

Pronounced light trapping effect and enhanced photo-electrochemical property of type (II) aligned graphitic-C₃N₄ with embedded 1-D ZnO nanostructures

S Singh¹ and M Khanuja²

¹ Shaheed Rajguru College of Applied Sciences for Women, University of Delhi, New Delhi 110096, India

² Centre for Nanoscience and Nanotechnology, Jamia Millia Islamia (A Central University), New Delhi 110025, India

sonal.singh0811@gmail.com, manikakhanuja@gmail.com

Abstract. Graphitic carbon nitride (g-C₃N₄) with embedded 1D-ZnO nanostructures was prepared by simple two step thermal decomposition process. Photocatalyst exhibited higher optical absorption than pure ZnO due to π - π conjugations of C₃N₄, which thus allow greater adsorption on its surface. Conduction band (CB) edge of g-C₃N₄ being more negative than ZnO and Valence band (VB) of ZnO is more positive than VB of g-C₃N₄; this alignment of Type (II) resulted in transfer of excited electrons in g-C₃N₄ to the CB of ZnO. This charge transfer created the internal electrostatic potential, which aided in reducing the recombination rate of charge carriers. Finally, samples were tested for photo-electrochemical activity measured by generated photocurrent density with respect to voltage and time under illumination conditions.

1. Introduction

Graphitic Carbon Nitride (g-C₃N₄) has already attracted much attention in the field of organic nanomaterials owing to its unusual excellent properties towards environmental protection and remediation through artificial photocatalysis, photo-electrochemical and other solar energy conversion related methods [1,2]. g-C₃N₄ is metal-free catalyst with a band gap of 2.7 eV, which is smaller than commercially used and much advanced inorganic TiO₂. It is regarded as the most stable phase of C₃N₄ at ambient conditions and with controlled structure and morphology at the nanoscale, it can possess properties such as high hardness, low friction coefficient, and reliable chemical inertness, which classify it as a suitable photoactive material. Moreover, it is highly sustainable being composed of nitrogen and carbon only [3,4]. However, the quantum yield of the system still remains low and the photocatalytic efficiency of pristine g-C₃N₄ is still not satisfactory due to factors like high recombination rate of photogenerated electron-hole pairs. Therefore, it is required to assist its activity in some sort. Several routes like chemical doping, non-metallic doping, and composite formation by coupling g-C₃N₄ with other semiconductors have been adopted and there is an effective strategy to modify the electronic structure as well as surface properties of semiconductors [3,5].

Although, various studies related to formation of ZnO nanostructures, such as nanosheets, nanotubes, and nanoparticles coupled with g-C₃N₄ as a composite have been reported for their photocatalytic activity so far, photoelectrochemical (PEC) properties of 1D-ZnO nanostructures, i.e. nanorods with embedded g-C₃N₄ are still poorly studied [6-9]. Studies reveal that individual materials, here ZnO, of different morphology (particles, rods, sheets, etc.) exhibit different optical and electronic properties



under the same conditions [10-14]. ZnO of 1D morphology, such as nanorods and nanotubes, has shown improved photoactivity by light trapping effect, wherein it achieves improved electron transport due to its internal electric field. So, we have purposely chosen this particular morphology and attempted to embed these nanostructures into a narrow band gap material, g-C₃N₄. The ability of 1D nanostructure to trap photons theoretically remains very high as compared to flat surface, which thus increases light absorption [15]. Coupling a wide band gap material with a narrow one is a promising approach to achieve high photoactivity, as it helps overcome the demerits of individual components and instigate a synergistic effect, such as improved photostability, enhanced harvesting of light, and efficient photo-excited charge separation [16,17]. Further, due to sp₂ hybridization, formation of the delocalized conjugated π structure of g-C₃N₄ brings effective charge separation in the photocatalysis. Adopting such strategy may help the material to overcome some of its existing drawbacks, such as (1) typical confinement below 470 nm wavelength due to insufficient sunlight absorption, (2) moderately low specific surface area, (3) low efficiency with low charge mobility, and (4) inability to oxidize water due to its inappropriate valance band (VB) position at about 1.4 V vs. NHE [18].

Herein, we attempted to prepare g-C₃N₄ nanofilms with ZnO nanorods embedded to it via simple two step thermal decomposition process and tested its PEC properties.

