Visible Light Active Nitrogen and Cobalt Co-doped TiO_2 Nanoparticles: Synthesis, Characterization and Photocatalytic Activity

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Research Article

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Abstract

A facile and room temperature approach to synthesize pure TiO_2 and different variants of nirogen and cobalt co-doped TiO_2 (CoN-TiO_2) catalysts is reported in this study. The successful synthesis and crystalline phase analysis was carried out via X-ray diffraction (XRD) which confirmed anatase phase with tetragonal structure. The spherical morphology, uniform size distribution in the range of 20-40 nm and presence of dopants in final product were validated by scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDS). Diffused reflectance spectroscopy (DRS) is deployed for study of optical properties. A reduction in band gap from 3.2 eV for pure TiO_2 nanoparticles to 2.34 eV for the 7 wt.%. doped CoN-TiO_2 was observed. The photocatlytic activity of pure TiO_2, and CoN-TiO_2 nanoparticles was studied against methyl orange.The photocatlytic activity of CoN-TiO_2 was almost double as compared to undoped TiO_2 which proves these catalysts to be very efficient and potential candidate for the wastewater treatment at industrial level.

Introduction

The essence of water in our lives can be understood from the fact that no living being can survive on the earth without water. However, water pollution has become a global concern because of the increased addition of different industrial contaminants to drinking water reservoirs. This polluted water is harmful to human beings, plants, animals and other aquatic life(Owa 2013). Out of different methods for wastewater treatment, photocatalysis has proven to be quite successful for converting toxic organic contaminants to fewer poisonous compounds(N. M. Soboleva 2007). In the past few decades, nanoscience has reached top benchmark in the applied sciences. Nanomaterials can have applications in almost every field of life, including electronics, medical, antimicrobial, water treatment, even in typical households(M. Qammar 2019, Findik 2021, Javier Lou-Franco 2021, Zhu 2021). Among different nanomaterials, which have been used as photocatalysts, TiO_2 is the most efficient due to its non-toxicity, chemical and photostability(Sopyan Iis 1994, I.M. Arabatzis 2003, Yin Zhao 2007). 1n 1958, Kennedy and his team investigated the photo-adsorption of oxygen onto the surface of TiO_2. They concluded that the electrons generated during the photoexcitation process could reduce oxygen, thus enabling the reduced oxygen to adsorb on the surface of TiO_2. In 1964, Kato and Mashio also discovered that TiO_2 could be used in different photocatalytic activities such as the oxidation of hydrocarbons and alcohols to produce hydrogen peroxide. Afterwards, Mclintock and Ritchie also studied the photocatalytic activities of TiO_2 towards the oxidation of ethylene and propylene. From this study, they concluded that organic compounds could be completely oxidized to carbon dioxide and water. Subsequently, various studies were reported on TiO_2 as a photocatalyst towards the degradation of different organic compounds(Kazuhito Hashimoto 2005).

However, one drawback associated with TiO_2 is its significantly wide band gap which restricts its utility as a photocatalyst in visible light range. TiO_2 is doped with different metals and non-metals to reduce

2019). Different dopants like Fe, Mn, Cr, and Co help to

improve the absorption range of TiO_2 and prevent electron-hole recombination(Chumanov 2005, M.A. Barakat 2005, Chien-Cheng Pan 2006, Ye Cong 2007, Q.R. Deng 2011). Doping of TiO_2 with different non-metals i.e., N, S, F, and C, is quite successful for tuning the absorption over a broad range of spectrum(Di Li 2005, Ye Cong 2007, P.V.R.K. Ramacharyulu 2014, Penghui Shao 2015). TiO_2 is also co-doped with different metals and non-metals. The photocatalytic ability of these co-doped catalysts was improved as compared to an un-doped and mono-doped TiO_2 (Guidong Yang 2010, M. Hamadanian 2010, R. Jaiswal 2015, Patil S. Basavarajappa 2020).

