RESEARCH ARTICLE

SYNTHESIS AND CHARACTERISATION OF C$_3$N$_4$ – V$_2$O$_5$ NANOCOMPOSITE AND ITS PHOTOCATALYTIC AND ELECTROCHEMICAL PROPERTIES

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ARTICLE INFO	ABSTRACT
	Nanotechnology is a fast growing area of research in various discipline carbon nitride vanadium oxide (C$_3$N$_4$ –V$_2$O$_5$) nanoparticles were synthesized by simple thermal decomposition method. Ultraviolet – Visible spectroscopy, Fourier transformed infrared spectroscopy (FT - IR), Raman spectroscopy x-ray diffraction (XRD) and Scanning electron microscopy (SEM) were employed to characterized the structure, light absorption capacity of the synthesized sample. The photocatalytic activity of C$_3$N$_4$– V$_2$O$_5$ nanoparticles was examined by using degradation of methylene blue (MB) as the model organic pollutant. The visible light irradiation of aqueous dye solution in presence of C$_3$N$_4$–V$_2$O$_5$ nanoparticles showed decrease in absorption maximum with shift in absorption maximum λ = 663nm. Further, absorbance of C$_3$N$_4$ – V$_2$O$_5$ Showed a maximum value of 0.37 before irradiation and decreased to a value of 0.05 after 120 min. It can seen that the C$_3$N$_4$ – V$_2$O$_5$ nanocomposite exhibits maximum efficiency towards the photocatalytic degradation of methylene blue. The electrochemical sensing properties of were studied using hydroquinone.

INTRODUCTION

Carbon nitride

Diverse polymeric carbon nitride which differ in their atomic proportion have been reported by thermal condensation of organic monomers. One of the most relevant is the polymeric form melon, H$_3$C$_6$N$_9$, a predominate architecture which is a consequence of an incomplete condensation of carbon nitride precursors (Lotsch *et al.,* 2007). Bojdys *et al.* reduce the hydrogen content to a reasonable C$_3$N$_4$ formulation by Condensation of dicyandiamide in salt melt of lithium and potassium chloride (Bojdys *et al.,* 2008). The result indicate that graphitic (g-) allotropes are the most stable phases under ambient condition for the C$_3$N$_4$ composition. Carbon nitride and related compounds are of great engineering interest as possible material for microelectronic devices, optical, magnetic and tribological application (Scharf *et al.,* 1999; Donnet and Erdemir, 2004; Li *et al.,* 2009; Zhao *et al.,* 2008). Porous polymeric C$_3$N$_4$ has been proved as an active metal-free catalyst in Friedel-Crafts reaction (Goettmann *et al.,* 2006; Thomas *et al.,* 2008; Thomas *et al.,* 2008). Graphitic carbon nitrides can also be an active support, Lewis-base character, for the dispersion of metal particles in heterogeneous catalysis (Kim *et al.,* 2007).

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Recently, Wang *et al*. have considered g-C$_3$N$_4$, as an abundant photocatalyst for hydrogen production from water (Wang *et al.,* 2009). In addition to mentioned perspectives, in the past decades, studies on the most stable polymorphs of C$_3$N$_4$ were motivated by a special interest for the synthesis of new low-compressible material (Lowther, 1999; Li *et al.,* 2007). The calculation have predicted the bulk modulus of b-C$_3$N$_4$ nearly equal to that diamond (Liu and Cohen, 1989). Theoretical simulations of super-hard crystalline phases composed of C$_3$N$_4$ seen justified (Kroke and Schwarz, 2004; Zhao and Fan, 2008). A crystalline material, C$_3$N$_4$, which contains at least three coordinate non-planer covalent C-N bonds, printed as iconic city and small bond length, look like a clear indication for low compressibility, (Cohen, 1989; Solozhenko *et al.,* 2001). The same principles work in the finding of cubic c-BC$_2$N as competitive with c-BN as the second solid (Enders *et al.,* 1997). Many reports have claimed the synthesis of hard covalent C-N solids, mainly g-C$_3$N$_4$ (Matsumoto *et al.,* 1999; Hwang *et al.,* 2007). However, the experimental evidence of highly condensed crystalline carbon nitride is unreliable and its existence is at least doubtful. More consistent appears the obtaining of graphitic C$_3$N$_4$ phase (g-), extended lamellar, or confined nanocage and nanotubular structures (Guo *et al.,* 2005; Zimmerman *et al.,* 2001; Li *et al.,* 2007). Carbon nitride architectures have now for long been examined as candidates for materials application. The proposal of super-hard C$_3$N$_4$ phases hard re-initiated the endeavor in covalently bonded

carbon nitride materials for the last two decades. It soon turned out that layered, C-sp^2, carbon nitride phase are thermodynamically favored over potentially denser, C-sp^3, network structures of C_3N_4. Carbon nanotubes have extraordinary mechanical properties electrical and heat conductivity. As polymers of pure carbon, they can be functionalized using the rich chemistry of carbon. This provides opportunities to adapt the structure to optimize its performance. These extraordinary characteristics give carbon nanotubes potential in numerous applications. Since Dillon *et al*. claimed that single-walled carbon Nanotubes (SWCNTs) can store hydrogen, this material has been considered as a candidate for hydrogen storage media, safe, efficient and compact hydrogen storage is a major challenge in order to realize hydrogen powered transport.

