Synergistic effect of Cobalt on Nitrogen and Carbon codoped Anatase Titania for Photodegradation under Visible Light

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ABSTRACT

This work reports on the synergistic effect of cobalt on Carbon and Nitrogen codoped anatase titania photocatalysts prepared via sol–gel method using urea as the nitrogen source. Visible light activity is achieved as result of anion doping and further improvement is manifested in the photocatalytic activity with the cobalt doping. The photocatalysts prepared are characterized using various analytical techniques. Diffuse reflectance spectral (DRS) analysis shows visible light absorption. Efficient dispersion of cobalt and anatase phase stability is clear from X-ray diffraction (XRD) patterns. Photodegradability under visible light is investigated using methylene blue which is a widely used dye in photodegredation studies. Titania upon C & N codoping shows good activity in very dilute solutions whereas with cobalt doping, the activity is retained even at higher dye concentrations. Reaction parameters are optimized to improve the photodegradation capacity of the prepared systems. Present systems show excellent activity even within 15 minutes and are found to be reusable as well.

Keywords: synergistic effect, cobalt doping, anion doped TiO_2, sol-gel method, photodegradation

1 INTRODUCTION

A dye is a colored substance that has an affinity to the substrate to which it is being applied and makes the world more beautiful. However, the release of coloured wastewaters poses a serious environmental problem and a public health concern. Colour removal, especially from textile wastewaters, has been a big challenge over the last decades, and till date there is no single and economically attractive treatment procedure available that can effectively decolourise dyes [1]. Titanium dioxide (TiO_2) has attracted much attention for the past few decades as the most promising photocatalyst because of its excellent capacity in the decomposition of pollutants in water and air by means of photodegredation, However, two major drawbacks in TiO_2 photocatalysis are the low quantum efficiency due to the high recombination rate of photoinduced electron–hole pairs (e^-–h^+) and the poor absorption ability in the visible-light region.

In order to improve the photocatalytic performance of TiO_2,there has been a large number of studies modifying TiO_2 catalyst in various ways. Some of the strategies adapted by researchers in this field include depositing noble metal on titania [2,3], doping with metal [4,5,6], doping nonmetal [7-10] and compounding TiO_2 with other materials [11,12]. Doping with metal and doping nonmetal were the most feasible methods for improving the photocatalytic performance of TiO_2.The doping of metal atoms can suppress the recombination of photo-induced electron-hole pairs so as to increase the photo quantum efficiency [9,9]. On the other hand, the nonmetal atoms can incorporate into the lattice structure of TiO_2, decreasing the band gap, and thus giving rise to a good response to the visible light [7-10].

Our objective was the preparation of a doped TiO_2 system where there is low band gap, so that visible light can be used effectively and the recombination of electron - hole pairs is low which will result in good quantum efficiency. Recently we had developed a highly active carbon and nitrogen codoped TiO_2. The system is found give 100% degradation of the dye pollutant within a short span of 10 minutes. But the main handicap we have faced with that catalyst was its decreased activity in solutions where the dye concentration is appreciably high. This motivated us to study the synergistic effect of transition metal on this carbon and nitrogen codoped system. The transition metal chosen here is cobalt. The effect of percentage of metal loading on the anion doped system is also investigated. The photoactivity is investigated using methylene blue (MB) degradation.

2 EXPERIMENTAL

2.1 Modified TiO_2 Preparation

Carbon and nitrogen codoped system is prepared following the reported procedure [13]. Cobalt loading is done on the