2. Experimental

All chemicals were of analytical grade and were used in experiments without any further purification. Pure ZnO nanorods were prepared by mechanical thermal decomposition method using [Zn(CH₃COO)₂·2H₂O], zinc acetate dehydrate as a precursor. 2 g of powder were kept in alumina crucible after mechanical grinding in mortar pestle for 45 min. To thermally decompose the powder, it was placed in programmable furnace at 500°C with ramp rate 4°C/min for 4 h. The obtained powder sample was washed several times with distilled water and then dried in oven for 8 h at 100°C. Graphitic carbon nitride sheets were synthesized via simple heat treatment method as reported in Ref. [19]. To prepare zinc oxide embedded g-C₃N₄, the as prepared ZnO nanostructures were added to the g-C₃N₄ precursors during its synthesis. In brief, the light-yellow powder of melamine (5 g) was obtained after annealing and kept for cooling overnight under ambient temperature. The sample was annealed with ramp rate of 4°C per min for 4 h at 550°C. The sample was treated with HCl (50 mL/g of g-C₃N₄, 18.5 wt. %) for protonation followed by addition of ZnO nanostructures to the solution at room temperature for 4 h. This suspension was diluted, filtered, and washed several times with de-ionized water and dried at 80°C for 6 h.

Transmission electron microscopy (TEM, FEI, Technai G2, 200kV) was used to study the morphologies and crystallographic structure of the as-prepared samples. To investigate the crystalline structure of pure g-C₃N₄, pure ZnO and ZnO embedded g-C₃N₄ samples, X-ray diffractometer (XRD) (Bruker, D2-Phaser) using CuK α (λ = 1.5403Å) X-ray was used. XRD spectrum was recorded from 2θ = 5 to 80° operating at 10 KV and 30 mA. XRD data peaks were verified with the help of JCPDS files. The photo luminescence (PL) emission spectra were examined using photo luminescence spectroscopy (RF 5301 PC, Shimadzu) with 325 nm excitation wavelength.

PEC performance of pristine ZnO and ZnO-embedded-C₃N₄ samples was evaluated and compared using three-electrode-electrochemical system. Chrono-amperometry and linear sweep voltammetry (LSV) measurements were carried out under illumination at bias potential of 0 V vs Ag/AgCl. The samples were prepared over conducting glass and used for PEC as working electrode keeping Pt and Ag/AgCl electrode as counter electrode and reference electrode, respectively. The electrolyte used was 1 M NaOH at pH 14. The film was spin coated on Fluorine-doped tin oxide (FTO) substrate/glass at 5000 rpm for 50 seconds and annealed at 350°C for 1 hr.

3. Results and discussion

Figure 1 shows the XRD spectra for both pure ZnO and ZnO-embedded-C₃N₄ sample. The XRD characteristic peaks were verified with the help of JCPDS card no (06-2151), which confirmed the successful formation of the samples. The as-calculated lattice parameters values for ZnO (a =3.25 Å,

$c=5.2$ Å) were consistent with the standard values for wurtzite hexagonal structure confirming its structure. XRD pattern for ZnO-embedded- C_3N_4 exhibited characteristic peaks of both ZnO and C_3N_4 . However, the strongest peak for C_3N_4 at (002) is not distinctly visible in the graph, as the intensity of the peak is proportional to its concentration compared to counter material in the composite. As the concentration of the material in the composite increases, the XRD peak intensifies. In our case, amount of C_3N_4 is less compared to ZnO. No phase change was observed for both the materials in nanocomposite rather change in value of peak intensities indicated a change in crystallinity. In case of C_3N_4 -ZnO, a decline in peak intensity values was observed for planes (100), (002), and (101) as compared to pure ZnO as shown in Table 1.

Figure 2 shows the transmission electron microscope micrographs for pure ZnO and C_3N_4 -ZnO samples. Figure 2a reveals the clear formation of 1-Dimensional morphology for pure ZnO in the form of nanorods. From Figure 2b, it is clearly observed that ZnO nanorods are completely incorporated in C_3N_4 nanosheets. The images of C_3N_4 -ZnO confirm the huge dispersion of ZnO nanorods in C_3N_4 nanostructures and thus lead to an establishment of close contact of latter with the former. This sets for prompt transfer of charges between the two.

Table 1. Data showing peak intensities for ZnO and C_3N_4 -ZnO at various planes.