Vanadium oxide nanoparticles [V_2O_5]

The multivalent nature of vanadium gives it interesting chemical properties along with distinct multifarious colors, which earn it the name of the Norse Goddess of beauty, Vanadis. By its inherent properties, vanadium attracts our attention in various applications; broadly speaking in oxidation reaction, oxidation coupling, organic toxic dye degradation, energy storage battery formulation and medicinal application (Rehder, 2013; Hirao, 1997). In the nano regime, these properties are affected to a noticeable extent. Different synthetic method lead to the formation of nano vanadium oxides with astonishing morphological behavior via nanosheet, nanotube, nanowire, nanobelt, nano-urchin, etc. formation, which in turn results in variation in the extent of their application. In the nano-regime, self-aggregation occurs in a spontaneous manner due to great surface energy. This self-aggregation can be prevented by the formation of one-dimensional (1D) nanostructure, e.g. nanobelts or nanowire. So with in this large variety of morphologies, special attention has to be paid to the formation of 1D nano structure, for their stability and applicability in various functions, due to their electronic confinement, high surface activity and high-surface area defects (Wang and Liu, 2009; Jiang and Peng, 2007; Spahr *et al.,* 1998). In developing countries, where industries are the economic backbone, the use of dye plays an important role; e.g. paper, textile, cosmetics, printing, etc. and therefore industries cause a direct threat to water bodies and ecosystem by creating unaesthetic pollution. One of the most studied dye is methylene blue (MB), which is used in the dyeing industry as well as in industries and has severe adverse effects on human health. Prevents photosynthetic activity, retards the growth of organisms, and the compounds chelate metal ions, which causes micro-toxicity in fish and other organism. In this study, V_2O_5 – carbon nitride nanocomposite was prepared by thermal decomposition method. In these studies have been reported on the photocatalytic properties of these materials and focused on the catalytic oxidation of drug and phenolic compound.

Scope of the present investigtion

Nanotechnology is a fast growing area of research in various disciplines including chemistry, physics, biology and medicine. Carbon nitride nanoparticles like carbon nitride-vanadium oxide, nanocomposite has been used as a photocatalytic materials. Synthesis of metal carbon nitride nanoparticles like carbon nitride-vanadium oxide by simple thermal decomposition method. Characterization of the nitride

nanoparticles like carbon nitride-vanadium oxide, nanocomposite by X-ray diffraction (XRD) analysis, Fourier transform infrared (FT-IR) spectroscopy, UV-Visible absorption (UV-Vis), scanning electron microscopy (SEM). Valuation of photocatalytic degradation property of the synthesized nanoparticles by using methylene blue (MB), the electrochemical sensing properties of hydroquinone.

MATERIALS AND METHODS

Synthesis of Nanocomphosite

Synthesis of carbon nitride nanoparticles

The graphitic C_3N_4 photocatalysts were synthesized using urea, The known amounts of urea were taken in alumina crucibles with covers. These were calcined at 550° C for 5 hrs at a heating rate of 5°C min^{-1}.

Synthesis of vanadium oxide nanoparticles

The vanadium oxide nanoparticles photocatalysts were synthesized using ammonium meta venadate, The known amounts of ammonium metta venadate were taken in alumina crucible with covers. These were calcined at 450° C for 5 hrs at a heating rate of 5° C min^{-1}.

Synthesis of carbon nitride-vanadium oxide nanoparticles

The graphitic C_3N_4 -vanadium oxide Nanocomphosite photocatalysts were synthesized using urea – V_2O_5 The 50:50 amounts of urea – V_2O_5 were taken in alumina crucible with covers. These were calcined at 450° C for 5 hrs at a heating rate of 5° C min^{-1}.

RESULT AND DISCUSSION

UV-Visible spectroscopy

The UV-Visible absorption spectrum of the carbon nitride-vanadium oxide nanocomposite is showed in Fig 5. The broad peaks in the range of 571 nm π^*-π^* nm are electronic states are contributions from CN (Xiang *et al.,* 2011). The synthesized carbon nitride nanoparticles are similar to the value reported in literature. Note that very few literatures reported the UV - Visible absorption of vanadium oxide nanostructures. The V_2O_5 absorption at 404 nm, it was observed that V_2O_5 showed an absorption band in the wavelength range of 200 to 600 nm, which results from them electronic transition of the $02_p/V_2d$. Generally V^{5+} showed absorption edged at wavelengths less than 600 nm. In this investigation V_2O_5 showed an absorption edged at around 404 nm which might be due to the presence of vanadium in the V^{5+} oxidation state. The UV-Visible absorption peak 404 and 571 nm 0f nitride and vanadium oxide nanocomposite. In the carbon nitride-vanadium oxide hybrid composite photocatalyst there is a small shift in the band edge position to a higher wavelength as compared with pure carbon nitride and vanadium oxide suggesting that the recombination rate of the electron-hole pair was successfully reduced in the hetero structured carbon nitride-vanadium oxide composite photocatalytic activity.