anion doped system by using cobalt nitrate as the precursor. The detailed preparation method is as follows. Cobalt loaded Nitrogen and Carbon codoped Anatase TiO2 catalysts using Titanium (IV) isopropoxide (Sigma Aldrich) as titanium precursor, Cobalt nitrate ((Hamburg Chemical GmbH) and urea (Merck) as cobalt and nitrogen source was prepared using sol-gel method at room temperature. 18.6 ml Titanium (IV) isopropoxide and 50 mL ethyl alcohol (Merck) were mixed (solution a), to this solution b which contains 50 mL ethyl alcohol, 12.5 mL glacial acetic acid and 6.25 mL distilled water was added. The resultant transparent solution was stirred for 3h. A mixture of Urea - water - alcohol with molar ratio of urea:ethanol:water, 1:5:0.5 and Cobalt nitrate solution to get the required loading of Co was then slowly added to the above solution until the N/Ti molar content of 20 was satisfied. It was again stirred for 3h, aged for 2 days and dried in an air oven at 80˚C. Ground into fine powder and calcined at 300˚C for 5h to obtain nitrogen doped TiO_2. The systems are designated as Ti, NT,1CoNT, 2CoNT, 3CoNT and 4CoNT whereas the numbers indicates the wt% of Co loading.

2.2 Photocatalyst Characterization

XRD patterns of the samples were recorded for 2θ between 3 and 80° on a Bruker AXS D8 Advance diffractometer employing a scanning rate of 0.02°/S with Cu Kα radiation (λ=1.5418). The FTIR spectra were recorded in NICOLET6700 FT-IRThermoscientific in the region 400–4,000 cm^{-1}. Diffuse Reflectance Ultraviolet - Visible spectroscopy (UV–Vis DRS) of powder catalyst samples was carried out at room temperature using a Varian, Cary spectrophotometer in the range of 200 to 800 nm.

2.3 Photoactivity Studies

Photodegradation of methylene blue is investigated as a model pollutant. The pollutant degrading capacity of the Cobalt loaded Nitrogen and Carbon codoped Anatase TiO2 catalysts was studied using a Rayonet type Photoreactor with visible light having 16 tubes of 8W (Associate Technica, India). In the reactor, 5 quartz tubes of 150 ml capacity, is concentrically arranged to get uniform illumination for all the systems. 50 ml of methylene blue (25mg/l) was placed in the quartz tube, containing a definite amount of the catalyst and is irradiated with visible light under continuous stirring. The methylene blue concentration was analyzed using a colorimeter (ESICO Microprocessor photo colorimeter model 1312) at a wavelength of 665 nm.

3 Results and Discussion

3.1 Characterization of the photocatalysts

XRD pattern of anion codoped sample is found to be amorphous in nature. We analyzed the cobalt incorporated samples to know about the crystallinity. All metal incorporated C and N codoped systems are found to contain anatase as the only phase. The absence of amorphous phase indicates that the metal incorporation accelerated the transition from amorphous to crystalline; of anion doped TiO_2 system. TiO_2 without any dopant also exists as anatase. The crystallite size of the systems is calculated using Scherrer equation [14]. Cobalt doping results in reduction in the crystallite size when compared to the TiO_2 system without the presence of any dopant. But increase in the percentage of metal dopant results in increase in the crystallite size, but still is less when compared to that of undoped system. Reduction in crystallite size indicates increased surface area. Efficient dispersion of Co is manifested from the absence of peaks for oxides of cobalt.

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System	Crystallite size (nm)	MB Degradation (%)
Ti	7.9891	14.5454
NT	-	87.0370
1CoNT	4.2040	94.5454
2CoNT	4.6338	96.3636
3CoNT	5.8567	89.0909
4CoNT	6.5585	85.5454

Table 1: Crytstallite size and photodegradation results over different systems.

