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Co-doped TiO_2 nanostructures as a strong antibacterial agent and self-cleaning cover: Synthesis, characterization and investigation of photocatalytic activity under UV irradiation

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ABSTRACT

The aim of this work was synthesis and investigation of various properties of Co-doped titanium dioxide nanostructures. However, dopant has no effect on XRD pattern of the host but it can influence on the various characteristics of host such as optical and electrical properties. The results of optical properties showed that absorption energy of TiO_2 decreases in presence of cobalt as dopant. Red-shift in absorption spectrum that may be due to the excitation of 3d electrons of Co ions to the conduction band of TiO_2 can be considered as a strong evidence to confirm the presence of Co as dopant in TiO_2 lattice. Photocatalytic activity of products was examined by degradation of three dyes including: Acid Red 1 (A.R.1.), Reactive Blue 21 (R.A.21.) and Acid Blue 74 (A.B.74.) under UV irradiation and antibacterial activity of this product was tested by inhibition of the growth of three bacteria: *Pseudomonas aeruginosa*, *S. aureus* and *E. coli*. High percent of dye degradation and decreasing the contact angle of surfaces in the presence of this product as a cover confirm that Co-doped TiO_2 can be used as a self-cleaning cover on various surfaces. The antibacterial activity is another property of this product as an antibacterial agent.

1. Introduction

Recently, environmental pollution has been a global problem, so researchers try to represent many ways for decreasing the pollutants [1–5]. One of the most important sections of this problem is water pollution that impresses healthy of human, animal and plants [6–9]. Textile dyes and organic materials that are entered to water by industries are examples of the pollutant sources, so removing of them is one of the most important necessities [10–14]. Photocatalysts are compounds that can decompose organic molecules and degrade textile dyes by photolysis process. Photolysis, chemical process by which molecules are broken down into smaller units through the absorption of light [15]. However, importance of photocatalysts led to many compounds with photocataytic properties were synthesized in recent years, but preparation of photocatalyst with good performance and the high yield is a challenge, up to now. Synthesis of photocatalysts in nanoscale, doping and preparation of nanocomposites are ways for improvement of photocatalytic performance and changing the operating range [16,17]. In summary, everything that increases the ratio of surface to volume and decreases the electron-hole recombination process can increase photocatalytic yield.

Titanium dioxide is a useful semiconductor with many potential applications in various fields. One application of it is photocatalytic performance that was discovered by Fujishima's and Honda's [18]. This semiconductor has three phases that anatase phase with band gap about 3.2 eV represents more photocatalytic activity than the others [19]. The operating range of photocatalysts is determined by band gap. Band gap is measured by distance between valence and conduction bands. In photocatalysts, energy of the incident beam should be equal to this parameter that can excite the electron and transfer to conduction band. By considering the band gap of anatase phase, it is considered as a photocatalyst under UV irradiation. According to the studies, sunlight at Earth's surface is around 52 to 55% infrared (above 700 nm), 42 to 43% visible (400 to 700 nm), and 3 to 5% ultraviolet (below 400 nm) [20]. So, preparation of photocatalysts with exciting energy in visible range or changing the required energy for exciting the electrons can be useful for using the sun light in order to purging of water. Whereas energy conversion and storage is the big challenge in the modernized world, over these problem is very important for the improvement of catalytic and electrochemical technology [21–24]. Doping is one of the most common methods to change the required energy for exciting of electrons in photocatalysts [25]. Doping can decrease or increase this energy, this change depends on type of photocatalyst and dopants [26]. In this work, Co was used as dopants in TiO_2 nanostructures and the

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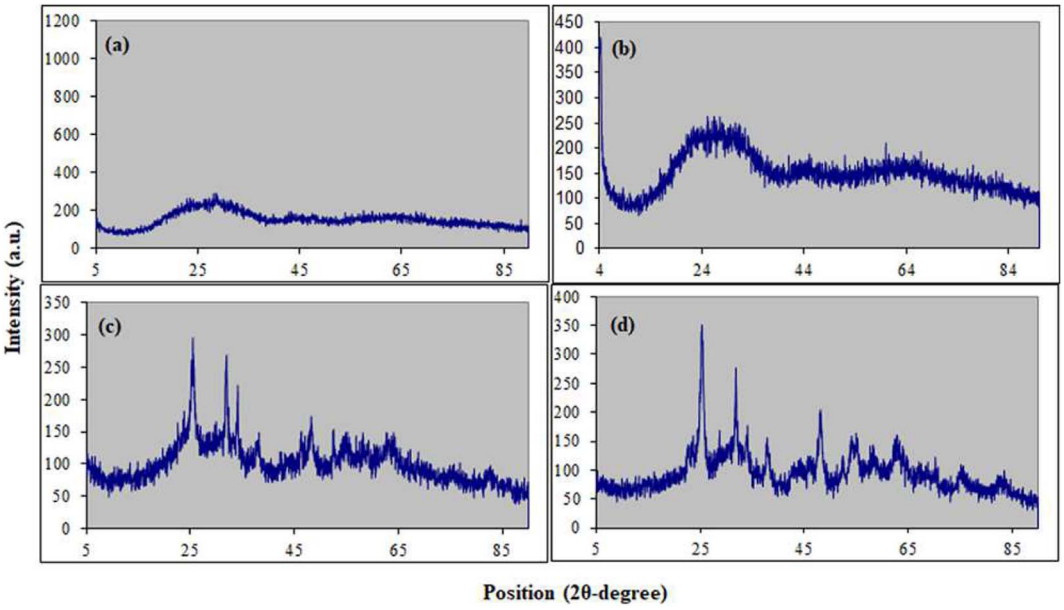

