (Osram) with a quartz cover positioned inside the solution, as an UV light source. The reaction temperature was kept at 25 ℃ using cooling water. Methylorange concentration changing under a 15W UV lamp was recorded by an UV spectrometer model Varian.

The photocatalytic activity has been shown in Fig. 5. According to these results, photocatalytic activity has increased with the application of co-doping and photocatalytic activity has increased in sample 3 (Co, Nd-TiO$_2$nanocomposite powder). It is presumed that the metal doping induced the formation of new states

closed to the valence band and conduction band, respectively. The co-operation leads to the much narrowing of the band gap and greatly improves the photocatalytic activity. Meanwhile, the co-doping can also promote the separation of the photogenerated electrons and holes to accelerate the transmission of photocurrent carrier. Consequently, sample 3 has the better photocatalytic activity in comparison with other samples.
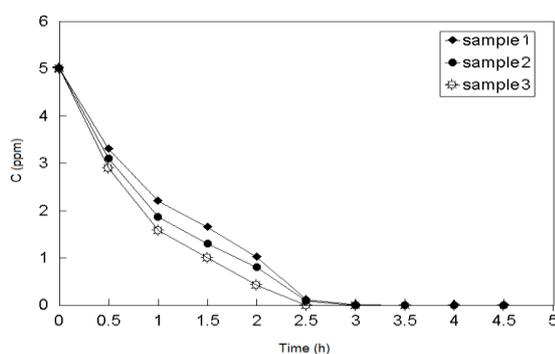

Figure 5.Photodegradation rate of Methylorange solution under UV irradiation

4. Conclusions

This study has confirmed that the photocatalytic activity of Co-TiO$_2$ and Nd-TiO$_2$nanocompsite powders can be improved using co-doped of these metals. Three samples (Co-TiO$_2$, Nd-TiO$_2$ and Co, Nd-TiO$_2$nanocomposites) have been prepared by a sol–gel method. The photocatalytic activity of the synthesized nanocomposites was investigated for degradation of methyl orange in water under UV-irradiation in a batch reactor. The results showed that the photocatalytic activity of the nanocomposites has been increased in presence of two metals and co-doped was effective on photocatalytic activity.

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