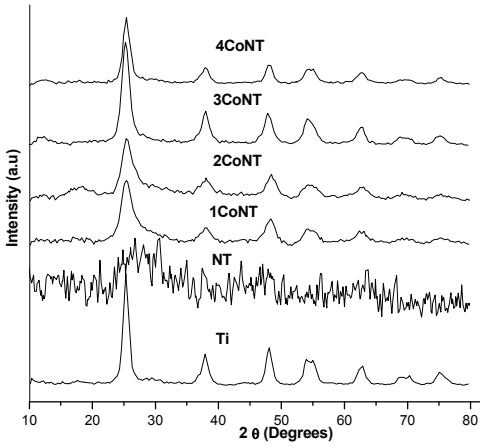

Fig. 1 XRD patterns of the prepared photocatalysts

The photocatalyst samples are found to be coloured, indicating absorption of visible light. The brownish yellow colour of NT remains unaffected after loading 1% Co. In 2CoNT the colour fades, but still remains as brownish yellow whereas 3CoNT and 4CoNT are green in colour. DRS analysis of the samples is done which shows absorption throughout the visible range. The incorporation of cobalt strengthens the visible absorption. This absorption feature suggests that these Co-doped TiO_2 can be activated by visible light. The reflectance spectra of the samples are given in figure 2. This broad-energy feature reflects the heterogeneity of Co, C and N impurities and associated charge-neutrality defects present on the samples.

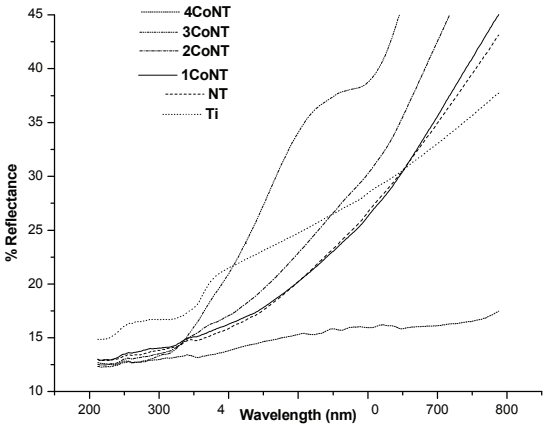

Fig. 2 UV-VIS diffuse reflectance spectroscopy of prepared photocatalysts

3.2 Photodegradation of dye pollutant

In order to assess the photocatalytic performance of Co loaded C, N codoped TiO_2 for their application in the pollutant removal processes, MB degradation is carried out. The reaction parameters are optimized to get better activity. The system selected for optimization studies is 2CoNT.

3.2.1. Effect of initial MB concentration

The effect of initial MB concentration on MB photodegradation is investigated (fig. 3). When we analyzed the activity of the catalysts using 10mg/L dye solution, all systems except that without any doping resulted in complete conversion. Thus we increased the concentration of MB to 25mg/L for further studies to get a comparison on the performance of different systems. The degradation result of 2CoNT for MB degradation over a range of concentration is studied and the result is given in Fig. 3. MB photodegradation decreases with increase in the initial concentration of MB, but still the activity is appreciable even for 100mg/L dye concentration for a short period of exposure to visible light. For NT system, the activity drops sharply with increasing dye concentrations [14] and is found to be effective mainly in dilute solutions within this short span of exposure to visible light. For concentration variation study the other two parameters were kept constant i.e. loading of photocatalyst (1g/L) and reaction time (15 min).

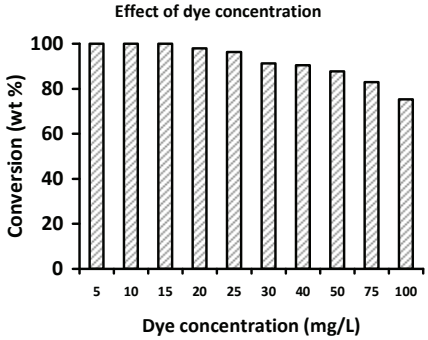

Fig. 3 Influence of dye concentration on % degradation in presence 0.1g/L catalyst for 15 min. irradiation

3.2.2 Effect of photocatalyst dose on degradation

Fig. 4 shows the effect of catalyst dose on MB degradation. It is apparent from the figure that with increase in the catalyst dose, the photodegradation increases up to dose of 0.05g. Further increase in the dose up to 0.1g does not affect MB degradation reaction. There is a marginal initial increase in the efficiency. This is because initial concentration of MB solution and light intensity is constant throughout the dose study. As the photocatalyst dose was increased from 0.01g to 0.05 g, the number of active sites increases, the extent of light absorption increases which in turn increases photoactivity. Further increase in photocatalyst dose to 0.15 g increases the opacity of solution, which decreases the penetration of light inside the solution with a slight decrease in the photodegradation of MB [15]. Thus the selected optimum catalyst dose is 1g/L dye.