Fig. 1. XRD patterns of (a) sample synthesized without calcination and samples calcined at (b) 200, (c) 350 and (d) 500 °C, respectively.

products were characterized by various analyses. Also, antibacterial and photocatalytic activities of this product were investigated. According to the results, this product can be used as self-cleaning cover. Besides, this product indicates antibacterial activities through inhibiting the growth of Gram positive and Gram negative bacteria. This property confirmed the application of this product as an effective cover on various surfaces with self-cleaning and antibacterial properties that can be useful for surgery rooms or other places.

2. Experimental

2.1. Materials

Titanium tetraisopropoxide (TTIP, > 99%) and isooctane (> 99%) were purchased from Sigma-Aldrich. Cetyl trimethyl ammonium bromide (CTAB), cobalt acetate and ethanol were obtained from MERCK. Acid Red 1 (A.R.1), Reactive Blue 21 (R.B.21) and Indigo carmine (A.B.74) were obtained commercially.

2.2. Synthesis of Co-doped TiO_2 Nanostructures

The Co-doped TiO_2 nanostructures were synthesized according to that reported in ref. [3] as follows:

At the first, 10 mL of TTIP was added to the emulsion that included 10 of mL isooctane, 2 mL of ethanol and 2 mL of CTAB solution (0.2 mol/L) to reach to R = 0.2 (R = V (aqueous): V (oil)). Next, 0.35 g of $Co(OAc)_2{\cdot}6H_2O$ as dopants source was dissolved in 2 mL water and was added dropwise to above emulsion in a sonicator bath at 60 °C for 2 h. Afterward, the particles produced within the as-formed nano-reactors were washed with ethanol and water to eliminate the organic phase and surfactants residuals. The as-prepared nanoparticles were dried at 100 °C in a vacuum oven. In order to investigate the effect of calcination temperature on morphology and purity of the products, the sediments obtained from previous step were calcined under three different temperatures: 200, 350 and 500 °C for 1 h. The products were characterized by various analyses such as: SEM (scanning electron microscopy), XRD (X-ray powder diffraction), DRS (diffuse reflection spectra) and TEM (Transmission electron microscopy).

2.3. Preparation of Sample for Photocatalytic Tests

The photocatalytic activity of Co-doped TiO_2 nanostructures was studied by degradation of dyes including: Acid Red 1 (anionic dye), Reactive Blue 21 (cationic dye) and Acid Blue 74 (anionic dye) as organic pollutants. The photocatalytic reactions were carried out under ultraviolet (UV) irradiation. The photocatalytic degradation reactions were performed in a quartz photocatalytic reactor and carried out with 1 L of 20 ppm dye solution containing 0.02 g of Co-doped TiO_2 as a photocatalyst. This mixture was aerated for 30 min to reach adsorption equilibrium. Then, the mixture was placed inside the photoreactor in which the vessel was 40 cm away from the UV and visible source. The quartz vessel and light sources were placed inside a black box equipped with a fan to prevent UV leakage. The photocatalytic tests were done at room temperature and the mixtures were exposed to radiation. During irradiation, agitation was maintained to keep the suspension homogenous, and at certain reaction intervals, 10 mL of sample was taken, centrifuged and analyzed by UV–Vis spectrophotometer.

2.4. Characterization

The XRD of products was recorded by a Rigaku D-max C III XRD using Cu Kα radiation. SEM and TEM images were obtained on Philips CM120. UV–visible absorption spectra were also measured by a Cecil CE9200 spectrophotometer. The source of UV and visible light to perform photocatalytic tests were OSRAM HTC 400 W (λ = 315–400 nm) and a 300 W xenon lamp with a 420 nm cut-off filter (λ > 420 nm), respectively.

3. Results and Discussions

3.1. XRD Patterns

The XRD patterns of sample without calcination and samples calcined at 200, 350 and 500 °C are shown in Fig. 1(a–d), respectively. As shown, the calcination temperature can influence on crystallinity of products. In Fig. 1a, there were no diffraction lines, so the amorphous phase was detectable. However, intensity of peaks in Fig. 1b was more than the Fig. 1a but it didn't show any phases and crystalline structures. By increasing the calcination temperature to 350 °C, diffraction lines were appeared (Fig. 1c). According to this pattern, all of diffraction