Solvothermal synthesis of C doped Co-Cu/TiO₂ based nanocomposite to study their photocatalytic activity

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Abstract

The solvothermal approach is applied to produce doped titanium dioxide nanoparticles in the mesoporous form using Pluronic F127 as a delicate mold. The formulated samples are investigated successfully via x-ray diffraction, ultraviolet-visible spectroscopy, photoluminescence spectroscopy, scanning electron microscope, energy dispersive x-ray, transmission electron microscope, nitrogen adsorption-desorption analysis, and Fourier-transform infrared spectroscopy. Analysis of XRD, SEM, and TEM demonstrates the existence of a nanocrystalline size range of the particles. Methylene blue, congo red, and malachite green dyes are used to evaluate the photocatalytic competence of the samples. The results verified that the TiO₂ including a peak quantity of copper (4%) shows maximum photocatalysis caused by the declined bandgap energy including effective charge separation of photoinduced charge carrier with a maximum surface area as revealed by ultraviolet-visible, photoluminescence spectroscopy & nitrogen adsorption-desorption analysis respectively.

1. Introduction

Water is frequently polluted by a broad range of poisonous chemicals and crude impurities by the growth of manufacturing industries [1]. Photocatalysis using metal oxides nanoparticles is one of the most efficient technique for wastewater treatment and is also known as the ‘green technology’ [2]. TiO₂ is the most efficient metal oxide semiconductor due to its excellent physical and chemical stability as compared to other metal oxides, innoxious nature, and easy availability. It is able to oxidize a broad variety of poisonous non-biodegradable impurities into non-toxic elements (CO₂ and H₂O) [3–7]. TiO₂ has a wide band gap, which requires the UV light for excitation and its high electron-hole recombination rate limits its photocatalytic efficiency [8]. Doping of N, F, C, and S (non-metal) is implemented to lower the bandgap energy [9]. Doping of metals such as Cu, Co, Ag, In, Ni, Au, and Pt are required to decrease the electron-hole recombination rate due to their efficiency to form a Schottky barrier with TiO₂ (semiconductor). With the increase in surface area, porosity also provided several physicochemical incidents like diffusion and adsorption, particularly in the mesoporous (2–50 nm) form [10]. Copper, Cobalt, and Carbon co-doped TiO₂ in the mesoporous form has been verified to be a very competent photocatalyst in the visible light exposure, attributed to its low bandgap energy, less recombination rate of charge-carrier, and capacity to offer a maximum surface area with huge pore volume, which consequently results in a large amount of surface reactive sites [3]. Numerous work has been done on doped TiO₂ to investigate its photocatalytic activity. Saba Habibi et al prepared carbon-doped TiO₂ via the sol-gel method for degradation of methylene blue [11]. Sarunas Varnagiris et al synthesized carbon-doped TiO₂ thin films for photocatalysis [12]. Chandni Khurana et al prepared cobalt doped TiO₂ as photocatalyst [13]. Maryam Hosseini-Zori prepared cobalt doped TiO₂ for antibacterial activity [14]. Nazli Turkten et al prepared copper doped TiO₂ for photocatalytic activity [15]. Yabin Yan et al prepared TiO₂-Cu/C for photocatalytic activity [16]. Anupama Chanda et al prepared undoped and cobalt doped TiO₂ to study its magnetic and
structural properties [17]. However, Carbon, copper, and cobalt doped mesoporous TiO$_2$ are never synthesized before for analysis of photocatalytic activity. By using the solvothermal method we can precisely control the shape, size, and morphology of nanoparticles. These parameters depend upon the solvent type, reaction temperature, reaction time, and type of surfactant.

In the present study, we are discussing the synergic consequence of doping with mesoporous morphology on the dye degradation competence of TiO$_2$.

Figure 1. Flow chart for the experimental process.

Figure 2. XRD pattern of all the samples.
2. Experimental

2.1. Material used
Titanium tetraisopropoxide (Ti\{OCH(CH₃)₂\}₄), Pluronic F127 (EO20PO₇₀EO20), Graphite, Copper sulfate pentahydrate (CuSO₄·5H₂O), Cobalt nitrate (CoN₂O₆), Methanol (CH₃OH), Methylene blue (C₁₆H₁₈ClN₃S), Malachite green (C₂₃H₂₅N₂), and Congo red (C₃₂H₂₂N₆Na₂O₆S₂) dyes. All chemicals are bought from Sigma Aldrich.

