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Synthesis, characterization and photodegradation activity of graphitic C_3N_4-$SrTiO_3$ nanocomposites

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ABSTRACT

Porous graphitic nitride (gC_3N_4) by template free simple condensation and $SrTiO_3$ nanocubes by sol-gel method were synthesized. Composites containing Different percentages of pGCN were prepared (x% pGCN-ST where x = 5, 10, 30, 50 & 70%). The as synthesized composites were characterized by various instrumental techniques such as X-Ray diffractometer, Fourier transform infrared spectrophotometer, BET surface area analyzer, UV Visible diffuse reflectance spectrophotometer, X-Ray photoelectron spectrophotometer, SEM with Energy dispersive X-ray analyzer (SEM/EDAX) and elemental mapping, Transmission electron microscope, Photoluminescence spectrophotometer and Electrochemical impedance. The composite catalysts were evaluated for their photocatalytic degradation of reactive blue 198 (RB 198), reactive black 5 (RB 5) and reactive yellow 145 (RY 145) in the presence of visible irradiation. Among the different composites 50% pGCN-ST catalyst showed remarkable decolourization of all the three dyes under different irradiation (UV, visible and solar). Kinetics studies were revealed that the photodecolourization reaction followed pseudo first order. TOC and COD studies confirmed that the dyes were mineralized significantly. A possible mechanism for photocatalytic degradation was also proposed in this study.

1. Introduction

Water which is an indispensable thing for all the living beings is being polluted by various industries such as textile, dye, leather, tanning, chemicals, paint, plastic, insecticides, pesticides, food and beverage etc. [1–3]. Among the industries, the dye industry contributes a lot to water pollution. 120–280 l of water is required in the dyeing process for one kilogram of cloth [4]. 17–20% water pollution is caused by the textile and dyeing industries. According to survey of Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) among 4000 tested dyes, 90% of them were found to have LD_{50} >2 g/kg [5,6]. Among the dyes azo, direct and basic dyes have high toxicity rates. Reactive dyes are highly water soluble and least taken up by the fabric during dyeing and therefore the effluent contains more of reactive dyes when compared to other dyes [7]. In addition, the reactive dyes are extremely difficult to remove. Some reactive blue dyes have the half life of about 45 years [8]. These non-biodegradable and carcinogenic dyes present in the effluents cause dreadful diseases and other health issues in living organisms [9–11]. Hence the effluent need to be treated by a clean, green and economically attractive method before it is let into the natural stream and water bodies. Several strategies such as biological treatment, reverse osmosis, ozonation, filtration, adsorption on solid phases, incineration, and coagulation, etc. have been practiced and reported [12,13]. However, these strategies have their own advantages and limitations. The conventional physical methods such as adsorption, filtration, reverse osmosis and coagulation are quite expensive and also these techniques do not eradicate the pollutants completely [14,15]. Elimination of pollutants in the environment in an economically attractive way has been the subject of researchers in the last few decades. Mitigation of pollutants by utilizing solar energy and semiconductor photocatalysts is one of the Advanced oxidation processes (AOPs). AOP employing semiconductor photocatalyst has been found to be an effective and alternative way for the treatment of organic dye stuffs. In the photocatalytic process, semiconductor photocatalyst mineralize organic molecules into nontoxic CO_2, H_2O and mineral salts at the atmospheric conditions

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[16–20]. Although titania based catalysts such as titanates are very good semiconducting materials, the bottlenecks of these titania based catalysts are their wide bandgap and poor visible light activity and hence they are not economically attractive [21]. We have already reported the modification of titania based photocatalysts to improve its visible activity [22–27]. Strontium titanate is also one of the titania based catalyst which has the shortcomings of wide bandgap and poor visible activity [28,29].

The graphitic carbon nitride (g-C_3N_4), a metal free semiconductor, due to its advantageous properties such as high chemical stability, tunable electron structure, abundant nature, ease of preparation has attracted the attention of scientific communities [30–33]. However GCN alone cannot be used as photocatalyst as it suffers from limitations such as narrow bandgap leading to quick recombination of electron-hole pairs, and small surface area. GCN has to be modified in order to make it as a robust and visible active photocatalyst. Several modifications such as hybridization or heterojunctioning with other semiconductors, doping of metal and non-metals and sensitization with dyes have been reported for various applications such as pollutant removal, solar cells, water splitting, etc. [34–41]. Among the different above approaches, heterojunctioning of GCN with semiconductor oxides is one of the best ways to improve the photocatalytic activity under visible light irradiation. We have also shown the heterojunctioning of GCN with BiOBr for the degradation of dyes [42]. One has to be very careful in choosing the semiconductor for fabrication as these heterojunctioning may cause lattice mismatch leading to defects which may be the active points for the recombination of e^-- h^+ pairs. Such mismatch may lead to poor photocatalytic activity. Herein we report the syntheses of strontium titanate nanocubes by sol-gel method, porous graphitic carbon nitride (pGCN) by template free simple condensation method and porous graphitic nitride-strontium titanate (pGCN-ST) composite catalysts by simple impregnation method. The novelty of this work is to fabricate the composite catalyst to alter the bandgap of strontium titanate catalyst by heterojunctioning with visible active porous GCN polymeric semiconductor to degrade the reactive dyes under visible irradiation. The characterization of the catalysts revealed that the composite catalyst has been formed and intact. To address the twin main issues such as wide bandgap and electron-hole pair recombination the composite catalyst has been synthesized. The photocatalytic activity of all the synthesized catalysts were tested towards the decolourization of three reactive harmful azo dyes namely reactive blue 198 (RB 198), reactive black 5 (RB 5) and