FT-IR Spectroscopy

The FT-IR spectrum of the carbon nitride-vanadium oxide nanocomposite is showed in Fig 6.
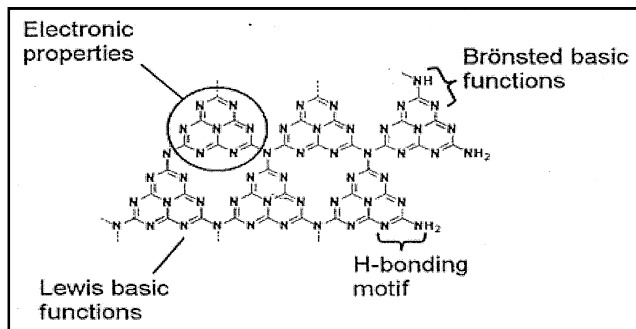
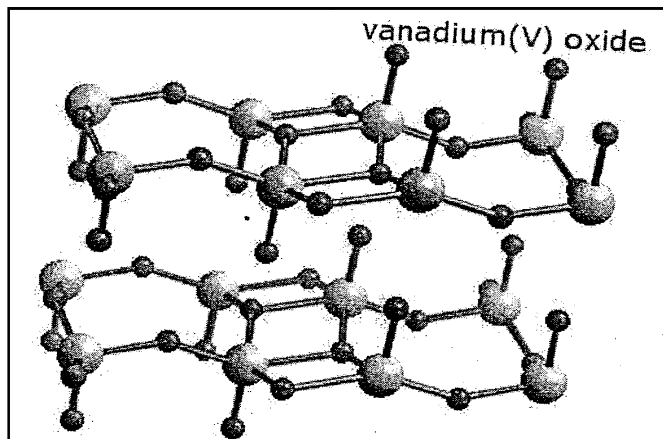**Fig. 1. Structure of carbon nitride nanoparticles**

Fig. 2. Reaction mechanism for the preparation of carbon nitride from thiourea

Fig. 4. Structure of vanadium oxide nanoparticles.

Fig. 5. UV – Visible spectroscopy of carbon nitride-vanadium oxide nanacomposite

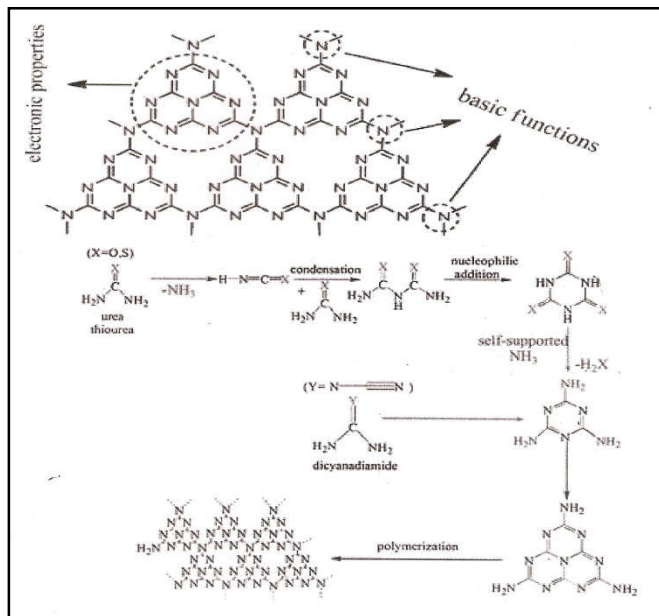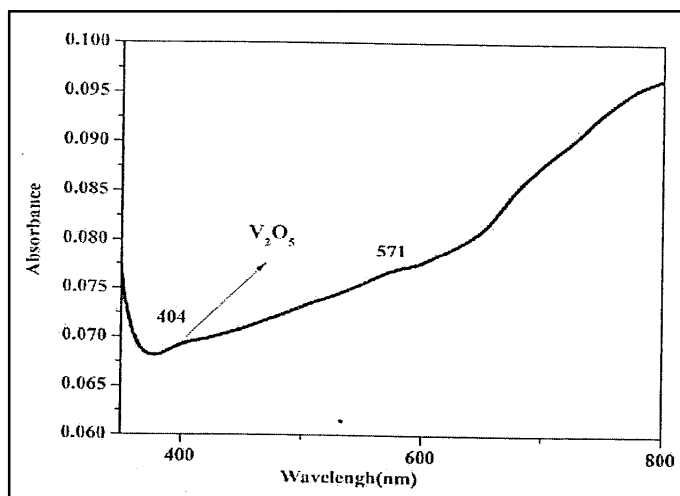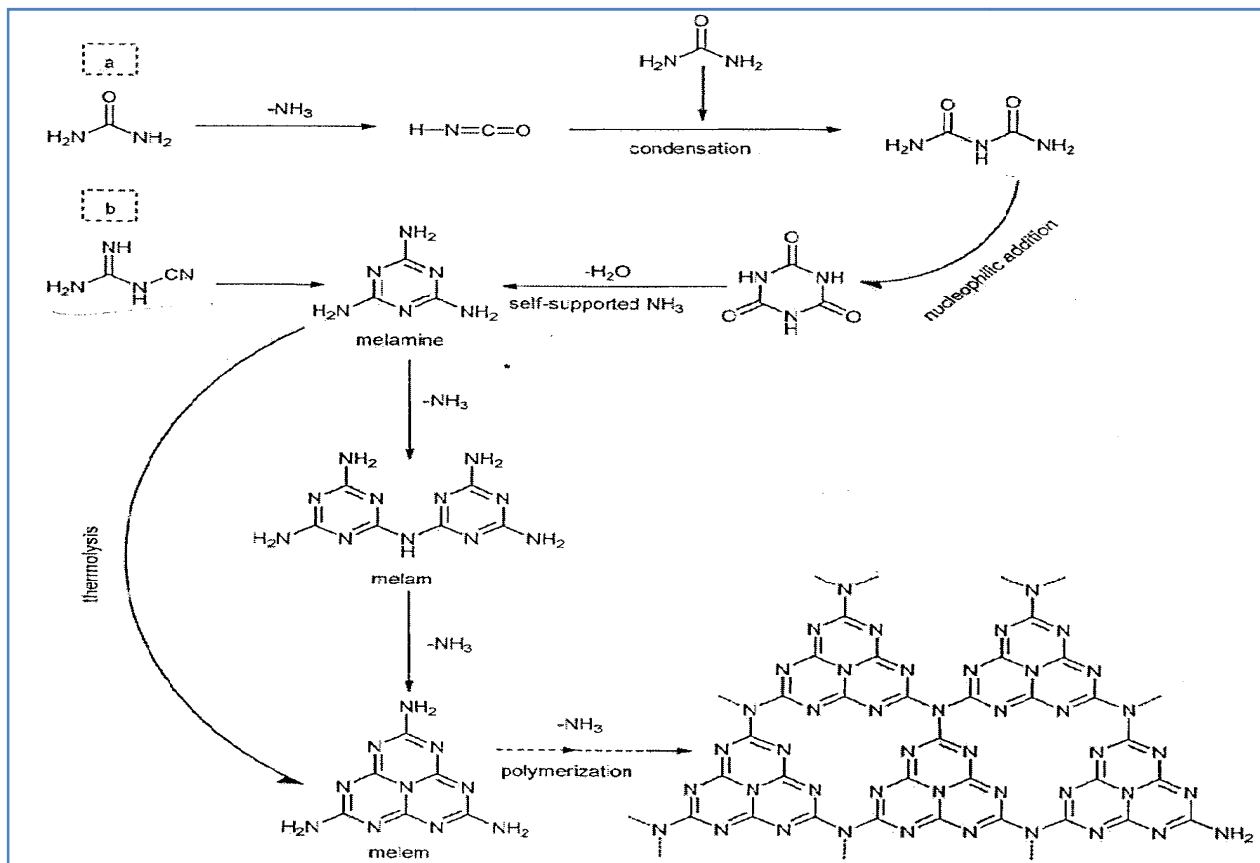**Fig. 3. Reaction mechanism for the preparation of carbon nitride from urea**
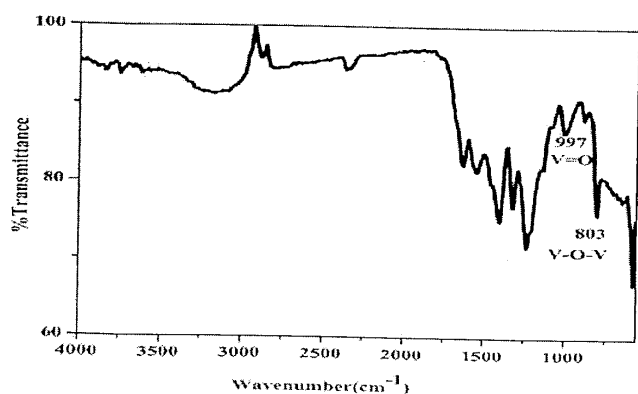
Fig. 6. FT-IR spectrum of carbon nitride-vanadium oxide nanocomposite

