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Effect of g-C_3N_4 loading on TiO_2/Bentonite nanocomposites for efficient heterogeneous photocatalytic degradation of industrial dye under visible light

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TiO_2/clay nanocomposites tend to have high photocatalytic efficiency than commercial TiO_2 (Degussa P25) due to their high porosity, surface area, the presence of active sites and optical transparency. However, its inactivity in the visible region of the solar spectrum makes it unsuitable for practical use. Hence, the nanocomposite of TiO_2 with bentonite clay has been coupled with visible light active graphitic carbon nitride (g-C_3N_4) by wet impregnation process at room temperature. The as-prepared nanocomposite was then used to photocatalytically degrade (90%) reactive brilliant red dye (RBR- X3BS) in 100 min of time under visible light irradiation. The high activity was attributed due to the suppression of electron-hole recombination as the electron was transferred from g-C_3N_4 to TiO_2 and there was a strong electrostatic interaction between g-C_3N_4 and bentonite clay. To investigate the reactive species responsible for the photodegradation of dye, different radical scavengers were employed and it was observed that the % degradation was highly affected by the addition of DMSO and ascorbic acid which indicated that electrons (e^-) and superoxide radicals ($O_2^{\bullet -}$) have played an important role in dye degradation. The reusability efficiency of the as-prepared nanocomposite was examined for 5 consecutive cycles. Complete photo-mineralization of the dye was confirmed by the evolution of CO_2 gas (37 ppm) which was monitored by gas chromatography (GC). From the comparative study of literature, it can be proposed that our as-synthesized g-C_3N_4/TiO_2/bentonite nanocomposites could be employed as an efficient photocatalyst for the degradation of RBX-3B dye.

1. Introduction

Clays have been well known for their role as effective support materials for several semiconducting materials like TiO_2 [1,2]. The TiO_2/clay nanocomposites tend to degrade several organic pollutants more actively than commercially available TiO_2 (Degussa P25) [3–5]. The high porosity, high surface area, optical transparency and presence of highly active sites are the key factors which make TiO_2/clay nanocomposites highly active photocatalyst than commercial P25 [6]. Despite all above-mentioned merits, the TiO_2/clay nanocomposites have a limitation of being inactive under visible light due to the wide band gap of TiO_2. In order to eliminate such drawback, few attempts have been reported such as elemental doping [7–9], coupling with metal oxides [10]/semiconductors [11,12], coinage metal loading [13–15] and dye sensitization [16]. Apart from all above-mentioned attempts, the coupling of TiO_2/clay nanocomposite with g-C_3N_4 can be highly promising since g-C_3N_4 is one of the highly attractive photoactive materials due to its special electronic structure which makes it one of the highly novel metal-free semiconductors. Moreover, its chemical and thermal stability at ambient condition, hardness, low density, layered structure, water resistivity and biocompatibility makes it highly promising in the field of photocatalysis and photovoltaics [17]. Its graphite-like two-dimensional planer structure having π conjugated systems enables the transport of charge carriers and a narrow band gap of 2.7eV provides it with light absorption around 460 nm [18]. Moreover, it can be easily synthesized from low-cost precursors like urea [19]. Despite all these advantages, its photocatalytic efficiency is limited merely due to fast charge recombination rate and marginally visible light absorption [20,21]. The fast recombination of charge carriers can be reduced upon its coupling with TiO_2 since least unoccupied molecular orbital

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(LUMO) of g-C_3N_4 lies above the conduction band (CB) of TiO_2 leading to electron transfer from g-C_3N_4 to TiO_2 [22–24]. Reduction in charge recombination of g-C_3N_4 has also been reported upon incorporating it on clays due to its strong electrostatic interaction with clay particles leading to high photocatalytic activity [25,26]. Thus, heterojunction formation of g-C_3N_4 with TiO_2 as well as its electrostatic interaction with clay particles can be expected to efficiently separate photogenerated charge carriers for better photoactivity.

Here, in this paper, we have taken bentonite clay to synthesize TiO_2/bentonite nanocomposites and incorporated g-C_3N_4 onto it by simple wet impregnation method at room temperature. The g-C_3N_4/TiO_2/bentonite nanocomposite was then used to degrade reactive brilliant red-X3BS dye (RBR-X3BS) under visible light irradiation.

2. Experimental

2.1. Materials

Bentonite clay [$Na_{0.4}Ca_{0.03}K_{0.01}$) ($Al_{1.6}Mg_{0.3}Fe_{0.1}$)$Si_4O_{10}(OH)_2$], titanium (IV) butoxide, urea were purchased from Sigma-Aldrich. The RBR-X3BS dye was obtained from a local textile industry in Ludhiana, India. All reagents were used without further purification. All the solutions were prepared in deionized water (18.2 MΩ cm).