Hui Li and his team synthesized a variety of nitrogen-doped TiO_2 catalysts and tested their photocatalytic activity against methyl orange. Among different N-TiO_2, TON-1 (N:Ti molar ratio= 36.47) showed the highest degradation efficiency (2.98 mmol g−1h−1) as compared to other N-TiO_2 and un-doped TiO_2 (<0.5 mmol $g^{-1}h^{-1}$). This high photocatalytic activity of N-TiO_2 that can result from the optimal volume ratio of ethylene diamine to sol is conductive enough to allow the formation of sufficient nitrogen-centres and oxygen vacancies, which ultimately increase the number of Ti^{+3} ions(Hui Li 2015). Anupama Chanda and his team studied the consequences of cobalt doping on structural and optical properties of TiO_2 nanoparticles. The crystallite sizes of un-doped TiO_2 samples were higher than single, triple, and seven-layered TiO_2 films, which indicated reduced particle size of cobalt-doped TiO_2 than un-doped TiO_2. Un-doped TiO_2 showed maximum transmittance of ~84%, which remained uniform throughout the visible region, whereas single-layered cobalt-doped TiO_2 showed maximum transmittance of ~92%, which started decreasing afterwards(Anupama Chanda 2021).

To the best of our insight, a limited work has been stated on N, Co co-doped TiO_2 (Penghui Shao 2015) In this work, we have successfully synthesized pure TiO_2 and N, Co co-doped TiO_2 with variable dopant ratios via the sol-gel route. All the catalysts were schematically analysed by XRD, SEM, and UV- VIS DRS. A comparative photocatalytic activity among pure and doped catalysts was performed against methyl orange, which showed an improved photocatalytic potential of nitrogen and cobalt co-doped TiO_2.

Results And Discussion

We have deployed a facile, economical, reproducible, and room temperature synthesis by using sol gel method for the successful synthesis of pure and 0.5, 1, 2, 6 and 7-wt.%. nitrogen, cobalt co-doped TiO_2 nanoparticles. They were tagged as CoN-TiO_2-1, CoN-TiO_2-2, CoN-TiO_2-3, CoN-TiO_2-4 and CoN-TiO_2-5. Pulverization at high temperature such that 450 °C leads to the improvement of the crystallinity and removal of all organic residues from the sample and grinding helped in breaking the lumps and the agglomerates. Fig. 1 shows the XRD spectrums of the synthesized catalysts. The peaks located at 25.3 °, 37.8 °, 48.06 °, 55.1 ° and 62.7 ° correspond to (101), (004), (200), (105), and (204) can be well indexed with the already reported JCPDS cards 96-900-908214 to 96-900-908214. They confirm the anatase phase formation(S. Mugundan 2015, Dongdong Liang 2019).

As we increased the concentration of dopant the peak broadening is observed but till wt.% 7% doping no significant additional peak is observed. Scherrer equation ($D=K\lambda/(\beta \cos \theta)$) was used to calculate crystallite size of each catalyst (PATTERSON 1939). The crystallite sizes of all catalysts have been summarized in the Table 1.

Table 1
Crystallite sizes of all samples

Sample Code	Crystallite size (nm)
TiO_2	26
CoN-TiO_2-1	10
CoN-TiO_2-2	10
CoN-TiO_2-3	9.7
CoN-TiO_2-4	8.75
CoN-TiO_2-5	8

SEM was performed to determine the morphology and particle size of the catalysts. The average particle sizes of doped catalysts were below 40 nm. SEM images of undoped TiO_2, and all variants of CoN-TiO_2 have been shown in the Fig. 2.

It can be observed from these images that the morphology of TiO_2 remain intact even after doping with nitrogen and cobalt. In case of undoped TiO_2, the average particle size is ~60 nm, and particle size ranges from 20- 40 nm for doped catalysts. The decrease in the particle size of the catalysts after doping are in the consensus with the decrease in the crystallite size mentioned in the Table 1. The spherical morphology of these nanoparticles is important for improving the photocatalytic properties of the catalysts (R. Lakshmi Narayana 2011). As the dopant concentration is too low to be detected in XRD, EDS is used to testify the successful doping. The EDS spectrum for each sample is shown in Supplementary information (SI) Fig. S1. and relative atomic wt. % of each element in every sample is summarized in Table 2.

