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NOVEL SYNTHESIS OF CU NANOPARTICLE GRACED GRAPHENE COATED ZNO NANOROD TO ENHANCE PHYSICAL ABSORPTION BAND FROM UV TO VIS -IR REGIONS

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Abstract

In this work synthesized Cu nanoparticle (NP) - graced graphene - covered ZnO nanorod (ZNR@Gr/Cu) by novel material and low cost solution methods .The morphologies of ZNR@Gr/Cu could be studied with (FE-SEM), (TEM), and (AFM), which specified that ZNR can good cover by graphene with 5 layers and graced by Cu (NP) size (10-15 nm). UV-Vis absorption spectra and photoluminescence spectra (PL) can be described the optical properties. As the result all samples with high absorption at UV region of spectrum. Then coated the ZNR by GO and decorated with Cu NP. Increased in physical absorption accrues at (300–1000) when the band gap decreases from (3.2 to 2.9, 2.7 and 2.2) e.v at ZNR, ZNR/Cu, ZNR@Gr, and ZNR@Gr/Cu that due to high reduced of recompilation of photo electron–hole pairs at range (350-800)nm at ZNR@Gr/Cu. We were synthesis all these types of thin films by simple, cheap and environmentally, method which made its favorable for huge -scale preparation in many applications as water splitting, sensor, solar cell, antibacterial and optoelectronic devices.
***Keywords*:** ZnO nanorod, graphene oxide, absorption, synthesis, Band gap, coated, composite materials.

Introduction

ZnO has a great attention Because of it is semiconductor materials, non-toxicity, low cost and controllable morphology (Muhammad Amin *el al*., 2012). Metal nano particles are particles of the size 1-100 nm. Nanotechnology is widely used in various fields including surface chemistry, organic chemistry, molecular engineering, semiconductor, and nano fabrication (Hongbo Fu *et al.*, 2008); (Shakeel Ahmed *et al*., 2016). ZnO has limited with large band gup 3.37 e.v, the optical absorption is specified to the UV region (Mundher *et al.,* 2012); (Yuan-Fong Chou Chau *et al*., 2014). To obtained broadband photo-response in the Vis. region, the Au, Ag, Al, Cu, Pt and Ni, NP structures should be deposited on ZnO semiconductor with fine domination on distribution and size (Cheng long Zhang *et al*., 2015). Graphene has large surface area and high thermal conductivity, high absorption in IR regain of light spectra there for, it is a novel material for energy storage applications (Ferrari *et al.,* 2015). In spite of ZnO & graphene composites have been a great reported, but there were few reports on ZNR with graphene coating. On the other hand, huge efforts have been focused towards enhancing the physical absorption by decorating with a metal (Ag, Au, Al or Cu) on the surface of the ZNR arrays (Su *et al.*, 2014); (Roozbeh Siavash Moakhar *et al.,* 2017). In this work, we synthesized a Cu NP, graced graphene - coated ZNR array (ZNR@Gr/Cu) and (ZNR/Cu) thin film. The hydrothermal method is a process of low cost, low temperature, large area uniformity and environmentally friendly method. The SEM, TEM, and AFM images show that graphene with 5 layers were good-coated on the surface of ZNR, and the average size of Cu NP (10-15) nm were uniformly decorated at the ZNR@Gr/Cu, ZNR/Cu to enhance physical absorption properties of ZNR thin film when reduced the energy gap.

Materials and Methods

The ZNR were synthesis in the FTO substrates were washed with 50 ml of water, 25 ml of ethanol, and 25ml acetone in an ultrasonic bath for 20 min at 90 C °.Ten drops of hexamethylenetetramine (HMTA, 0.5 M) from New Delhi-110002 (INDIA) and ten drops of Zn $(NO_3)^2$ solution from (Shanghai, China), (0.5 M) were alternately distilled onto the FTO (fluorine-doped tin oxide) substrate. After 10 min, the solution on (FTO, 2× 3 cm^2) substrates was distributed by using a spinner. FTO was annealed at 200 C° for 20 min. To be sure that the seeds are formed on the substrate all above process should be repeated for 3 times by using hydrothermal method. Samples of ZnO nano seeds substrates were prepared with were stood up right into stainless-steel autoclave at 122 C° for 4h then two days at room temperature including the blended solution of 0.05 M HMTA and 0.05 M Zn $(NO_3)^{2.}$ Then, all the samples were cleaned by deionized water and dried at 100 C° for 4 h.