Sample	(100)	(002)	(101)
ZnO	8525	6424	14160
C_3N_4 -ZnO	4733	3789	8426

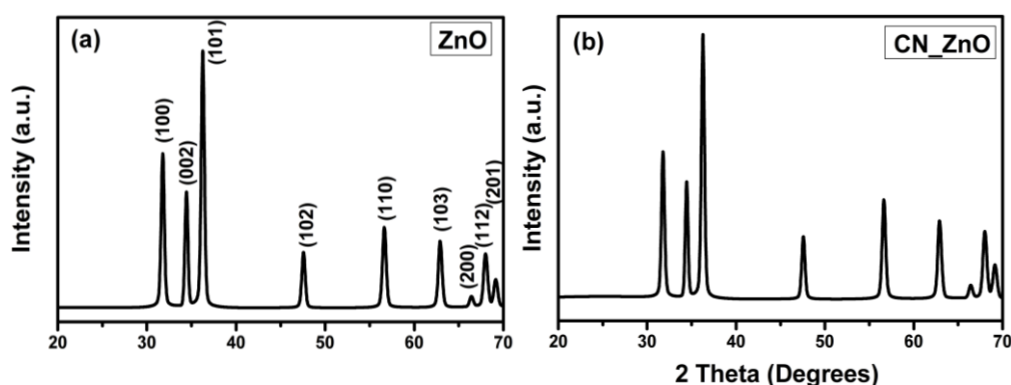


Figure 1. XRD patterns of (a) pure ZnO and (b) C_3N_4 -ZnO nanostructure.

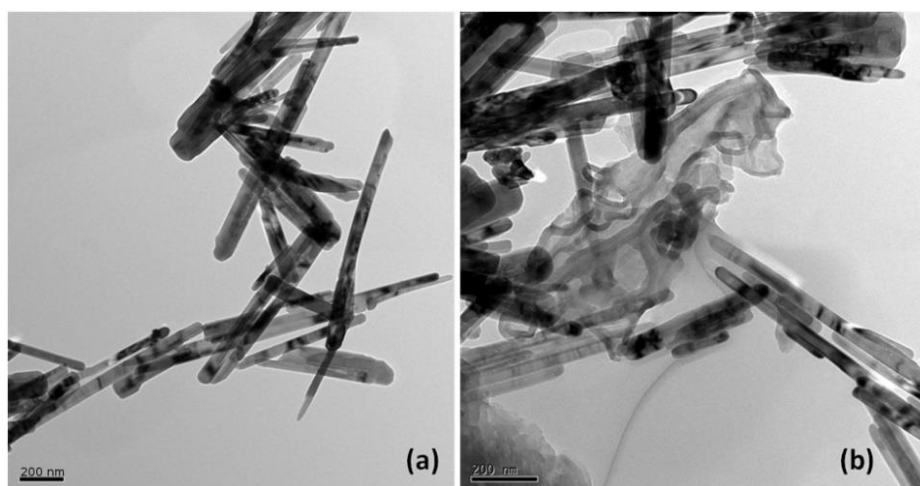


Figure 2. TEM micrograph of synthesized (a) ZnO nanorods and (b) C_3N_4 -ZnO nanostructures. Scale-bar 200 nm.

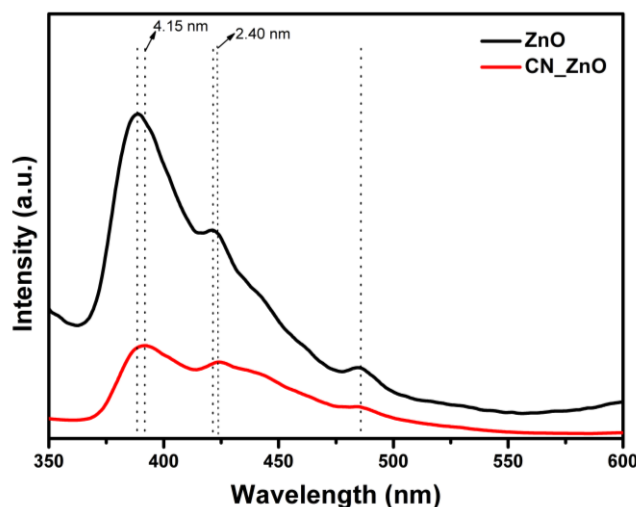


Figure 3. PL spectra for ZnO and C₃N₄-ZnO nanostructure.