The Fourier transform infrared spectroscopic measurement, which implies the existence of condensed aromatic CN heterocyclic. The stretching vibration near at 1539 and 1619 cm^{-1} are attributed to C=N stretching, while the three bands at 1228, 1320 and 1406 cm^{-1} to aromatic C-N stretching. The peak at 887 cm^{-1} belongs to triazine ring mode, which correspond to condensed CN heterocyclic. A broad band near at 3160-3500 cm^{-1} correspond to the stretching modes of NH_2 or =NH groups, are mostly due to typical vibration of C-N that contain C-N heterocyclic and are generally associated with skeletal stretching vibration of these aromatic ring (Zhou *et al.,* 2012). The FT-IR spectrum of the vanadium oxide nanoparticles as expected the metal oxygen stretching vibration in V_2O_5 nanoparticles bands at 997 and 803 cm^{-1}. The band at 997 cm^{-1} is attributed to the VO_3 symmetric stretching vibration and bands at 803 cm^{-1} are connected to the VO_3 anti symmetric stretching vibration. The band at 583 cm^{-1} is corresponding to the symmetric stretching mode of V-O-V units. The FTIR spectrum of carbon nitride-vanadium oxide nanocomposite shows the symmetric and asymmetric V-O vibrational modes at 803 and 997 cm^{-1}, respectively. We found that V-O vibration modes are shifted to higher wavenumber upon interaction with carbon nitride. It is reported that, the NH-O=V bond promotes a displacement of the vanadium ion position in direction to the VO_4 plane. This increases the V=O bond length and the interaction between the oxygen of planar base and vanadium ion, increasing the wavenumber corresponding to symmetric and asymmetric V-O vibrational modes. From this, it is concluded that the VO_5 square pyramid in carbon nitride-vanadium oxide nanocomposite is less distorted than in V_2O_5.

Raman Spectroscopy

The Raman spectrum of the carbon nitride-vanadium oxide nanocomposite is showed in Fig 7. It can be clearly seen that carbon nitride nanosheets, which is indicating that the retain the crystal structure as exfoliation. However, the carbon nitride nanosheets shows a lower shift, which is due to the phonon confinement effect of exfoliated nanosheets. The Raman peak observed at approximately 688 and 987 cm^{-1} are attributed to the different types of ring breathing modes of s-triazine, which is present in the carbon nitride structure. The above result are in good agreement with the FT-IR result (Kawaguchi and Nozaki, 1995). The Raman bands are observed at 1038, 516, 476, 402 and 284 cm^{-1}. The band at 1038 cm^{-1} is attributed to the VO_3 symmetric stretching vibrations and bands at 769 cm^{-1} are connected to the VO_3 antisymmetric stretching vibrations. The band at 516 cm^{-1} is corresponding to the symmetric

stretching mode of V-O-V units. Furthermore, the band observed at 1390 cm^{-1} is caused by overtone band. The Raman spectrum of the carbon nitride-vanadium oxide nanocomposite it is implies the existence of condensed aromatic CN heterocyclic and vanadium oxide. The peak at 1038, 156, 476, 402 and 284 cm^{-1}. All the characteristic peaks of carbon nitride and vanadium oxide were observed in the carbon nitride-vanadium oxide nanocomposite.

