Cobalt doped TiO_2 nanosheets: an efficient visible-light-driven photocatalyst for degradation of Tetracycline antibiotic

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Abstract

TiO_2 nanosheets (TNs) and cobalt doped TiO_2 nanosheets (Co-TNs) were prepared by one-pot hydrothermal method**.** The synthesized samples were identified by various analyses including PXRD, FESEM/EDX, elemental mapping, DRS and Raman spectroscopy. The synthesized samples were used to remove of antibiotic tetracycline (TC) under visible and UV irradiation. In the presence of 100 mg TNs and Co-TNs, the percentage removal of 100 mLTC (30 mg/L) after 180 minutes of visible light irradiation was 36% and 60%, respectively and it was 77% and 68% respectively after 140 minutes of UV irradiation. Co-TNs exhibited the higher photocatalytic activity due to faster electron-hole separation and extend the absorption spectrum of TiO_2 into visible region by cobalt dopant.

Keywords: TiO_2 nanosheets,Cobalt, Tetracycline, Photocatalytic removal.

1. Introduction

The water pollution has become a serious problem and the removal of different pollutants such as heavy metals, organic dyes, radionuclides, oils, and so pharmaceutical hazardous components has become a hot topic. Also, the presence of antibiotics including TC in water sources is a public health concern and their removal is a challenge for scientific community. Recently, advanced oxidation processes (AOPs) utilizing heterogeneous photocatalysis using photocatalysts such as zinc oxide (ZnO) and titanium dioxide (TiO_2) has attracted much attention for degradation of hazardous organic compounds[1]. Among various photocatalysts, there is a meaningful attention on using TiO_2 because of low toxicity, chemical stability, insolubility in water, and low price. However, because of the wide band gap of TiO_2 (3.2 eV), it can be hardly activated in the visible region and this is the main drawback. The high tendency of photogenerated electrons and holes to recombine rather than the contribution in the formation of reactive radicals is another limiting factor controlling photocatalytic efficiency of TiO_2. Several attempts have been performed to enhance the photocatalytic activity[2]. Doping of TiO_2 photocatalysts by metal ions can improve the interfacial charge-transfer efficiency, utilize wider spectral range of visible light and retard the recombination of charge carriers. Among metal ions, Co^{2+} is an efficient TiO_2 dopant because of its optically active nature; doping Co^{2+} could boost the light response and improve the activity of TiO_2 under visible light. Recently, cobalt doped TiO_2 photocatalysts have shown significant performance for degradation a wide range of organic pollutants[3].In the present work, we synthesized TiO_2 nanosheets (TNs) and cobalt doped TiO_2 nanoheets (Co-TNs) by one-step hydrothermal synthesis method, characterized the structural and morphological properties by different analyses and used the prepared samples for photocatalytic removal of Tetracycline (TC) antibiotic under visible light and UV irradiation.

2. Experimental

2.1. Materials

Tetraisopropyl orthotitanat (TIP) (Merck No. 8.21895), anhydrous ethanol (Merck No. 818760), Cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$) (Merck No: 102539) and hydrofluoric acid (Merck No: 100337) purchased from the US Research Nanomaterials, Inc. Company, were used for photocatalyst preparation. Tetracycline hydrochloride (Batch No.161026) was selected as a probe molecule for photocatalytic experiments; it was purchased from Hakim Pharmaceutical Company.

2.2. Synthesis of cobalt doped TiO_2 nanosheets (Co-TNs)

We used mentioned procedure in Ref [4]with some modification for samples preparation.

13.0 mL anhydrous ethanol and 89 mg $CoCl_2.6H_2O$ were added into the beaker and the suspension was stirred for 5 min. Then, 1.75 mL TIP and 0.2 mL hydrofluoric acid were added into the beaker while stirring. After 3 min, the dispersion was transferred into a Teflon lined autoclave. The hydrothermal reactionwas carried out for 24 h at 180°C. After reaction, the system was filtered and washed 3 times. Also, we synthesized pure TiO_2 nanosheets (TNs) with similar method in the absence of cobalt source.