Table 2
Atomic percentage of constituent elements in catalysts

Sample Code	Atomic % of Ti	Atomic % of O	Atomic % of Co
TiO_2	24.33	75.77	----
CoN-TiO_2-1	27.83	72.03	0.13
CoN-TiO_2-2	27.26	72.46	0.27
CoN-TiO_2-3	25.75	73.65	0.60
CoN-TiO_2-4	18.07	79.23	2.70
CoN-TiO_2-5	24.60	72.64	2.76

Every element shows its own characteristic peak in EDX spectra. We can clearly see the signal for titanium, cobalt, and oxygen in the EDX spectra of samples. DRS was carried out to calculate the band gap energy co-doped catalysts. As the band gap energy of the pure TiO_2 nanoparticles is 3.2 eV, so they absorb in the UV region only. After doping TiO_2 with nitrogen and cobalt, the band gaps were reduced, thereby shifting the absorption of TiO_2 in the visible region. The band gap energies for all catalysts along with Tauc's plots have been presented in the Fig. 3.

The photocatalytic potential of the catalysts was measured by using them for photodegradation of methyl orange. As pre-adsorption of dye is important for effective charge transfer and affects the photocatalytic degradation rate, therefore all the samples were kept in dark for two hours to attain adsorption-desorption equilibrium. After that, the solutions were kept under LED lamp with continuous stirring. All the experiments were conducted under visible light and ambient conditions. Aliquots of 5 mL were taken after every hour and after centrifugation, their absorbance was measured by using UV-VIS spectrophotometer. The decrease in absorbance showed that concentration of methyl orange was also decreasing as shown in Fig. S2. Activity and efficiency of all catalysts against degradation of methyl orange have been shown below in Fig. 4 and 5 respectively.

It can be seen from above figures that undoped TiO_2 showed lowest degradation efficiency than other catalysts. Furthermore, nitrogen and cobalt co-doping improved the photocatalytic performance of TiO_2. The photo degradation efficiency of the catalysts has been shown below in the Table 3.

Table 3
Comparison of degradation efficiency of all catalysts

Sample	Degradation Efficiency (%)
TiO_2	32
CoN-TiO_2-1	59
CoN-TiO_2-2	65
CoN-TiO_2-3	69
CoN-TiO_2-4	75
CoN-TiO_2-5	80

The degradation rate calculation parameters for methyl orange have been shown in Table S1. This table shows that absorbance and concentration of methyl orange was decreasing with time. Among all catalysts the highest photocatalytic activity was observed for CoN-TiO_2-5. This improvement in photocatalytic potential of all the co-doped catalysts can be the result of decreased particle size due to the introduction of dopants into TiO_2. Reduction in particle size results in an increase in surface area, which eventually improves adsorption of dye on the surface of catalyst, and hence increase the photocatalytic activity. In addition, anatase phase was dominant in all samples which is found to be the most active phase in the photocatalytic degradation process. Along with that, intense absorption of light in the visible range and a red shift in band gap energy resulted in generating more charge carriers thereby increasing the efficiency of photocatalytic process. More generation of hydroxyl free radicals means more degradation of methyl orange. Low degradation efficiency of undoped TiO_2 can be the result of high band gap (3.17 eV), which produces a smaller number of OH free radicals and therefore less degradation of methyl orange occurs.

Mechanism of Methyl orange degradation

The mechanism of photodegradation of methyl orange was explained by Akpan and Hameed in 2009 (U.G.Akpan 2009). According to this mechanism, when a photon of light ($hv \geq E_g$) falls on catalyst, valance electrons are excited to conduction band leaving behind the holes in the valence band. These photogenerated electrons react with the oxidant to produce a reduced product, and photogenerated holes react with a reductant to produce an oxidized product. In case of methyl orange degradation, the photogenerated electrons can either reduce the dye or can produce superoxide radical anion O^{2-} by reacting with water present on the surface of TiO_2. The photogenerated holes can either directly oxidize the methyl orange or can produce hydroxyl free radical by reacting with water or OH^-. The $OH^{\bullet}$ is such a strong oxidizing agent that it can produce mineral end products by complete oxidation of methyl orange.

According to this mechanism, most of the reactions occurring during the photodegradation of methyl orange can be explained by following equations (Liming Bai, et al. 2019).

$$CoN - TiO_2 + hv \rightarrow h^+ + e^-$$

1

$$h^+ + OH^- \rightarrow \bullet OH$$

2

$$h^+ + H_2O \rightarrow \bullet OH + H^+$$

3

$$e^- + O_2 \rightarrow \bullet O_2^-$$

4

$$H_2O + \bullet O_2^- \rightarrow HO_2\bullet + OH^-$$

5

$$HO_2^{\bullet} + e^- + H_2O \rightarrow H_2O_2 + OH^-$$

6

$$H_2O_2 + \bullet O_2^- \rightarrow \bullet OH + H^+$$

7

$$\bullet OH + Dye \rightarrow CO_2 + H_2O$$

8

$$\bullet O_2^- + Dye \rightarrow CO_2 + H_2O$$

9

Photodegradation Kinetics

The order of reaction was determined for CoN-TiO_2-5 by plotting a graph between -ln C_t/C_o versus time and has been shown below in Fig. 6.

