

## Preparation, characterization and photocatalytic activity of TiO<sub>2</sub>/CoO nanocomposite

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TiO<sub>2</sub>/CoO nanocomposites were prepared by the sol-gel method with and without additives such as carboxymethyl cellulose (CMC), polyvinylpyrrolidone (PVP), and hydroxypropyl cellulose (HPC). The structures and properties were characterized with FT-IR, XRD, SEM, and EDAX techniques. The photocatalytic activity under UV-irradiation to remove organic pollutants was investigated. The results revealed that additives have a significant effect on the particle size distribution and photocatalytic activity of TiO<sub>2</sub>/CoO nanocomposites. SEM pictures showed that the particle size of TiO<sub>2</sub>/CoO powder with additives was smaller than that of samples without any additive.

**Keywords:** Sol-Gel, TiO<sub>2</sub>/CoO Nanocomposite, Photocatalytic activity

### INTRODUCTION

In textile industry, the largest group of coloring materials is that of azo dyes [1–3]. These substances are some of the most important sources of environmental pollutants. In recent years, titanium oxide (TiO<sub>2</sub>) is recognized as the most efficient semiconductor photocatalyst for environmental applications due to its potential application in removing of all types of organic pollutants [4–7].

The use of titanium oxide as a photocatalyst has the following advantages: strong oxidizing power, non-toxicity, high photochemical corrosive resistance and cost effectiveness. However, due to the wide band gap (3.2 eV) which requires the use of UV light, TiO<sub>2</sub> is active only under UV irradiation [7].

In order to improve the efficiency of photocatalytic activity and the response to visible irradiation, the catalyst can be modified using various additives. For example, metals or metallic oxides can be added into the TiO<sub>2</sub> structure by doping.

For the preparation of Co-doped TiO<sub>2</sub> nanocomposites several methods were reported, e.g., solid-state method, impregnation method, and chemical coprecipitation method [7–9].

The sol-gel method has significant advantages, such

as high purity, good uniformity of the powder microstructure, low-temperature synthesis, and easily controlled reaction conditions and therefore it has been used for the preparation of TiO<sub>2</sub>/CoO nanocomposites [4, 7, 10–13].

In this study, Co-doped TiO<sub>2</sub> nanocomposites were prepared by the sol-gel method in presence of CMC, PVP, and HPC in order to investigate the effect of additives on the photocatalytic properties. The synthesized nanocomposites were characterized by Fourier transform infra-red spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDAX). The influence of additives on the photocatalytic activity under UV-radiation was assessed in the decolorization of methyl orange in water using a batch reactor.

### EXPERIMENTAL

#### Materials and Equipments

Titanium tetraisopropoxide (TTIP) (AR analytical grade, Merck Chemical Company) was the titanium source. Cobalt (II) nitrate.5H<sub>2</sub>O, glacial acetic acid, di-ethanolamine (DEA), absolute ethanol, methyl orange, and deionized water were purchased from Merck Chemical Company and carboxymethyl cellulose (CMC), polyvinyl pyrrolidone (PVP), and hydroxypropyl cellulose (HPC) from Sigma-Aldrich Company. The characteristics of the nanocomposites were determined by the following methods. FT-IR

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spectra of pellets were recorded in the range of 4000 to 500 cm<sup>-1</sup> on a Shimadzu FT-IR spectrophotometer. XRD measurements for identifying the nanocomposites phases were performed on a Philips x'pert pro MPD diffractometer with CuK<sub>α</sub> radiation from 10 to 80 (2θ) at room temperature. Morphology and microanalysis of the samples were studied by SEM (SEM-XL30, Philips). Ultraviolet-visible (UV-vis) absorption spectra were obtained on a Varian Carry 300 UV-vis spectrometer.

#### Preparation of Nanocomposites:

TiO<sub>2</sub>/CoO nanocomposite powders were prepared using the sol-gel process according to the following procedure.

*Preparation of TiO<sub>2</sub> sol:* Yellow-colored TiO<sub>2</sub> sol was prepared at room temperature in 3 steps:

Step 1) solution I: TTIP was dissolved in absolute ethanol (at a molar ratio of 1: 9) under vigorous stirring for 10 min.

Step 2) solution II: Acetic acid and deionized water were added to absolute ethanol (at a molar ratio of 6: 1: 10).