2.3. Photocatalytic performance

In each photocatalytic degradation experiment, the beaker containing the optimum amount of photocatalyst and 100mL TC aqueous solution (30 mg/L) was stirred first for 30 min, in the dark, for adsorption/desorption equilibrium. After the time, the lamp turned on for 180 min for photocatalytic degradation. The visible light source was Halogen, ECO OSRAM 500W lamp (350-800 nm, with a 400 nm cut-off filter). After predetermined intervals, 2mL of solution was taken, filtered and analyzed using Rayleigh UV-2601 UV/VIS spectrophotometer (λ_{max}=355 nm).

3. Results and discussion

3.1. Characterization of the samples

3.1.1. X-ray diffraction analysis

The crystalline phases of the synthesized samples were characterized by PXRD analysis (Fig. 1). The major diffractions were observed at 2θ=25.4°, 37.8°, 48.0°, 54.4°, 62.5°, 69.3°and 75.2° that well matched to the anatase phase of TiO_2 (JCPDS No. 21-1272)[5], demonstrating the high crystallinity of the samples and successful formation of anatase phase through the one-step hydrothermal synthesis. In PXRD pattern of cobalt-containing TiO_2 nanosheets (Fig. 1b), no other crystalline phases of cobalt was observed (for example Co_3O_4 at 2θ=38.55 and 74.12 based on the PDF#42-1467) [6] . Therefore, considering the sensitivity of PXRD, the results confirmed the high homogeneity of doping and the absence of secondary phases in the sample. Also, the diffractions intensity of the Co-TNs sample were smaller than the un-doped nanosheets (Fig. 1a) related to the strong interaction between cobalt ions and TiO_2 support [7].

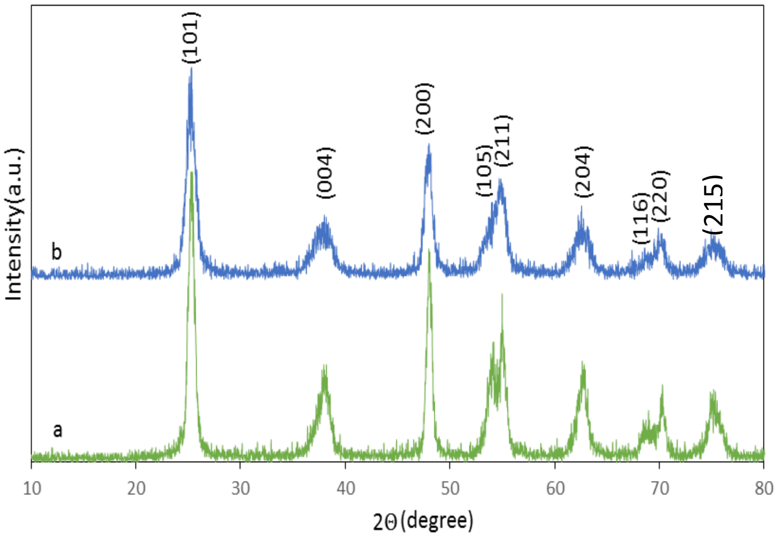

Fig. 1. The powder XRD patterns of a)TNs and b)Co-TNs

3.1.2. Raman spectroscopy

The Raman spectra of the prepared samples are shown in Fig. 2. The main Raman bands of the anatase phase at 145, 390, 514, and 632 cm^{-1} are observable for all the samples[8]. Similar to PXRD results, the peaks intensity of the cobalt-containing sample were lower than the un-doped nanosheets related to the strong interaction between cobalt ions and TiO_2 nanosheets and again confirming the doping of cobalt into TNs lattice.