The relationship between concentration and time can be explained by following equation

$$-\ln(C_t/C_o) = K_{app}t$$

Where C_t is the concentration of methyl orange at a particular time, C_o is the initial concentration of methyl orange, and k_{app} refers to apparent reaction rate constant. The slope of the graph indicated the apparent reaction rate constant (K_{app}) and the linearity of graph represents that the reaction is pseudo first order.

Experimental

Materials and reagents used

Titanium (IV) tetraisopropoxide (99.999%), urea (99%), cobalt (II) nitrate hexahydrate (98%), nitric acid and 2-propanol were procured from Sigma Aldrich. All chemicals were used as it is, without any purification.

Samples preparation

Typical sol gel route was deployed for the synthesis of samples (Dongdong Liang 2019). A solution comprising of 5 mL of Titanium (IV) tetraisopropoxide (TTIP) and 6 mL of 2-propanol was labelled as A. An aqueous solution of HNO_3 (pH=2) was designated solution B. Solution A was added dropwise into solution B along with vigorous stirring. The mixture was stirred overnight at room temperature. Resulting product was dried in rotary evaporator and annealed at 450°C for 4 hours in the furnace followed by the 60 min. grinding.

For nitrogen, cobalt co-doping of TiO_2, urea was added to solution B and different amounts of cobalt nitrate were added to solution B. Just like before, the solution A was added to solution B followed by overnight stirring. The solvent from resulting product was evaporated prior to calcination and grinding. The obtained powder was of green colour and darkening of colour was observed with the increase in dopant concentration. As prepared samples were subjected to characterization by XRD, SEM, EDX and UV-VIS spectroscopy.

Characterization

The crystal structure of pure and doped TiO_2 nanoparticles was characterized by using JEOL-JDX- II, X-ray diffractometer with Cu Kα radiation (λ = 0.1542 nm). Samples were scanned with an incident beam in scan range between 10-80° operated at 40 kV and 30 mA. The morphology, particle size and elemental composition were estimated via JEOL JSM-6460 equipped with energy dispersive X-ray spectroscopy (EDS) operated at 10 kV. Optical properties of the catalysts were studied by UV–VIS–NIR spectrophotometer and calibrated powdered barium sulphate ($BaSO_4$) was used as reference for the baseline correction.

Photocatalytic Degradation Experiment

As prepared catalysts were used for the photocatalytic degradation of pure methyl orange. An aqueous stock solution of 0.1 mM was prepared and further diluted to 0.01 mM. For the photocatalytic experiment, 50 ml solution was taken in a conical flask to which 50 mg catalyst was added. These solutions were allowed to stir for two hours to ensure adsorption-desorption equilibrium. Then solutions were kept under LED lamp with continuous stirring. All the experiments were performed at ambient conditions. After an interval of 60 min., 5 mL aliquots were taken and after centrifugation, their absorbance was measured by using UV-VIS spectrophotometer. The photocatalytic degradation rate of methyl orange was determined by using the following equation:

Degradation rate= $(1-A/A_0) \times 100\%$

Where A_o represents the initial concentration and A represents the concentration of methyl orange at a particular time.

Conclusions

In summary, visible light active nitrogen and cobalt co-doped TiO_2 catalysts were successfully fabricated through sol-gel method by using TTIP, 2-propanol, urea and cobalt nitrate. The ratio of nitrogen was fixed for all catalysts whereas cobalt doping was carried out in different ratios. Different characterization methods e.g., XRD, SEM, EDX and DRS confirmed the successful synthesis of all the catalysts. XRD results confirmed the presence of anatase phase in all the synthesized catalysts. SEM results showed that all the catalysts have their particle size <40 nm. UV-DRS results showed reduction in band gap from 3.21eV for undoped TiO_2 to 2.34 eV for CoN-TiO_2-5. It was found from the photocatalytic degradation experiment that all the nitrogen, cobalt co-doped catalysts showed superior performance compared to undoped TiO_2. However, CoN-TiO_2-5 showed highest degradation efficiency of 80% among all the catalysts, which can be the result of lowest band gap, decreased particle size and high surface area. These results show that nitrogen, cobalt co-doped TiO_2 has the potential to be used for photocatalytic degradation of harmful organic contaminants in polluted water.