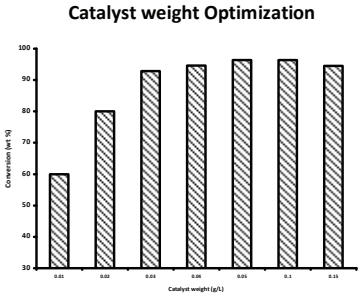

Fig.4 Effect of photocatalyst dose on the photocatalytic degradation of 25mg/l MB, for 15 min. irradiation

3.2.3 Effect of Time

The reaction is done continuously and the degraded solutions are analyzed with an interval of 5 min. It is found that the conversion reaches maximum within 15 minutes and then remains constant. Fig. 5 explains the influence of time on photodegradation of MB.

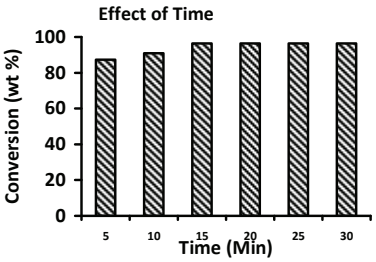

Fig. 5 Effect of reaction time on the degradation of 25mg/L MB with 0.1g/L catalyst.

3.2.4 Effect of metal loading

Effect of percentage (wt %) of metal loading on C and N codoped TiO_2 is investigated in the above selected optimum conditions. It is found that metal loading improved the activity of anion doped TiO_2. The activity increases and reaches maximum at a metal loading of 2% which then decreases. The activity of 4% metal loaded system 4CoNT is found to be even lower than that of anion doped system without any metal. The probable reason for the decreased activity with increase in metal loading may be because excess-doped metal introduce electron–hole recombination centers in the structure. Thus among the different systems 2CoNT, the 2% cobalt loaded, carbon and nitrogen codoped system is showing maximum photoactivity. The results are shown in table 1. In order to make sure about the synergistic effect of cobalt loading on the anion codoped TiO_2, degradation is done on 2% cobalt doped system without any anion doping. System preparation is done exactly as before, but eliminating the step for the addition of urea. The cobalt doped TiO_2 shows a degradation of 20.37%, which is very low when compared to the anion codoped systems.

3.2.5. Recycle ability

The reusability of TiO_2 photocatalyst was one of the key steps to make heterogeneous photocatalysis technology for practical applications. We did the reusability tests of the best system 2CoNT for 6 repeated runs and found to show appreciable activity for 3 cycles which then decreases down sharply. The results are shown in fig. 6.

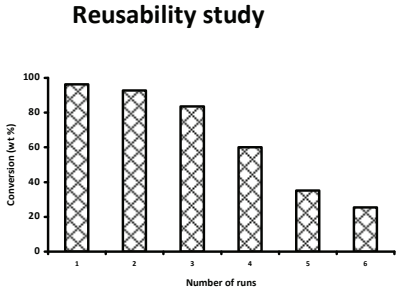

Fig. 5 Effect of reaction time on the degradation of 25mg/L MB with 0.1g/L catalyst.

3 CONCLUSIONS

In the present study, the successful preparation of a novel, improved photocatalyst, cobalt loaded carbon and nitrogen codoped TiO_2 is shown. Cobalt containing doped systems is found to be anatase in nature and is more photocatalytically active compared to carbon and nitrogen codoped TiO_2 without any metal doping, which is amorphous. The system, 2% cobalt loaded carbon and nitrogen codpoed TiO_2 showed excellent photoactivity for methylene blue degradation over a wide range of dye concentration within a short period of time. Reusability is another advantage of this doped system. The increased activity is assumed to be due to the synergistic effect of cobalt doping on the carbon and nitrogen codoped TiO_2. Further studies on the nature of dopants on TiO_2 and on the mechanism of photodegradation are required.

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