XRD

The X-ray diffraction pattern of carbon nitride-vanadium oxide are presented in Fig 8. The XRD pattern confirmed the of graphite like stacking carbon nitride structure. The two peak are observed in the XRD pattern for graphitic carbon nitride prepared from urea. The 2θ peak observed at 27.85° corresponds to the in-plane structure packing motif of tristriazine units and in indexed as the (002) peak (Goettmann *et al.,* 2006). This corresponds to the hole-to-hole carbon nitride and the presence of uncondensed amino groups. The XRD pattern of the as-prepared vanadium oxide (JCPDS No. 70-1532). The observed diffraction peaks 2θ=32.83, 35.70,38.90,48.88,53.67,58.12° respectively. No peaks from other impurity phases have been detected, indicating that the sample is highly pure. In the XRD pattern of carbon nitride-vanadium oxide nanocomposite, diffraction peaks at 2θ= 32.83, 35.70, 38.90, 48.88, 53.67 and 58.12° vanadium oxide. Whereas, the broad diffraction peak due to the periodicity parallel to the polymer chains of carbon nitride was not clearly observed at the 2θ value of 27.85 due to the weak intensity in comparison to the vanadium oxide diffraction peak. Further, the characteristic peak intensity of vanadium oxide in carbon nitride-vanadium oxide nanocomposite was significantly which can be explained by the formation of carbon nitride layer on the vanadium oxide nanoparticles.

SEM

of the photocatalyst was investigated by SEM. The SEM images of carbon nitride-vanadium oxide are shown in Fig 9. The grain size of g-C_3N_4 was distributed from 1 to 3 μm. The layered shape morphology is clearly shown in Fig 9b. The layered was agglomerated sheet like morphology of carbon nitride. It can be seen that the SEM image shows free standing nanosheet with diameters of a few nanometers. The edges of the sheets tend to be ranged in order to minimize their surface area. The surface morphology of the as anodized vanadium oxide as shown in Fig 9b, is a nanotubular structure with an average diameter of 3 μm. The nanoparticles calcined at 550°C 5hrs. The wall thickness was growth on nanosheets. The dispersed nanospheres will have potential applications in photocatalysis due to larger available surface areas.

Photocatalytic

Photocatalytic activity of the carbon nitride-vanadium oxide nanoparticles was examined by using degradation of methylene blue (BM) as model organic pollutant. Fig 10. Shows the absorption spectrum of 5×10^{-5} MB. The solution during different time intervals in presence of carbon nitride-vanadium oxide nanoparticles respectively. Fig 6. Shows time course degradation of MB. The visible light irradiation of aqueous dye solution in presence of carbon nitride-vanadium oxide nanoparticles showed decrease in absorption maximum with shift in absorption maximum (λ=663 nm).
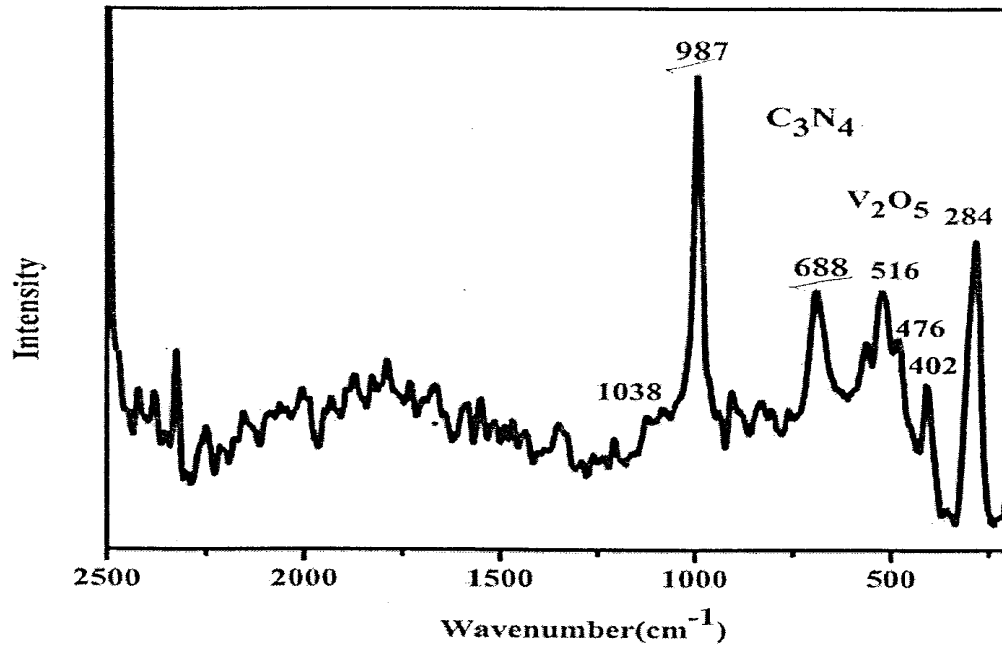
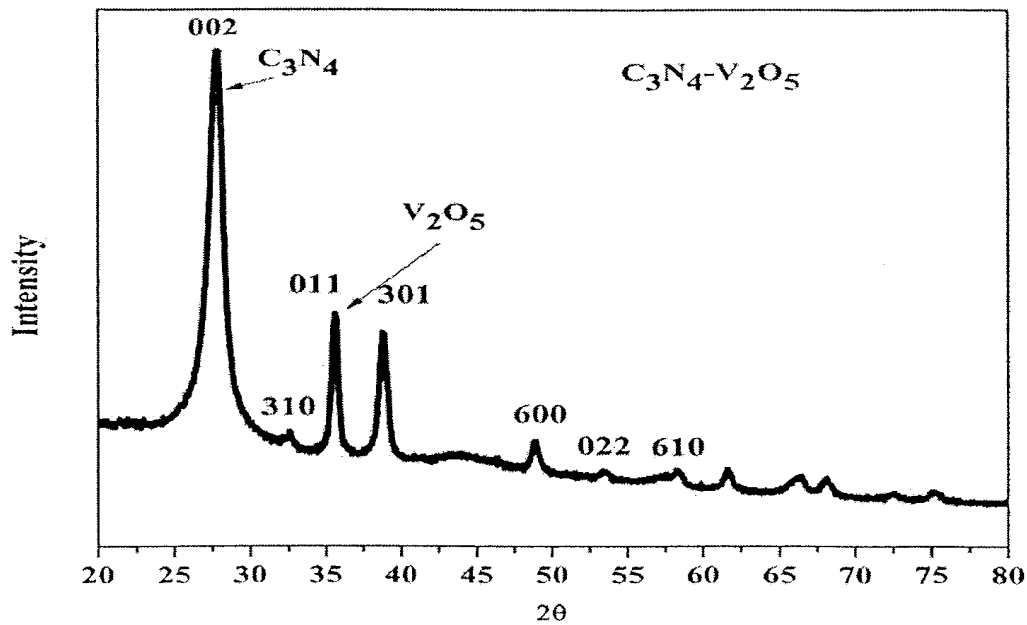**Fig. 7. Raman spectroscopy of carbon nitride-vanadium oxide nanocomposite**