Declarations

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Ethics approval and consent to participate

Consent for publication

Not applicable

Availability of data and materials

All the data generated or analysed during this study are included in this published article and supplementary information.

Conflicts of interest

Authors have no conflicts to declare.

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Author's Contributions

AroosaJaved: Investigator, Conceptualization Methodology, Investigation, Data Curation, Data Acquisition, Formal Analysis, Validation, Writing-Original Draft.

Memoona Qammar: Methodology, Formal Analysis Validation, Visualization, Writing-Review-Editing.

Rooha Khurram: Methodology, Formal Analyses, Writing-Review-Editing.

Zaib-un-Nisa: Methodology, Formal Analyses, Writing-Review-Editing.

Dr. Habib Nasir: Conceptualization, Project administration, Supervision, Funding acquisition.

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Figures

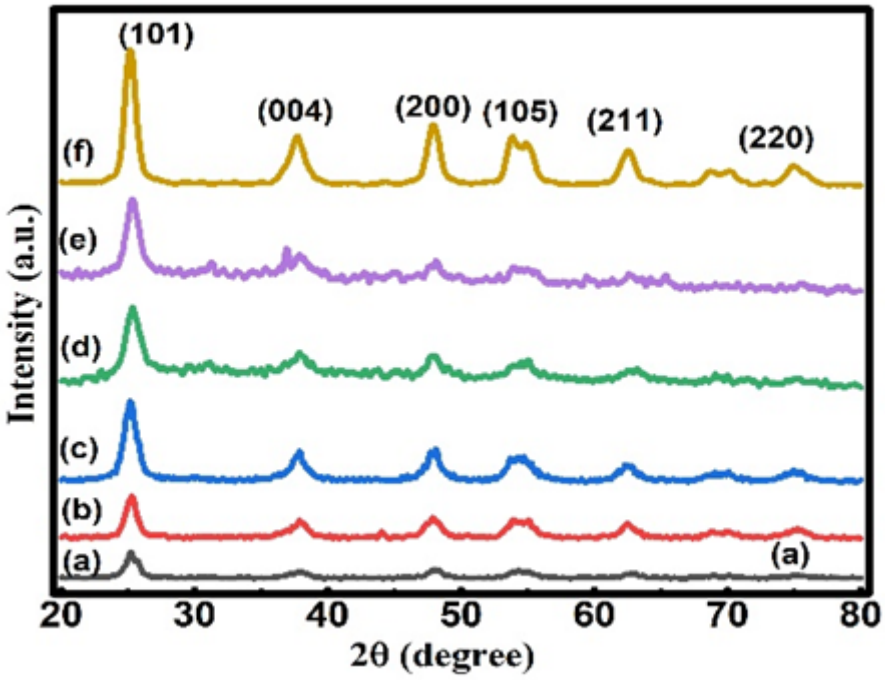

Figure 1

XRD Pattern of (a) TiO2 (b) CoN-TiO2-1 (c) CoN-TiO2-2 (d) CoN-TiO2-3 (e) CoN-TiO2-4 (f) CoN-TiO2-5