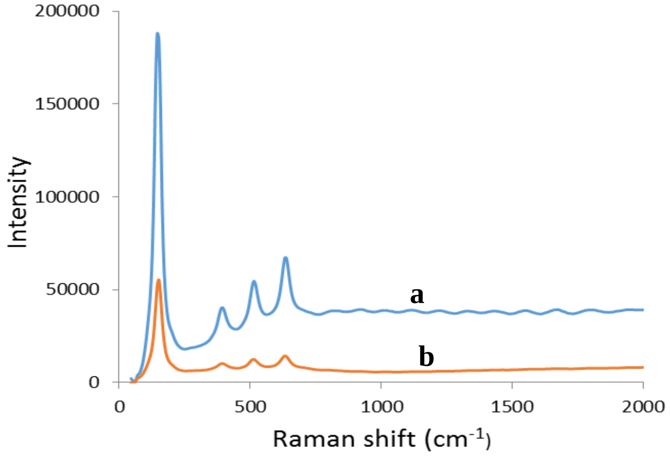

Fig.2. The Raman spectra of prepared samples a)TNs and b)Co-TNs

3.1.3. FESEM/EDX/ Elemental Mapping analysis

The field emission scanning micrographs, EDX patterns and the elemental mapping images of the prepared samples are presented in Fig.3. The smaller dimensions of nanosheets after cobalt doping compared to the pure TNs is the result of FESEM images. Cobalt addition into titania probably hinders the growth of TiO_2 nanosheets. It seems that cobalt cations form complex with the TiO_2 surface oxygen, hence, suppress the growth of TiO_2 crystallite[9].

The EDX patterns of the synthetized samples show two peaks around 0.2 and 4.5 keV related to TiO_2. The peaks of cobalt are appeared at different energies including 0.6, 6.9 and 7.5 keV in Fig.3b [9]. Therefore, the presence of cobalt atoms in the Co-TNs sample was confirmed by EDX results.

According to the elemental mapping images , the distribution of titanium atoms are similar to sheet structure and cobalt atoms are homogeneously distributed in the TiO_2 nanosheets lattice. This shows excellent interaction of cobalt and TiO_2 nanosheet over the hydrothermal synthesis procedure.