Step 3) solution II was added slowly into solution I under vigorous stirring for 15 minutes to obtain a yellow transparent sol.

*Preparation of CoO sol:*

Step 1) solution I: Co(NO<sub>3</sub>)<sub>2</sub>.5H<sub>2</sub>O was dissolved in absolute ethanol (at a molar ratio of 0.1 : 110).

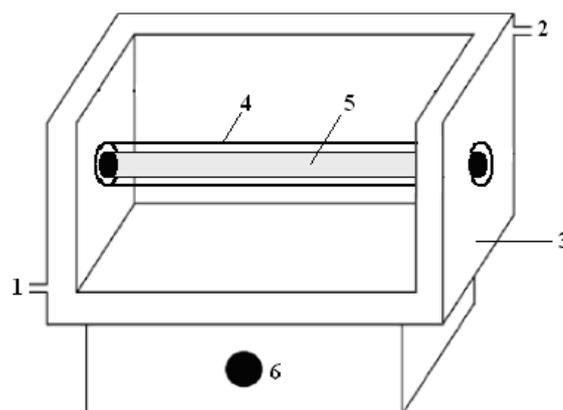
Step 2) solution II: di-ethanolamine and deionized water were added to absolute ethanol (at a molar ratio of 2: 1: 10).

Step 3) solution II was added dropwise into solution I under stirring for 15 minutes to obtain a transparent sol. Then, this sol aged for 72 h to allow it is formed as a gel. Ultimately, obtained gel was calcinated at 500 °C for 2 h.

#### Photocatalysis conditions:

The photocatalytic activity of the samples was studied on solutions of methyl orange (with a concentration of 5 mg L<sup>-1</sup>) in deionized water as a pollutant. All experiments were carried out in a photoreactor system with a capacity of 1 liter, shown in Fig. 1.

Firstly, 0.2 g of photocatalyst powder was added into 1 L of pollutant solution and was let in dark for 24 h to eliminate the absorptive effect of the solution on the catalyst. Then it was placed in the photoreactor system which consisted of a cubic borosilicate glass reactor vessel, a cooling water jacket and a 15W UV lamp (Osram) as a light source placed in a quartz tube. The reaction temperature was kept at 25 °C using cooling water.



**Fig. 1.** Schematic diagram of the photoreactor system: 1-water inlet, 2-water outlet, 3-glass jacket, 4-quartz cover, 5-UV lamp, 6-stirrer

The changes in methyl orange concentration were monitored by an UV spectrometer.

## RESULTS AND DISCUSSION

#### FT-IR spectroscopy:

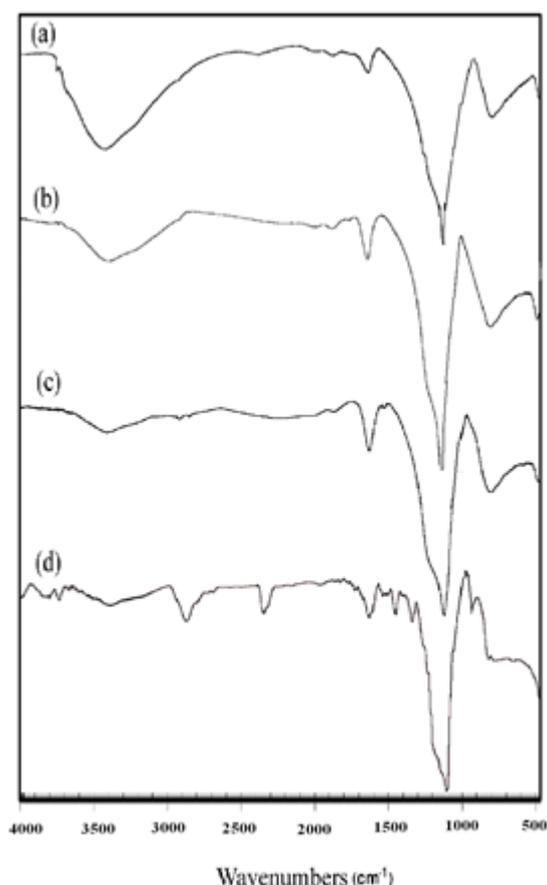
The FT-IR spectra of the TiO<sub>2</sub>/CoO nanocomposite samples are presented in Fig. 2. The stretching vibration of the OH group and molecular H<sub>2</sub>O leads to the appearance of the bands at about 3300–3550 cm<sup>-1</sup> and 1620–1635 cm<sup>-1</sup>, respectively. Hydrolysis of titanium tetraisopropoxide produced a large amount of propanol, which confirmed the presence of hydroxyl ions in the structure of the samples [13]. The peaks around 550 and 700 cm<sup>-1</sup> can be attributed to symmetric stretching vibration of the Ti-O-Ti bond and O-Ti-O flexion vibration, respectively [14,15]. The peak at 1035 cm<sup>-1</sup> may correspond to Ti-O-C bending [16]. The interaction between the Ti-O network and the organic polymers (CMC, PVP or HPC) may cause Ti-O-C bonding. Moreover, the bands at 1117 cm<sup>-1</sup> in the samples can be assigned to asymmetric stretching vibration of the Ti-O bands [17-19]. The peak at 602 cm<sup>-1</sup> can be assigned to symmetric stretching vibration of the Ti-O-Ti group [18-20].