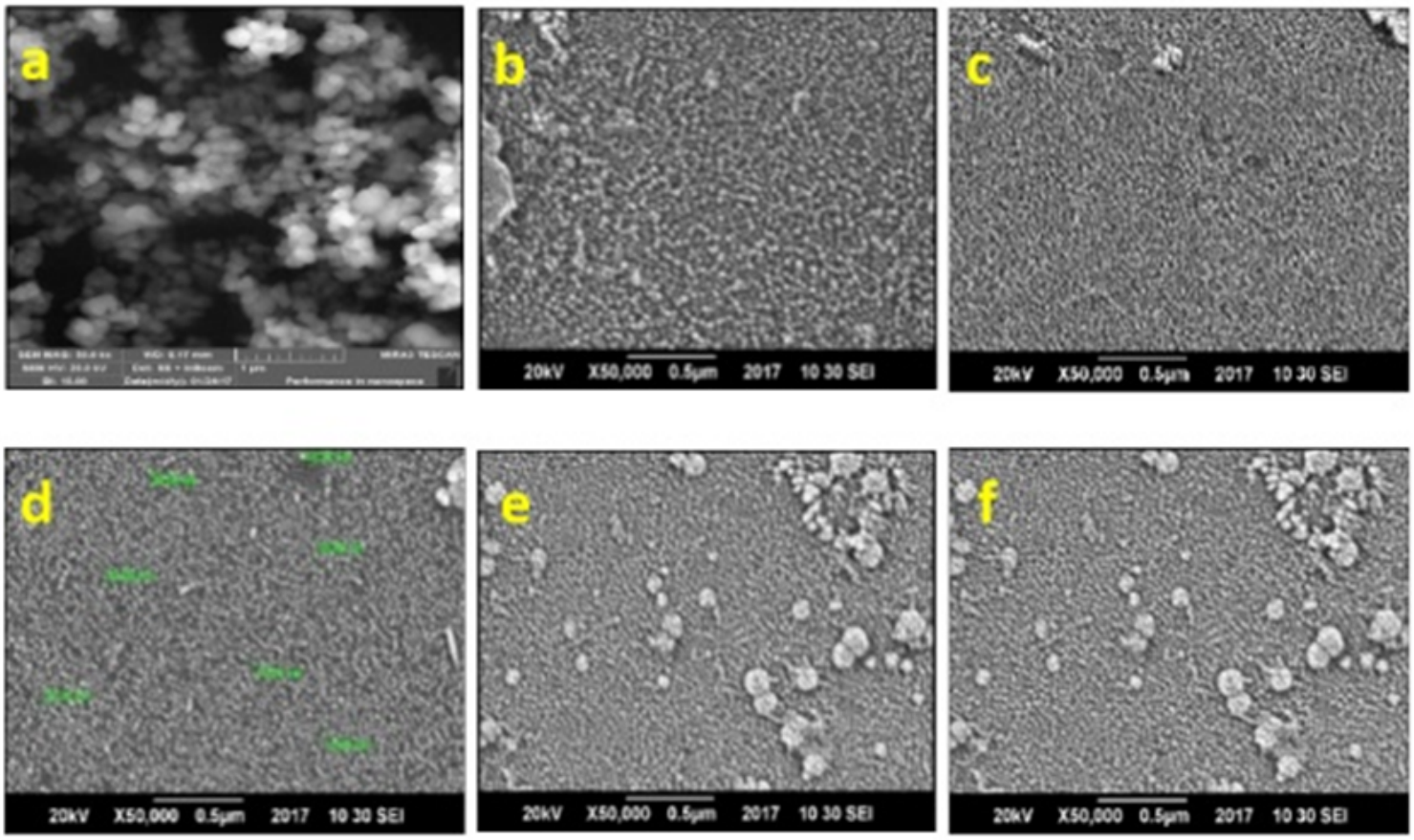

Figure 2

SEM micrographs of (a) Pure TiO2 (b) CoN-TiO2-1 (c) CoN-TiO2-2 (d) CoN-TiO2-3 (e) CoN-TiO2-4 (f) CoN-TiO2-5