2.2. Preparation of pure and co-doped mesoporous TiO₂
0.5 g of F127 is put into 20 ml methanol (solution 1) under stirring followed by addition of 20 ml of TTIP (in the absence of light) (figure 1). 2 ml of HCl is added to the above solution to control the pH and citric acid (0.2 g) is

Table 1. Chemical conformation with symbols of the samples.

| Sr no. | Chemical composition | Sample codes |
|--------|----------------------|--------------|
| 1      | Pure mesoporous TiO₂ | T₁           |
| 2      | Carbon (4%) + Cobalt (2%) and copper (2%) doped mesoporous TiO₂ | T₂           |
| 3      | Carbon (4%) + Cobalt (2%) and copper (3%) doped mesoporous TiO₂ | T₃           |
| 4      | Carbon (4%) + Cobalt (2%) and copper (4%) doped mesoporous TiO₂ | T₄           |

Table 2. Crystallite size of the pure and doped TiO₂ samples and their correlated bandgap energy.

| Sample | Highest peak | FWHM | Diffraction angle | Crystallite size (nm) | Bandgap E_g (eV) |
|--------|--------------|------|-------------------|-----------------------|------------------|
| T₁     | 12.99        | 2.112| 25.35°            | 4.03                  | 3.36             |
| T₂     | 7.42         | 0.768| 25.05°            | 11.06                 | 2.40             |
| T₃     | 12.27        | 0.576| 25.20°            | 14.77                 | 2.00             |
| T₄     | 31.67        | 0.576| 25.25°            | 14.77                 | 1.80             |
Figure 4. SEM images of sample T₄.

Figure 5. TEM Images of sample T₁.
used as a chelating agent. The whole solution is allowed to stir for 30 min and after that subjected to stainless steel coated digestion vessel for 24 h at 110 °C. After that subjected to filtration and washing and allowed to calcinate for 5 h at 400 °C to remove the soft template. For the preparation of doped samples, the considered quantity of Graphite (4%), Cobalt (2%), and Copper (2%, 3%, & 4%) have been added to the solution 1 (before the addition of TTIP). Chemical conformation with symbols of the samples is provided in table 1.

2.3. Photocatalytic degradation of methylene blue, congo red, and malachite green dyes
Various evaluations are carried out for different dyes using the four samples (photocatalyst). $10^{-5}$ mol/liter concentration of dye is prepared in each case. 100 ml of the dye solution with 0.05 g of the photocatalyst is subjected to sonication in dark for 45 min. After that, this solution is subjected to exposure of phosphor plated mercury vapor lamp, as a provenance of visible light (440–540 nm using a filter) with stirring. After a fixed time interval of 20 minutes this solution is removed and after filtration and centrifugation, checked by the UV–vis spectrophotometer to analyze the percentage of dye degradation with time.
3. Results & discussion

3.1. Structural studies

Figure 2 shows the x-ray diffraction pattern of all the samples. The pattern of pure TiO₂ shows the diffraction peak at 25.25°, 37.66°, 47.93°, 53.78°, 55.01°, 62.57°, 68.47°, 70.42°, 74.83° related to their corresponding planes (101), (004), (200), (105), (211), (204), (116), (220), (215) which shows the existence of anatase phase of TiO₂ (JCPDS card no. 84-1285) [18]. Broad diffraction peaks of all the samples show the existence of nanoscale dimensions of the particles. XRD pattern of all the doped samples manifests that only minor change in the XRD peak is observed with the addition of carbon and a rise in the concentration of copper. Crystallite size is 4.03, 11.06, 14.77, and 14.77 for the sample T₁, T₂, T₃, & T₄ respectively as determined by using the Debye–Scherrer
formula [19] as given in table 2. It is observed that crystallite size is the same for the sample T3 & T4 (maximum) and minimum in case of sample T1.

3.2. Morphological and chemical studies
To determine the crystallite size and shape of the samples, SEM and TEM examination of samples are carried out. SEM and TEM analysis of the two samples (T1 & T4) is shown by the figures 3–4 and figures 5–6 respectively. Mesoporous assembly of nanometer-sized particles is clearly visible in the SEM images, sample T1 & T4 are used because they show the minimum and maximum concentration of dopants respectively. Particle size shown by SEM images is large as compared to XRD analysis because it does not show the actual particle size, only the size of agglomerates is visible [20]. So analysis by TEM instrument of both the samples is carried out to show the actual size, shape with the Miller indices of the crystal. Figures 5 and 6 show the results obtained from TEM analysis with 10–20 nm of crystal size with tetragonal shape. To determine the elemental compositions of samples EDX analysis was performed. Figure 7 shows the obtained EDX spectra of the samples. The existence of oxygen, cobalt, copper, carbon, and titanium is clearly visible.

The existence of mesoporosity in the samples T4 is shown via the occurrence of the type IV curve by nitrogen adsorption-desorption analysis shown by figure 8, BJH desorption graph in figure 9 and multipoint BET plot in
The existence of pores by tapered mouths (ink-bottle pores), comparatively consistent channel-resembling pores, as shown by the H2 hysteresis loop [21].