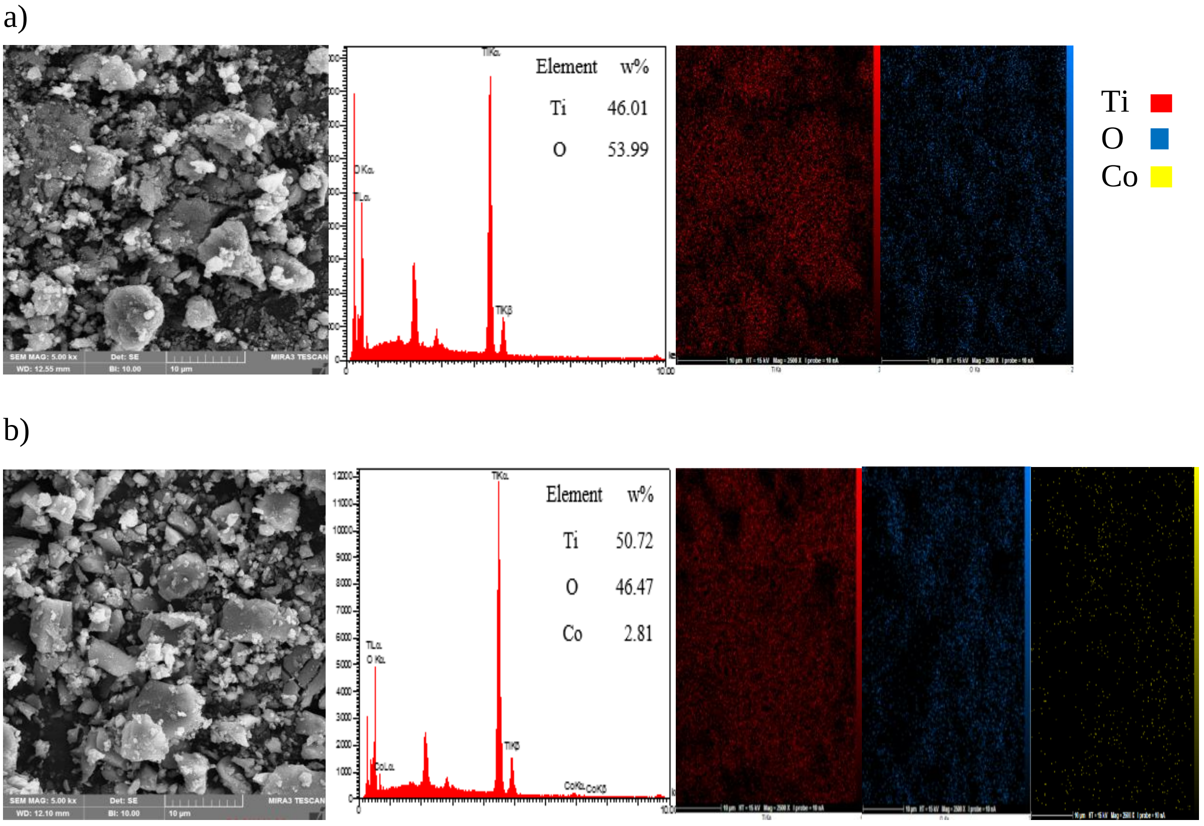

Fig.3. The FESEM , EDX and Elemental mapping results of a)TNs and b)Co-TNs

3.1.4. Diffuse reflectance spectroscopy (DRS)

The diffuse reflectance UV-vis spectra of the prepared samples are displayed in Fig.4A. The absorption spectrum of pure TiO_2 (TNs) consists of single narrow intense absorption around 200-400 nm, whereas, the spectrum of the Co-TNs consists some additional absorption peak at around 700 nm. In addition, this phenomenon may be the reason for the better photocatalytic performance of this sample under visible light than TNs[10].

Fig. 4B shows the Kubelka-Munk curves for the synthesized samples. According to Fig.4B the band gap energy of the TNs and Co-TNs samples are 3.0 and 2.6 respectively that show the band gap energy of the Co-TNs is slightly smaller than the TNs. This may be due to the 3d electrons migration of transition metals to the conduction band of TiO_2, in fact ,suggesting the successful introduction of Co^{2+} into the lattic of TiO_2 nanosheets [11].