To understand the high rate of charge carrier migration and get an insight into the mechanism process in case of close contact formation in composite, PL analysis was carried out. Figure 3 shows the PL spectra for pure ZnO and C₃N₄-ZnO with 325 nm excitation wavelength. Analysis of PL spectra is based on two primary factors: (a) peaks intensity and (b) peaks shift. As shown in Figure 3, major emission peak for pure ZnO sample corresponds to the light energy being almost equal to the band gap of ZnO. After adding ZnO to C₃N₄, it is clearly observed that there is a significant decrease in intensity of peaks for C₃N₄-ZnO PL spectra, along with the slight red-shift of the spectra. It is well known that decrease in intensity of peaks indicates reduced recombination rate of photogenerated charge carriers, which is the case in our C₃N₄-ZnO sample. This fact of prolonged electron-hole separation in the material contributes significantly towards improved charge transfer between ZnO and C₃N₄ and overall enhanced PEC activity of the material. Further, the shift in the spectra of C₃N₄-ZnO confirms the existence of close contact between the two materials, which is consistent with the results obtained for TEM micrographs. The shift of spectra towards red region of visible region also indicates a reduction in band gap as compared to pristine sample, which further aids in the superior photoactivity of the composite material.

PEC performance of pristine ZnO and C₃N₄-ZnO samples with respect to voltage and time is shown in Figure 4. LSV measurements under illumination conditions clearly show an increase in current linearly of +4.6 mA for C₃N₄-ZnO as compared to +2.0 mA for ZnO and almost 0 mA current for ZnO in dark. It is clearly visible that C₃N₄-ZnO shows the enhanced current and maximum current density with respect to pure ZnO, which does not produce sufficiently high current. The results obtained for LSV were found to be consistent with those of current density vs. time curves. C₃N₄ showed maximum photocurrent density and thus was the most stable with respect to time as compared to other samples.

Based on the PEC results obtained in this work, mechanism for boosted photoactivity is proposed in Figure 5. With the PEC results, it was clearly observed that ZnO alone was not able to contribute to the photoactivity as it could not be excited in solar visible region due to large band gap. Whereas, C₃N₄-ZnO exhibited remarkable photo electrochemical activity. The energy potentials for Conduction Band (CB) and Valence Band (VB) of C₃N₄ lies at -1.12 eV and 1.57 eV, respectively. The conduction band edge potential of ZnO is 0.5 eV, which is more positive than that of C₃N₄. The photoinduced electrons reaching the CB of C₃N₄ from its VB, can now easily transfer or inject to the CB of ZnO due to well-developed close contact between the two materials. The CB of ZnO now has excess of electrons reaching via VB of ZnO and CB of C₃N₄. This route of direct injection of charges from C₃N₄ to ZnO reduces the amount of energy required for the excitation of the material, thus making the material active in visible region of solar spectrum. This promotes the photo-electrochemical reactions of the composite material. Also, the reduced recombination rate of electron-hole pairs results in prolonged separation of charges further enhancing its photoactivity.

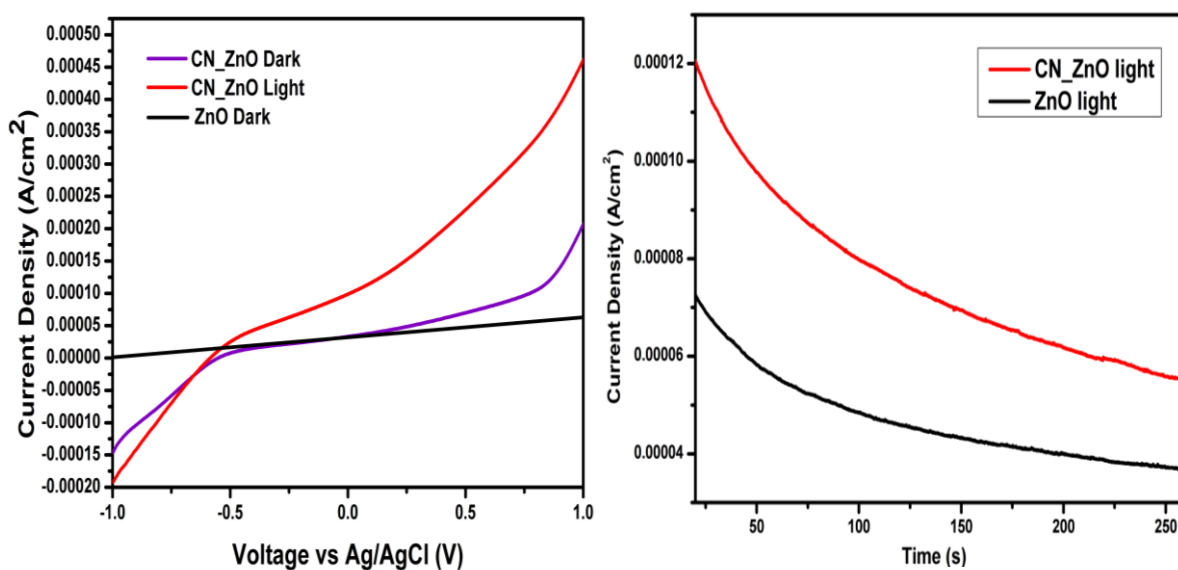


Figure 4. PEC performance of ZnO and C₃N₄-ZnO samples with respect to voltage and time.