3.3. UV–visible spectroscopy analysis
Because TiO$_2$ is an indirect band semiconductor, thus the exact value of bandgap energy of all the samples is shown by plotting $(\alpha h \nu)^{0.5}$ Vs $h \nu$ shown in figure 11 and absorption spectra in figure 12, and it shows that the value of bandgap energy declined constantly with an increase in the percentage of dopants. The calculated value of bandgap energy is 3.36, 2.40, 2.00, & 1.80 eV and shown in table 2. There is a direct correlation between the value of the bandgap and the crystallite size in our research (the crystallite size rises and bandgap energy reduces continuously with an increase in doping). The value of the absorption wavelength increases with rising in the number of dopants. Thus, a red-shift takes place [22].

3.4. Photoluminescence spectroscopy (PL) analysis
It can be noticed from figure 13 that the intensity of the co-doped samples is inferior to that of pure TiO$_2$. These outcomes specify that there is successful suppression in the recombination strike of the charge carrier by the co-doping. The samples exhibit two sturdy peaks at 390.9 and 469.7 nm. The previous shows the free excitation
emission. The second peak is ascribed to the charge-transport change as of Ti$^{3+}$ to oxygen anion exists in the TiO$_6$ octahedral compound. The PL spectra show the passage of electrons from the excited level (defect bands or conduction bands) to the ground position (defect bands or the valence band). As compared to sample T$_1$, the decline in emission intensity arises due to the distinction in the electronic configuration of all the three doped samples (T$_2$, T$_3$, and T$_4$), based upon the formation of a few novel defects, for example, oxide ion vacancy [23].

3.5. Fourier transform infrared spectroscopy analysis

FTIR spectra of all the samples in the 400–4000 cm$^{-1}$ range is shown in figure 14. It has been concluded from the obtained spectra that the bonding system existing inside the pure anatase TiO$_2$ remains intact from the effect of co-doping. All the samples have an about alike pattern. Bending vibration around 1300–1700 cm$^{-1}$ shows the incidence of hydroxyl functional group in all the photocatalyst sample. The stretching of the O=C=O bond is

Figure 13. PL spectra of all the samples.

Figure 14. FTIR spectra of all the samples.
described via the subsistence of the peaks in the mid of approximately 2300 cm\(^{-1}\). In a photocatalyst, the hydroxyl group engages a significant function in the creation of hydroxyl radicals \([24]\).

### 3.6. Photocatalytic degradation activity

Three dyes of different chemical nature i.e. malachite green and methylene blue (basic dye) & congo red (acidic azo dye) are used to check the versatile degradation action of the samples. The maximum absorption wavelength for MB, MG, & CR is 668 nm, 617 nm, and 497 nm respectively. Results of the percentage of degradation of dyes with time are shown in figures 15–17. Photocatalyst act in the same way (degradation increases with an increase in the concentration of dopants) on different dyes, but the percentage of degradation varies for different dyes, as shown in table 3. Maximum degradation of 88% has been achieved by sample T4, in the case of methylene blue dye. The increase in degradation affinity of co-doped samples can be explained in terms of the reduced bandgap energy to 1.80 eV and suppression in the redundant recombination of charge carrier as confirmed by the UV–vis & PL investigation. The decreased bandgap energy shifts the light sensitivity of TiO\(_2\) nanoparticles toward visible light. Copper and cobalt play an important role in suppression in the rate of charge carrier recombination percentage. This increased charge separation results in the increased life of \(\cdot OH\) radicals \([25]\) which act as a
powerful oxidizing agent during photocatalysis. An increase in photocatalytic activity can also be explained in terms of the mesoporous nature of the samples. Sample T4 shows the surface area of 599.5 m² g⁻¹ responsible for providing maximum adsorption sites with the 4.03 nm of small crystallite size responsible for its maximum degradation action among all the samples against all three dyes.

4. Conclusion

Copper and cobalt with carbon-doped of TiO₂ nanostructures are prepared favorably by using surfactant F127 in the solvothermal method. The presence of a crystallite extent of 4.03–14.77 nm is perpetrated by the XRD data evaluation. Purpose of doping, to promote the electron-hole separation for charge transfer and to decrease the bandgap energy to enhance the visible light susceptibility of TiO₂, has been attained successfully and is confirmed by analysis of PL and UV data. Prepared samples acquired some functional groups such as O=\text{C}=\text{O} &–\text{OH}, which comes from the reagents used during the synthesis process and is confirmed by analysis of FTIR data. SEM analysis shows that the mesoporous flocs are formed without undergoing collapse during calcination. Crystalite size and shape with mesoporous nanoparticles are affirmed by the TEM analysis. The existence of all elements in the samples (TiO₂ with dopants) is verified by the respective peaks in EDX spectra. The existence of type 4 hysteresis loop proves the mesoporous morphology and 599.5 m² g⁻¹ of surface area, 0.86 cm³ g⁻¹ of pore volume, 5.63 nm of pore diameter, also calculated by nitrogen-adsorption desorption analysis. During the photocatalytic evaluation, three different dyes are used and it is confirmed that TiO₂ in the combination of copper, cobalt, and carbon along with mesoporous form shows enhanced photocatalytic activity in the existence of the visible light source.

Declaration of interest

The authors have no conflict of interest.
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