Furthermore, a band at 2366 cm<sup>-1</sup> was observed which can be assigned to Co-TiO<sub>2</sub>. The peaks at 400 and 1400 cm<sup>-1</sup> were attributed to the vibration mode of Ti-O bond and those at 1240, 1160 and 1080 cm<sup>-1</sup> should be due to the Ti-OH bond [21-23].

#### XRD analysis:

The crystalline structures of the samples were studied by X-ray diffraction analysis and the results are shown in Fig. 3.

In all samples, significant peaks were observed at 2θ=25, 48 which were related to anatase phase (the base peak in the range of 20<2θ<30 is an

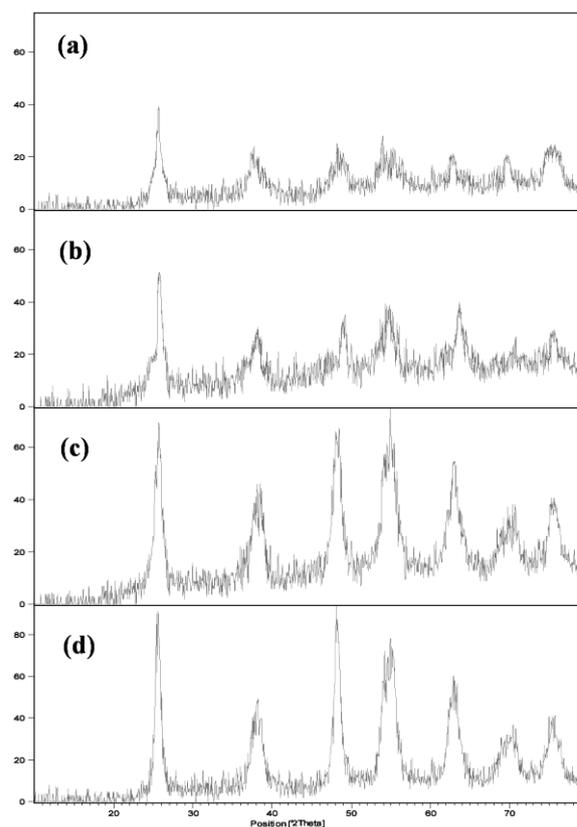


**Fig. 2.** FT-IR spectra of the sample sols. (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4

evidence of anatase phase); detectable peaks indexed as TiO<sub>2</sub> with rutile structure  $2\theta=27$  were also observed but the anatase phase dominated. According to the XRD patterns, anatase structure was formed to a lesser extent in sample 1 than in the other samples. As can be seen, in the other samples containing additives, the anatase phase increased and for sample 4 containing HPC additive, the anatase phase peak is sharper than for other samples. This reveals that sample 4 is a very good option for its photocatalytic and self-cleaning ability.