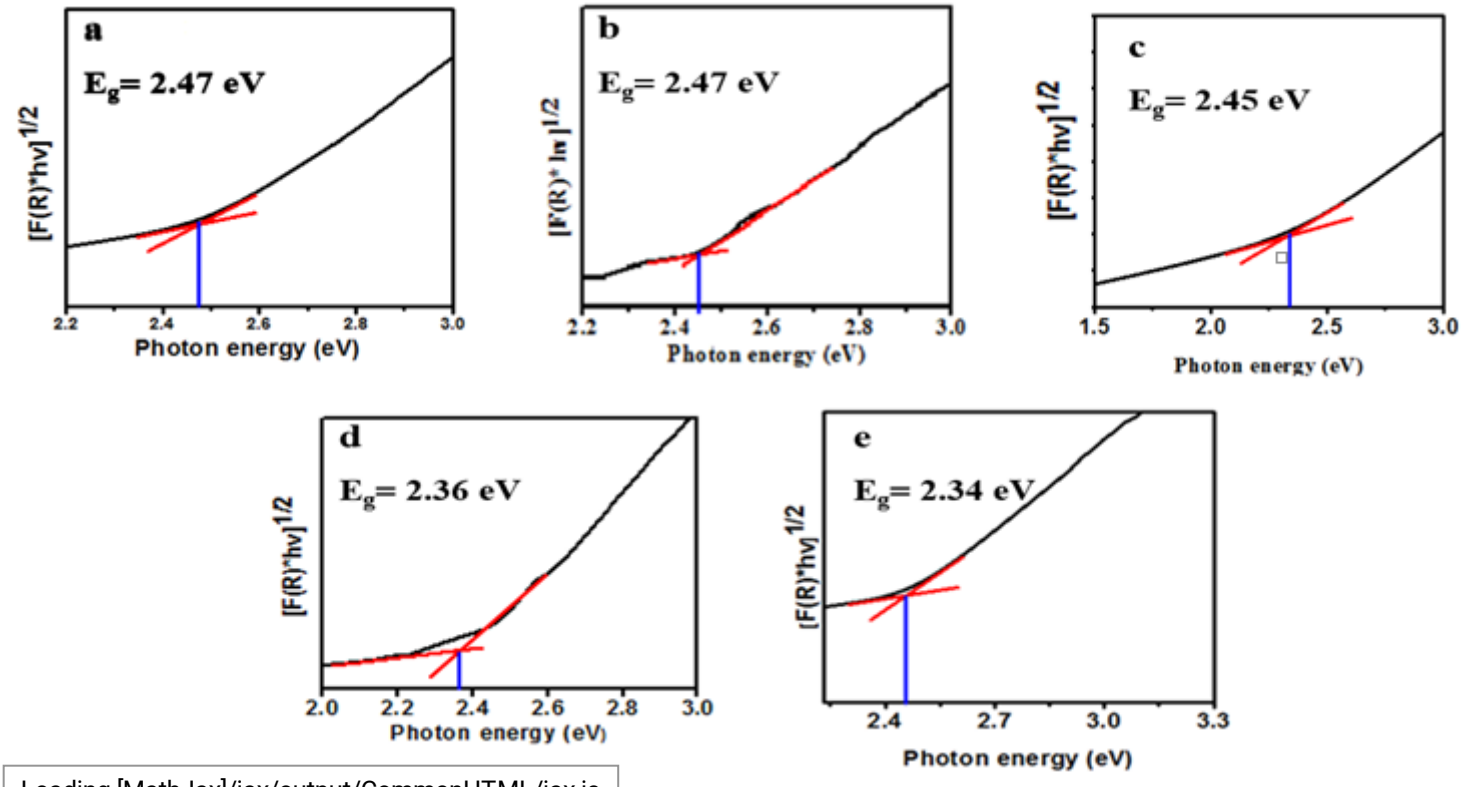

Figure 3

Tauc's plot of (a) CoN-TiO2-1 (b) CoN-TiO2-2 (c) CoN-TiO2-3 (d) CoN-TiO2-4 (e) CoN-TiO2-5.

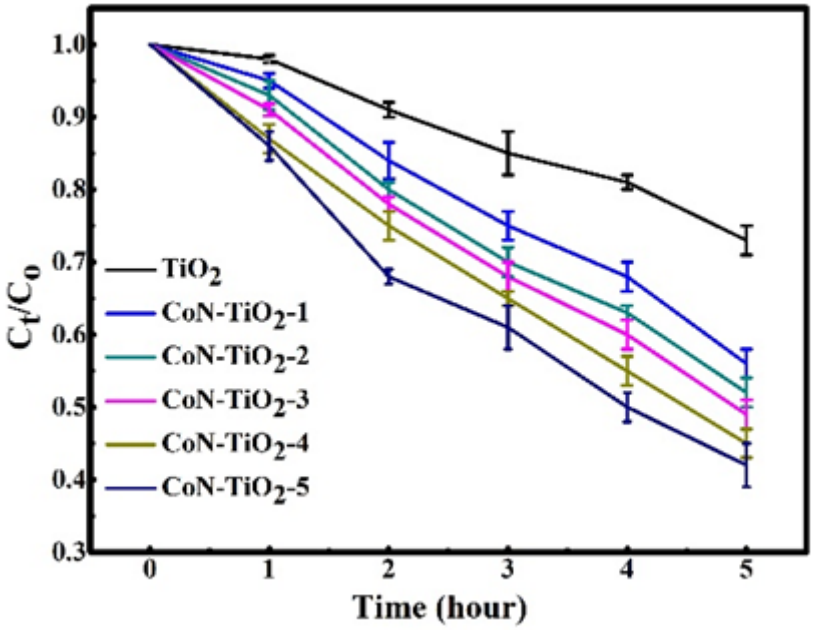

Figure 4

Photocatalytic activity of all catalysts against methyl orange degradation in visible light