Preparation of graphene oxide

To production graphene oxide (GO) can be used Hummers method William S. Hummers *et al*., 1958). In summary, 1 g of graphite powder with partial size (6-8 nm) from (sky spring nanomaterials Inc.2935 west hollow Drive. Houston, TX.77082.USA) was added to 23ml of H_2SO_4 98% (LOBA -Chemie) with 5g of sodium nitrate $NaNO_3$ 99.5 % (Sigma- Aldrich) for 15 min. Then 3 g of $KMnO_4$ 99% (Sigma-Aldrich) can be added with 500 ml deionized water and then, the solution putted on the magnetic stirrer for 24 h at 35 C°. 5 ml, H_2O_2 (30%) from (Sigma-Aldrich) was added. Then the solution was washed by 5%M of HCl (11.25) +H_2O (88.75) 37.5% (Fluka). Finally, to obtain GO the solution was heated at 100 C° for 3 h.

Synthesis of graphene covered ZNR (ZNR@Gr)

Electrostatic self-assembly method was used to cover ZNR arrays with graphene. The ZNR surface can be modified with APTM S aminopropyltrimethoxysilane was bought from Aladdin (Shanghai, China), in 5% APTMS/ethanol solution obtained a positively charged surface. 5 mL 0.1 mg mL^{-1} negatively charged. Graphene oxide (GO) is gained using the modified Hummers' methods. Selected size by using centrifuged at 8000 rpm for 25 min. Then increase to 100 mL and managed by ultrasonic for 20

min. The modified samples were submerged in GO solution with heating at 65 C° for 4 h. Subsequently, the samples could be cleaned with deionized water and dried at 80 C°. lastly, to get the ZNR@GO could anneal at 500 C° for one hour to obtain ZNR@Gr nanorod.

Synthesis of ZNR@Gr/Cu and ZNR/Cu

0.1mL $HCuCl_4$ (25mM) and 0.15 mL $CuCl_2$ (25 mM) from (Sigma-Aldrich) aqueous solutions can be added in a 50 mL beaker with 50 mL deionized water, 50 m PVA from (Sigma-Aldrich) (PVA/(Cu) 0.5, weight ratio), Cu NP size range (10-15) nm (china) and $NaBH_4$ (Sigma-Aldrich) ($NaBH_4$/ (Cu) 5, molar ratio) mingled solution as mixed into the beaker with stirred continuously. The formed ZNR and

ZNR@Gr arrays can be submerged in the solution for 4 h and washed with water. The ZNR@Gr/ Cu and ZNR/Cu samples were obtained after drying at 70C°for 2 h as shown in Fig. 1.