#### SEM analysis:

Surface morphology of the synthesized nanocomposite powders was evaluated by SEM and the results are shown in Fig. 4. SEM pictures showed that nanoparticles in sample 1 (without additives), contains scattered particles which have different sizes and are agglomerated. Sample 2 with CMC is less agglomerated. The particle size of sample 3, containing PVP is smaller than that in the two previous samples and its distribution is more monotonous [5, 9, 11, 20]. Sample 4 containing HPC has the smallest particle size and the most uniform particle distribution with low



**Fig. 3.** XRD patterns of sol-gel synthesized Co-TiO<sub>2</sub>.

(a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4

agglomeration in comparison with the other samples [7, 8, 21].

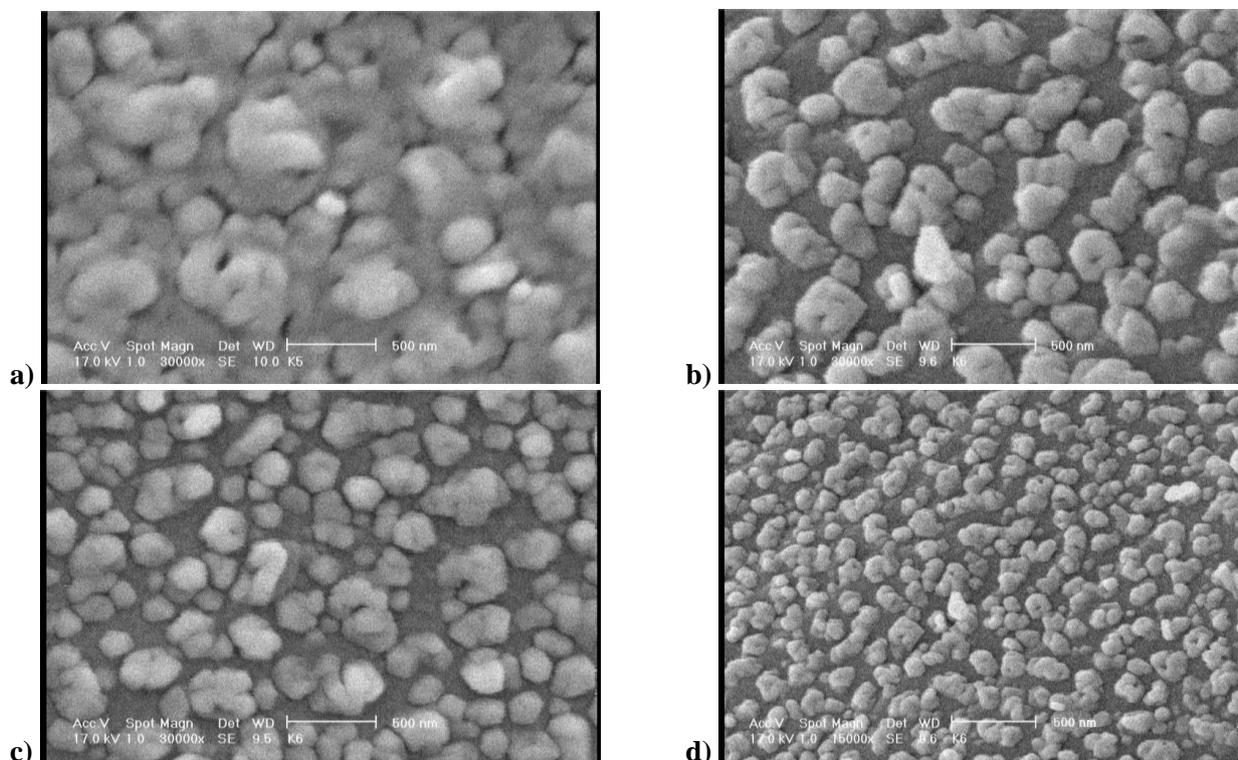
EDAX analysis has revealed that TiO<sub>2</sub>, SiO<sub>2</sub> and Co are present in all samples. All components and their weight percentages are shown in table 1.