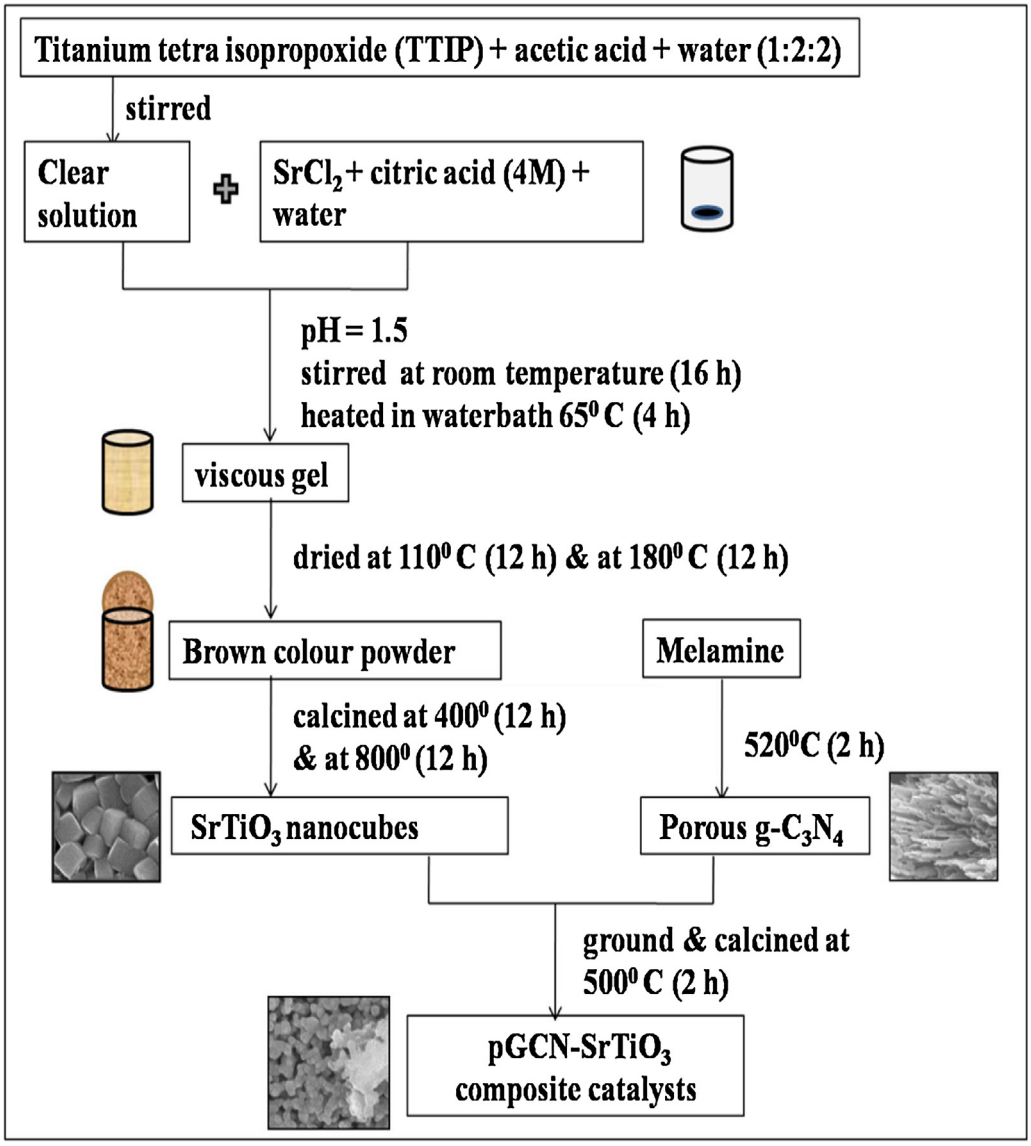

Fig. 1. Flow chart of pGCN-ST synthesis.