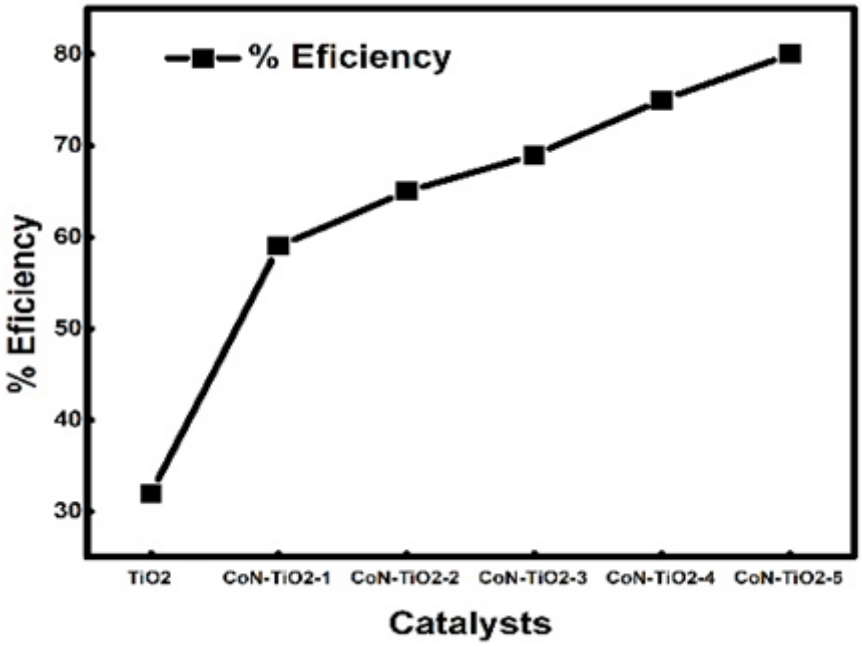

Figure 5

Comparison of percentage efficiency of all catalysts against methyl orange degradation in visible light

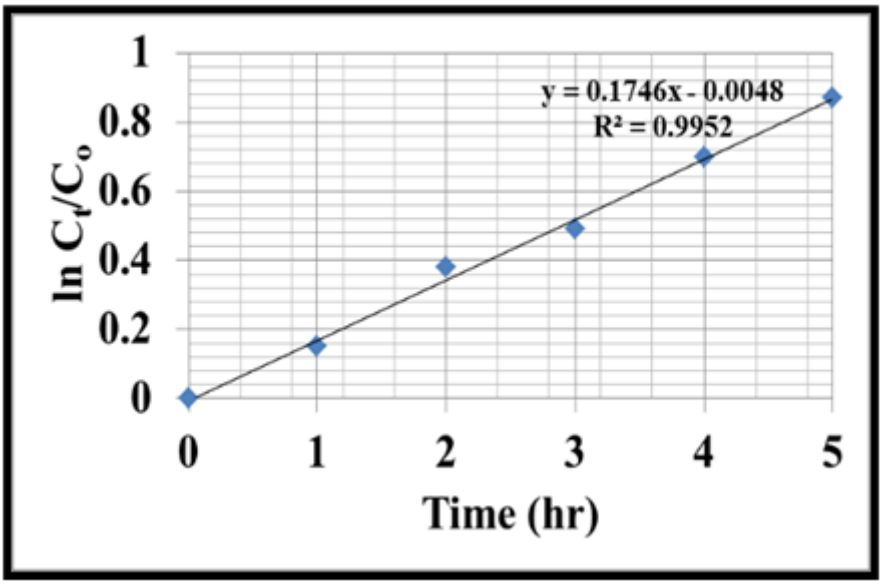

Figure 6

Plot between Ct/CoVS time for methyl orange degradation by usingCoN-TiO2-5

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- SupplementaryInformation.docx