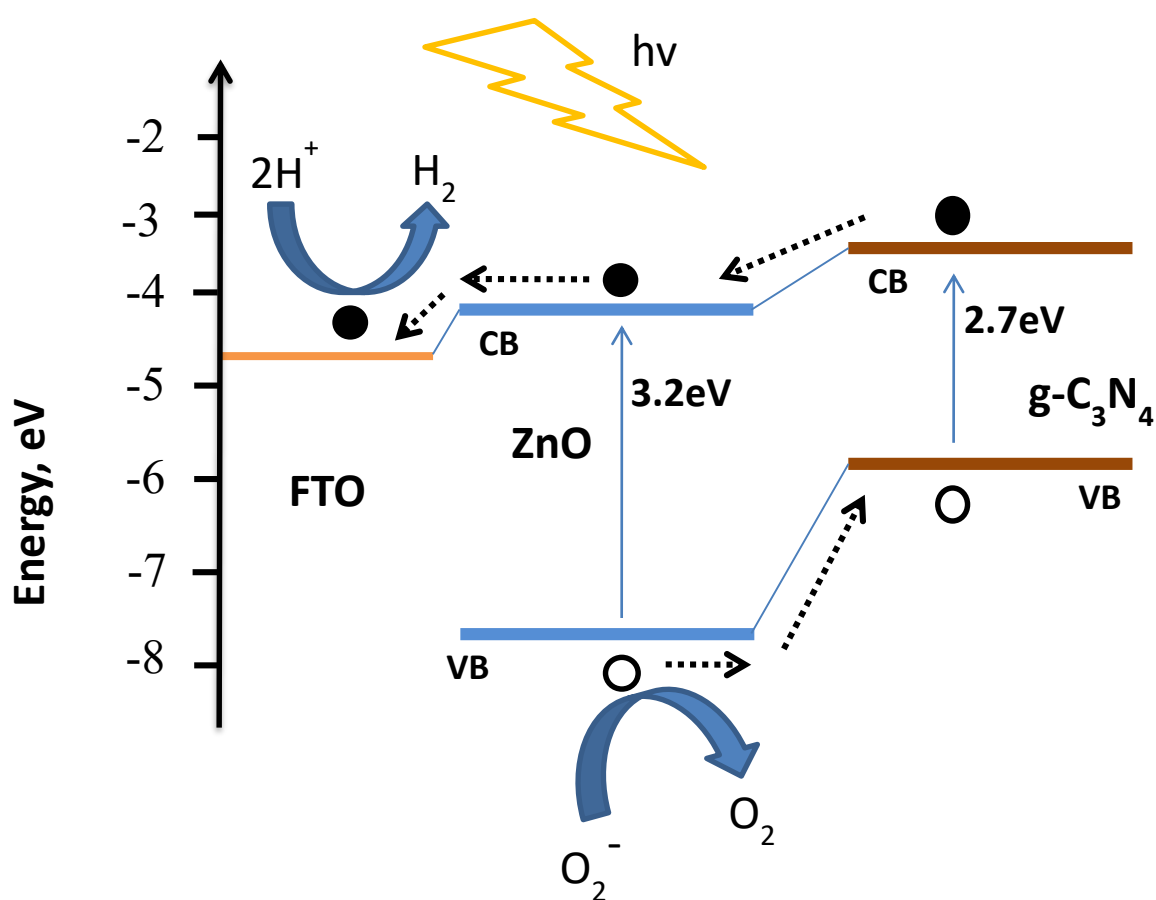


Figure 5. Schematic diagram of PEC action of C₃N₄-ZnO nanorods.

4. Conclusion

In summary, graphitic-C₃N₄ nanosheets embedded with 1D-ZnO nanorod structures were successfully formed by two step thermal decomposition process to test their photoelectrochemical activity and compare the results with that of pure ZnO. It was found that ZnO-embedded-C₃N₄ sample showed an overall increase of +2.6 mA current density as compared to pristine ZnO, which was attributed to the fact that close contact and type (II) alignment between the two materials promoted prompt and easy charge transfer. Further, 1D structure of ZnO contributed towards improved light trapping effect, which reduced the photon losses and increased average lifetime of charge carriers. Reduction in band gap of ZnO and increased electron-hole pair separation assisting to its pronounced photoelectrochemical activity is proposed with possible action mechanism.

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