#### Photocatalytic activity:

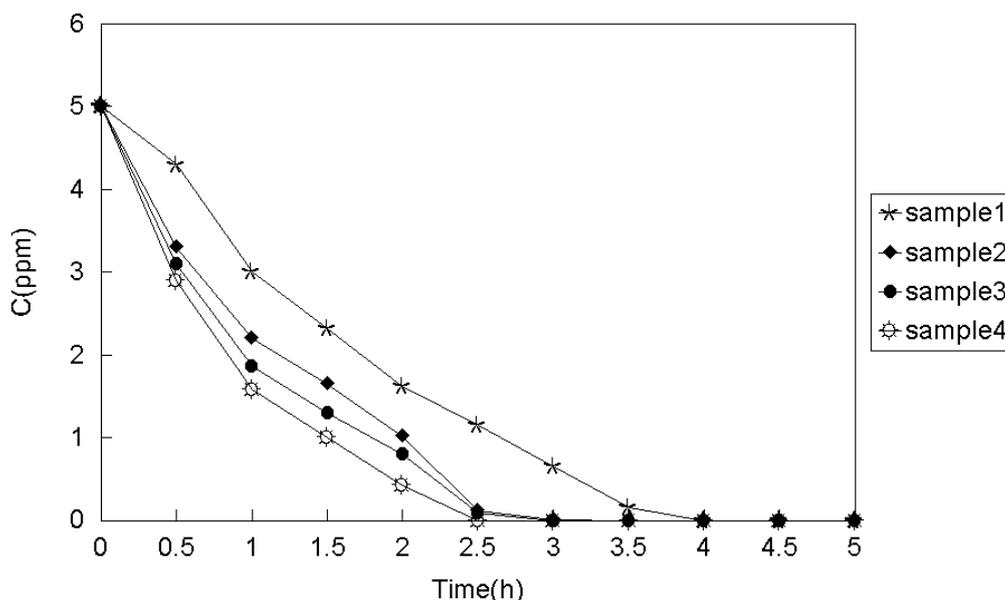
To evaluate the photocatalytic activity of the synthesized samples and to examine the role of additives, the solution of methyl orange (with a concentration of 5 ppm) in deionized water was selected as a pollutant solution for photodegradation. Fig. 5 shows the photocatalytic activity of the nanocomposites for decolorization of methyl orange as a function of time at  $\lambda = 465$  nm. The photocatalytic activity of the sample was enhanced in the presence of additives [2]. Sample 4 containing HPC displayed the highest photocatalytic activity in comparison with the other samples. About 2.5 h after starting the reaction, the absorbance of the methyl orange solution reached 0. Hence, it may be concluded that the organic polymers act as a dispersing factor to avoid accumulation of the nanocomposite particles [23–25].

**Table 1.** Component and weight percentages of the samples according to EDAX analysis

Component	Wt%(sample1)	Wt%(sample2)	Wt%(sample3)	Wt%(sample4)
TiO <sub>2</sub>	89.52	89.75	90.11	91.05
Co	10.48	10.25	9.89	9.95
Total	100.00	100.00	100.00	100.00



**Fig. 4.** SEM images of the samples: (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4



**Fig. 5.** Photodegradation rate of a methyl orange solution under UV radiation

### CONCLUSIONS

This study confirmed that the photocatalytic activity of TiO<sub>2</sub>/CoO nanocomposite powders can be improved using additives. Four samples of TiO<sub>2</sub>/CoO nanocomposites were 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. It follows from the XRD results that the anatase phase was the dominant phase in all samples and sample 4

showed the best photocatalytic activity. The SEM images indicated that in presence of HPC, both the density of the particles and their size distribution were improved. The results showed that the photocatalytic activity of the nanocomposites increased in presence of additives and HPC was more effective than others.

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#### ПОЛУЧАВАНЕ, ОХАРАКТЕРИЗИРАНЕ И ФОТОКАТАЛИТИЧНА АКТИВНОСТ НА НАНОКОМПОЗИТИ ОТ TiO<sub>2</sub>/CoO

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(Резюме)

Получени са нанокomпозити от TiO<sub>2</sub>/CoO по метода зол-гел с и без добавки, като карбоксиметил-целулоза (СМС), поливинилпиролон (PVP) и хидроксипропил-целулоза (HPC). Структурата и свойствата им са охарактеризирани с FT-IR, XRD, SEM и EDAX. Изследвана е фотокаталитичната активност за отстраняване на органични замърсители при облъчване с UV-лъчи. Резултатите показват, че добавките имат значителен ефект върху разпределението на частиците по размери и фотокаталитичната активност на нанокomпозитите. SEM-изображенията показват, че размерите на частиците в праховете от TiO<sub>2</sub>/CoO с добавки са по-малки от тези в проби без добавки.