Fig. 8 XRD pattern of carbon nitride-vanadium oxide nanocomposite
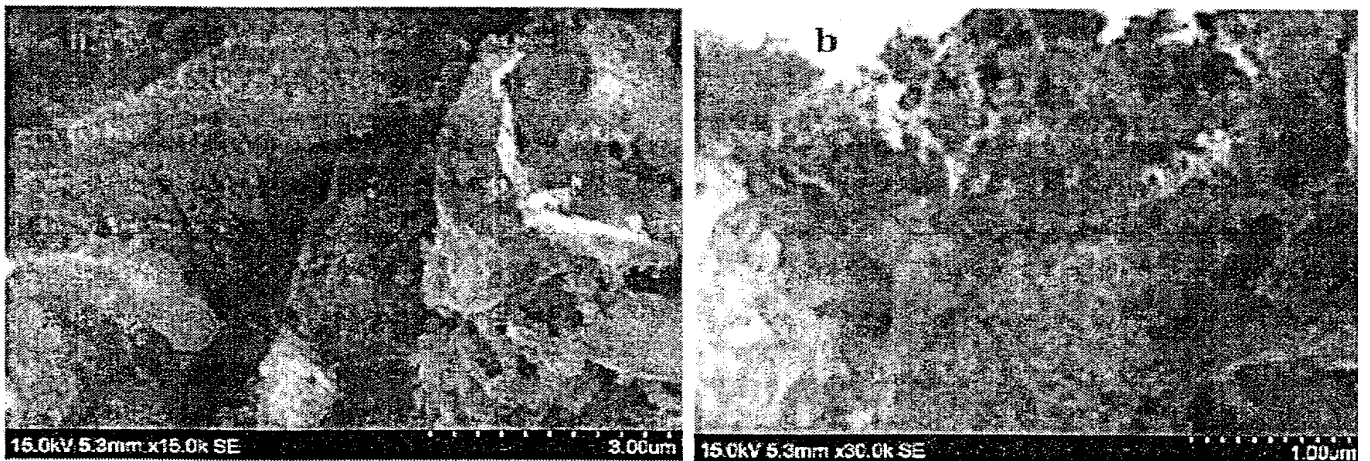