2.2. Preparation of g-C_3N_4/TiO_2/bentonite nanocomposites

2.2.1. Preparation of TiO_2/bentonite nanocomposites

About 2 g of dry bentonite clay was dispersed in 500 ml of water and the pH of the slurry was kept at ~3 by adding 1 M HCl solution with continuous stirring for 24 h. The transparent TiO_2 precursor sol was prepared by adding 2 ml of titanium (IV) butoxide in 50 ml of absolute ethanol with continuous stirring to obtain the milky white suspension followed by addition of concentrated HCl until the milky suspension turned transparent. This transparent sol was slowly added to bentonite suspension and the final slurry was stirred for another 12 h, maintaining pH ~3 by adding 1 M NaOH solution. The amount of suspension was added in such a way that, the concentration of TiO_2 was kept to 5 mM/g of bentonite. The slurry was centrifuged and washed with water for five times, dried at 80 °C and finally calcined at 550 °C for five hours.

2.2.2. Preparation of g-C_3N_4

About 12 g of urea was dissolved in 60 ml of water in a crucible and kept at 60 °C for re-crystallization. The re-crystallized urea was then kept in a furnace at 550 °C for 2 h at a heating rate of 10 $^{\circ C/min}$

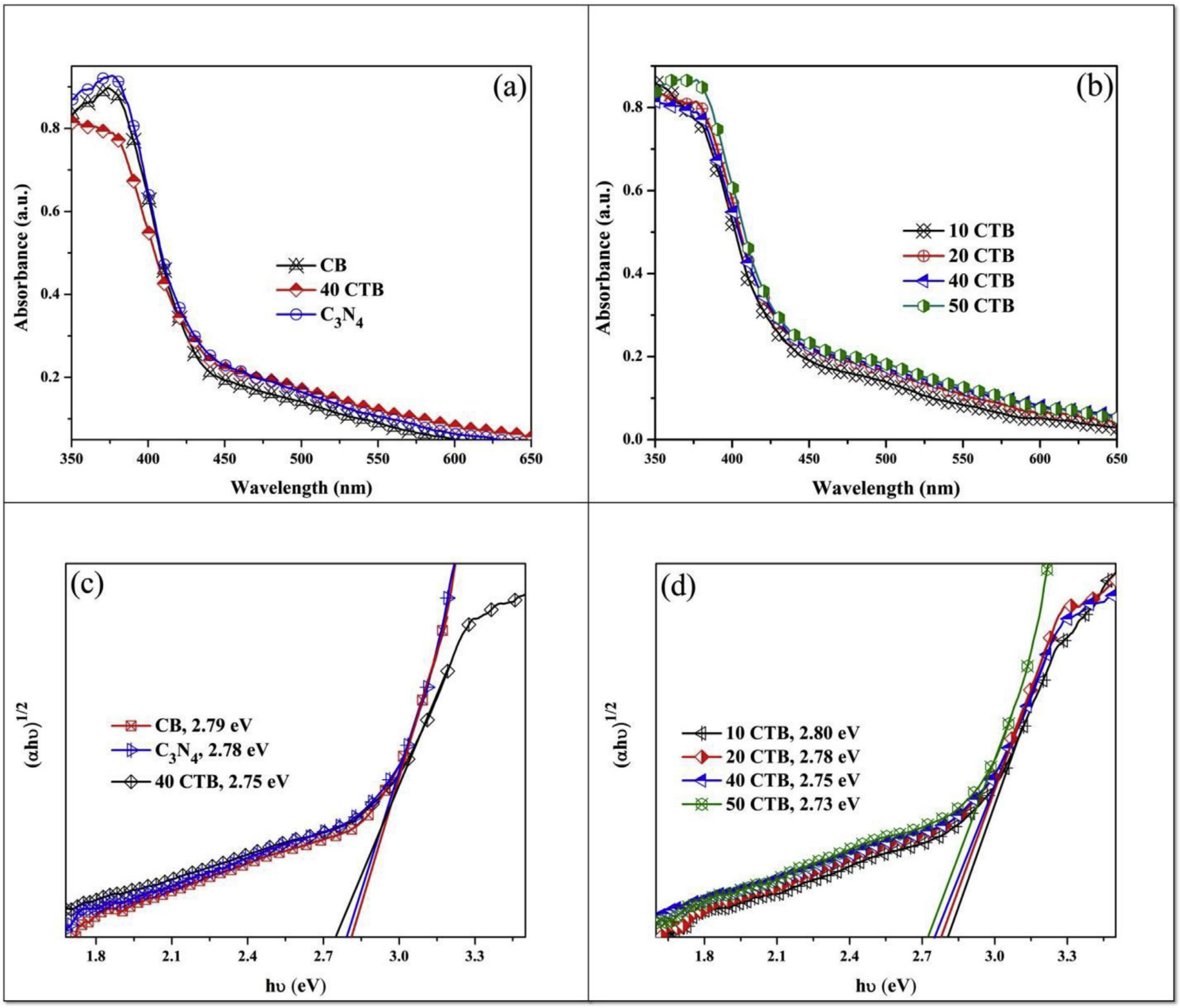

Fig. 1. (a)–(b) UV–Visible diffuse reflection spectra of g-C_3N_4/TiO_2/bentonite nanocomposites (CTB) and (c)–(d) their respective tauc plots.