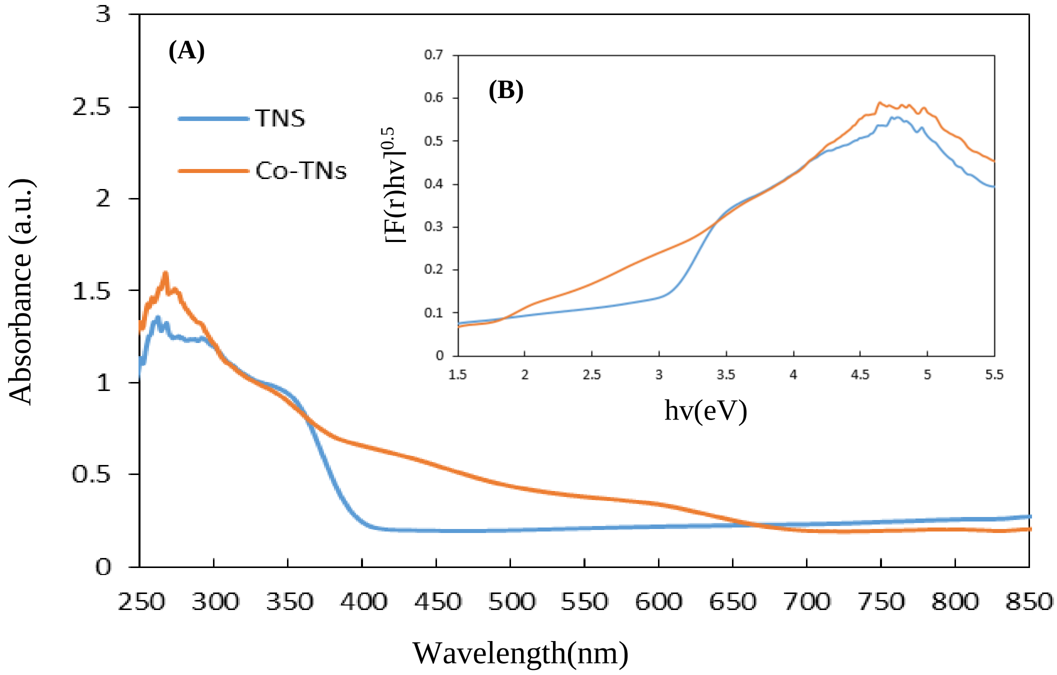

Fig.4. A) Diffuse reflectance spectra, B) Kubelka-Munk curves

3.2. Photocatalytic removal of tetracycline (TC)

To investigate the photocatalytic performance of the synthesized samples, based on the experiments performed, the Co-TNs sample showed better photocatalytic performance after 180 minutes under visible light irradiation with 60% degradation compared to pure TNs (36%). This suggests that doping cobalt into TiO_2 contributes to narrowing of the band gap of TiO_2 to take advantage of visible light. Also, the TNs sample showed 77% degradation after 140 minutes under UV irradiation, which is better than the doped sample (68%). The degradation results under UV light in Fig.5B show a better relative performance of the un-doped TiO_2, which is simply because TiO_2 is most efficient under UV light. These results in turn suggest that the doping of cobalt helped the absorption of visible light as designed, leading to a higher reaction efficiency[4].

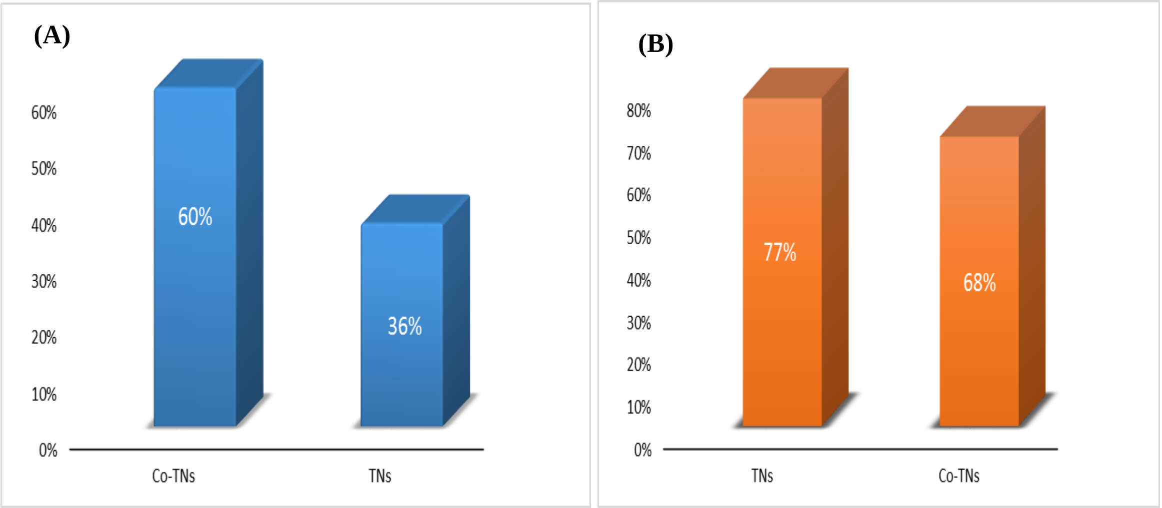

Fig.5. Photodegradation of TC in the presence of synthesized samples under A) visible light B)UV light

4. Conclusions

In summary, in the present work, cobalt doped TiO_2 nanosheets successfully synthesized through a one-pot hydrothermal method. It was observed that the Co-TNs sample presented an increased photocatalytic performance in degradation of tetracycline (TC) under visible light and exhibited expansion in the spectral response range shifted to the visible area. Tetracycline degradation percentage in the existence of TNs and Co-TNs after 180 min irradiation of visible light were obtained equal to 36% and 60% respectively. This enhancement can be attributed to the special properties of cobalt dopant that promoted separation of photogenerated carriers and extended the absorption spectrum of TiO_2 into visible region.

Acknowledgements

The authors are thankful to the financial support of University of Tehran for supporting this research.

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