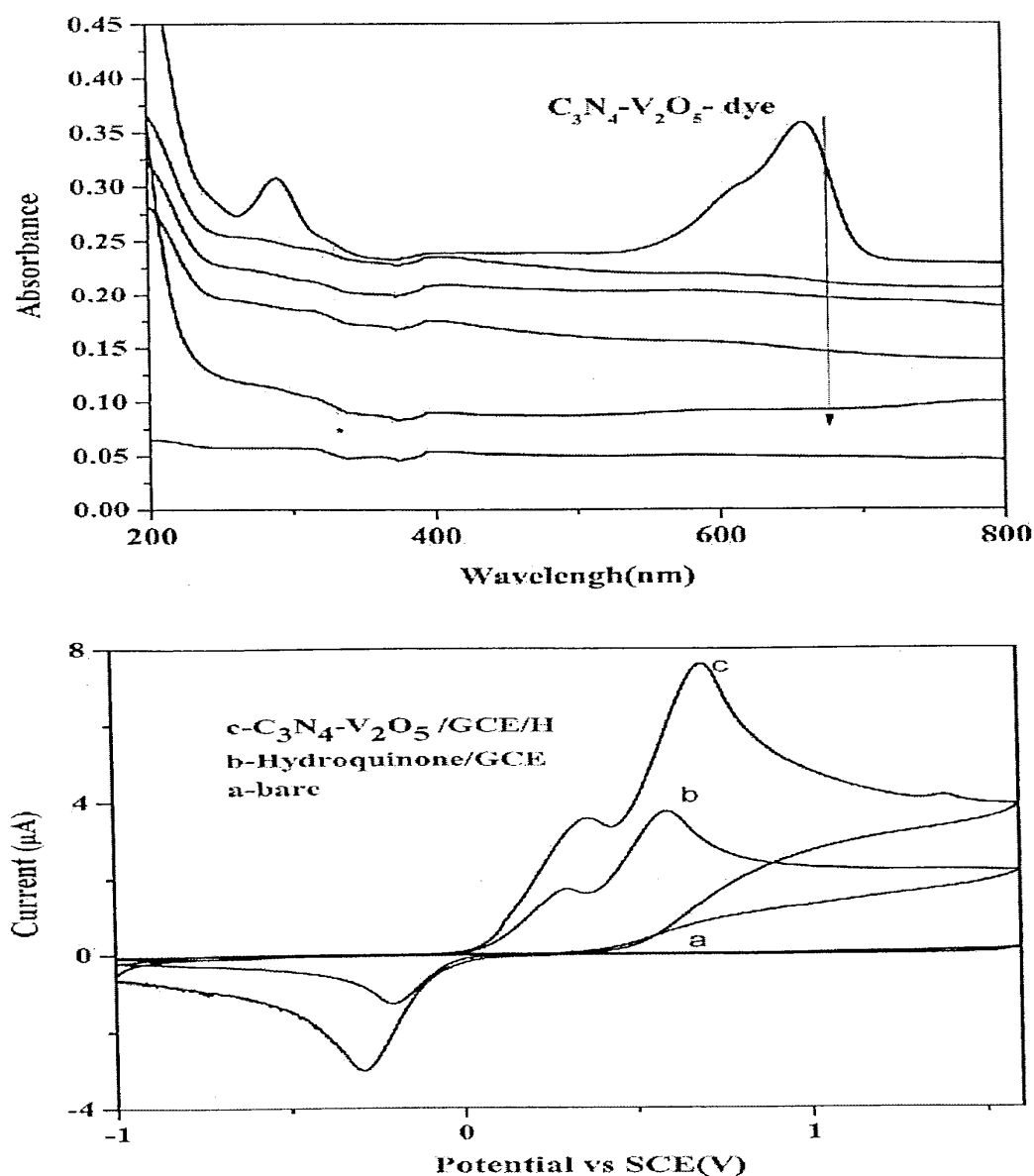**Fig. 9 SEM image of carbon nitride-vanadium oxide nanocomposite**

Fig -11, Cyclic voltammetry for (a)- bare, (b)- hydroquinone/DCE and (c) – carbon nitride-vanadium oxide/GCE nanocomposite.
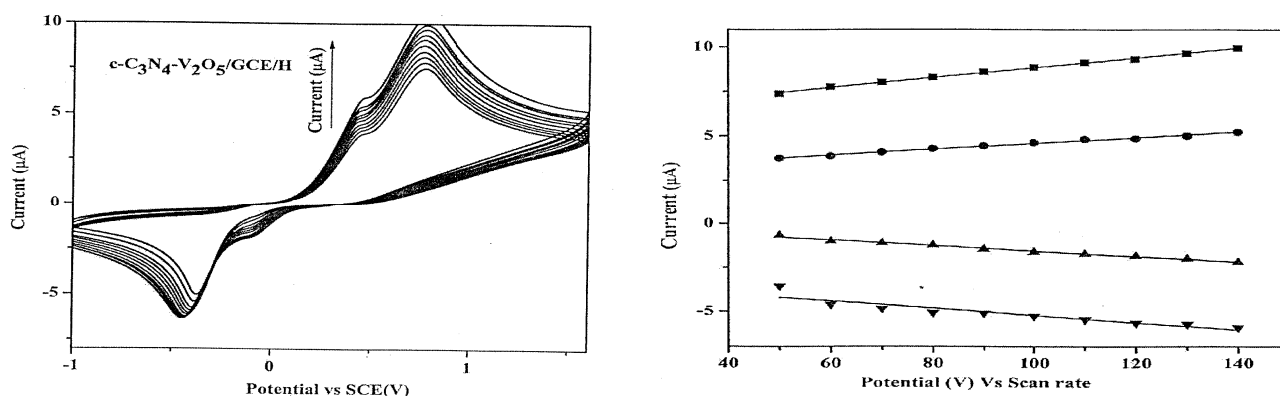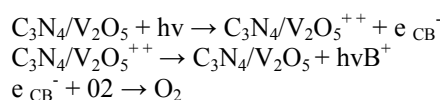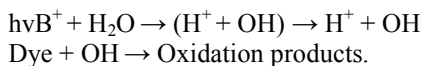

Fig. 12. Cyclic voltammetry for 50-130 scan rate – carbon nitride-vanadium oxide nanocomposite/GCE

It suggests that the complete decolourization of MB solution was purely due to the photocatalytic degradation ability of carbon Joithride-vanadium oxide nanacomposite. Further, absorbance of carbon nitride-vanadium oxide showed a maximum value of 0.37 before irradiation and decreased to a value of 0.05 after 120 min. It should be mentioned that the contained irradiation of visible light for another 35 min did not give any decrease in absorbance at 663 nm. Therefore, the photocatalytic efficiency and the rate constant values were

calculated with that carbon nitride-vanadium oxide value of absorbance and the degradation time of 120 min. It can be seen that the carbon nitride- vanadium oxide nanocomposite exhibits maximum efficiency towards the photocatalytic degradation of MB.

$$C_3N_4/V_2O_5 + h\nu \rightarrow C_3N_4/V_2O_5^{++} + e_{CB}^-$$
$$C_3N_4/V_2O_5^{++} \rightarrow C_3N_4/V_2O_5 + h\nu B^+$$
$$e_{CB}^- + 02 \rightarrow O_2$$

$hvB^+ + H_2O \rightarrow (H^+ + OH) \rightarrow H^+ + OH$

$Dye + OH \rightarrow$ Oxidation products.

Electrochemical sensing properties of modified GCE/Carbon Nitride-Vanadium oxide Nanocomposite

Fig 11. Shows the cyclic voltammogram (CV) of 1Mm a hydroquinone bare and carbon nitride-vanadium oxide nanocomposite modified GCE. The CV of hydroquinone the modified GCE shows a peak at about 0.6 mV. It is well known that the oxidation hydroquinone at bare GCE is generally believed to be totally irreversible and requires high over potential. However the hydroquinone voltammogram obtained for carbon nitride-vanadium oxide nanocomposite modified GCE showed an oxidation and reduction of hydroquinone 0.69 and -0.3 mV with enhanced peak current the bare GCE. Hence the carbon nitride-vanadium oxide nanocomposite modified electrode has improved the electron transfer kinetics and oxidation and reduction peaks for anodic peak potential (V) =0.69 mV, anodic peak current I (μA) = 7.6 (μA) and cathodic peak potential (0.29), cathodic peak current (-3μA). The anodic peak potential is shifted to the positive direction by ~0.1mV indicates the eletrocatalytic ability of the modified electrode and cathodic peak potential is shifted to the negative direction by ~0.1mV indicates the electrocatalytic ability of the modified electrode.

Fig. 12. shows the effect of scan rate on carbon nitride-vanadium oxide nanocomposite modified GC electrode in 1mM of hydroquinone. The slight towards higher value of the oxidation and reduction peak potential with increasing scan can be observed; indicating a kinetic limitation in the reaction between redox sites of carbon nitride-vanadium oxide nanocomposite modified GC electrode hydroquinone. However, the anodic peak and cathodic current for hydroquinone at carbon nitride-vanadium oxide nanocomposite modified GC electrode are linearly related to the scan rate the range of 50-140 mV s^{-1}. Which indicated that the electron transfer reaction was controlled by adsorption process. In order to determine the adsorption behavior of hydroquinone, we have performed the following experiment. The carbon nitride-vanadium oxide nanocomposite modified GCE was used for the determination of hydroquinone, there was a voltammetric for the oxidation and reduction of hydroquinone. The confirming that hydroquinone was adsorbed controlled at the carbon nitride, vanadium oxide nanocomposite modified GCE during oxidation and reduction process.

Summary and conclusion

- Synthesis of metal carbon nitride nanoparticles like carbon nitride-vanadium oxide, by simple thermal decomposition method.
- Characterization of the metal venadate nanoparticles carbon nitride nanoparticles like carbon nitride-Tantalum oxide, carbon nitride- vanadium oxide, carbon nitride-silver and carbon nitride-zinc nanocomposite by X-ray diffraction (XRD) analysis, Fourier transformed infrared (FT-IR) spectroscopy, UV-Visible absorption (UV-Vis), field emission scanning electron microscopy (FE-SEM), and energy dispersive X-ray spectroscopy (EDX).
- UV-Visible absorption peak 404 and 571 nm of nitride and vanadium oxide nanocomposite.

- The FT-IR spectrum of the vanadium oxide nanoparticles as expected the metal oxygen stretching vibration in V_2O_5 nanoparticles bands at 997 and 803 cm^{-1}. The band at 997 cm^{-1} is attributed to the VO_3 symmetric stretching vibration and bands at 803 cm^{-1} are connected to the VO_3 anti symmetric stretching vibration. The band at 583 cm^{-1} is corresponding to the symmetric stretching mode of V-O-V units.
- The Raman spectra bands at 1038, 516, 476, 402 and 284 cm^{-1}. The band at 1038 cm^{-1} is attributed to the VO_3 symmetric stretching vibrations and bands at 769 cm^{-1} are connected to the VO_3 antisymmetric stretching vibrations. The band at 516 cm^{-1} is corresponding o the symmetric stretching mode of V-O-V units.
- In the XRD pattern of carbon nitride-vanadium oxide nanocomposite, diffraction peaks at 2θ= 32.83, 35.70, 38.90, 48.88, 53.67 and 58.12^o vanadium oxide. Whereas, the broad diffraction peak due to the periodicity parallel to the polymer chains of carbon nitride was not clearly observed at the 2θ value of 27.85 due to the weak intensity in comparison to the vanadium oxide diffraction peak.
- Evaluation of photocatalytic degradation property of the synthesized nanoparticles by using methylene (MB) as model organic pollutants and industrial effluent (IE) by $C_3N_4 - V_2O_5$ nanoparticles.
- Electrochemical properties of hydroquinone – carbon nitride-vanadium oxide nanocomposite.

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