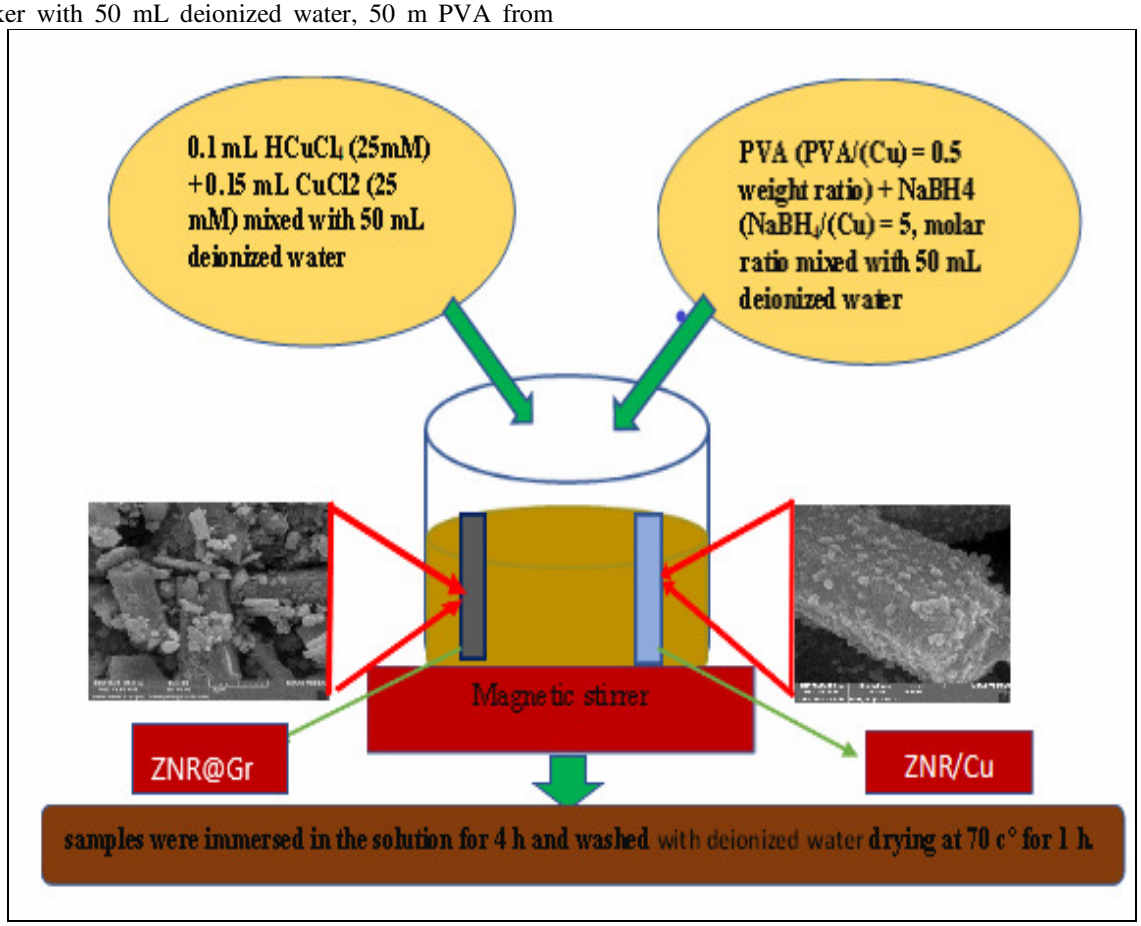

Fig. 1 : Refers to the steps of synthesizes, ZNR@Gr/Cu and ZNR/Cu**.**

Results and Discussion

Characterizationof ZNR@Gr/Cu and ZNR/Cu

The (EDX) given in Fig. 2 (a) showed the presence of (Zn, O) and Si, comes from substrate), That mean the formation of the ZnO nano rod structures was due to the presence of a suitable surfactant, (b)refers to (Zn, O, C and Si from substrate graphene oxide appeared and (O) intensity increased when coated the ZNR by graphene oxide. Fig. 2 (c) refers to (Zn&Cu) with high intensity beak was good reacting when doped the ZNR, by Cu ((10-15) nm NP powder) and without graphene oxide coated. then at Fig. 2(d) the(C), intensity with the seam intensity at fig2(b)and was good reacting between Zn & Cu but the intensity of Cu larger than Zn while at fig 2(c) the intensity of Zn was larger than Cu NP. Fig. 3 shows the morphologies SEM and TEM images of ZNR, ZNR/Cu, ZNR@Gr and ZNR@Gr/Cu. The ZNR arrays can be good aligned on the FTO substrate, which was shown in Fig. 3(a) while (b), (c) and(d) are the SEM and TEM of ZNR@Gr, we can observe graphene connecting the ZNR arrays, the graphene observed in the SEM image was already comparatively thick. It was shown at the TEM images that the surface of ZNR was good coated by graphene, most of which is not more than 5 layers of thick. Fig3(e) and (f) are the SEM and TEM of ZNR/Cu respectively, which display the well-dispersed Cu NP on ZNR with the size of about (10-15) nm, which displays Cu NP random alloy nanoparticle. agree with (Mohammed Khenfouch *et al.*, 2012). (Fig. 3(g),(h) and (i)refers the SEM and TEM image of ZNR@Gr/Cu graphene covers most of the ZNR surface ,and Cu NP are uniformly dispersed on the ZNR@Gr surface, the Cu NP were also found to be decorated onto the graphene connecting the ZNR arrays of display the detailed interstitial structure of ZNR@Gr/Cu. Fig. 4(a, b, c) and (d) shows AFM topography (Atomic force microscopy AFM JPK nano wizard ll Germany) of ZNR, ZNR@Gr, ZNR/Cu and ZNR@Gr/Cu. It could be seen that of image a, are uniform and homogenies, which appeared better nucleation centers for the formation of well arrangement. Image b. of ZNR@Gr, was uniform with average range size distribution less than 90 nm with roughness average (22,6) nm while, the distribution average size of ZNR less than 10.05 nm and with roughness average (3.5nm).

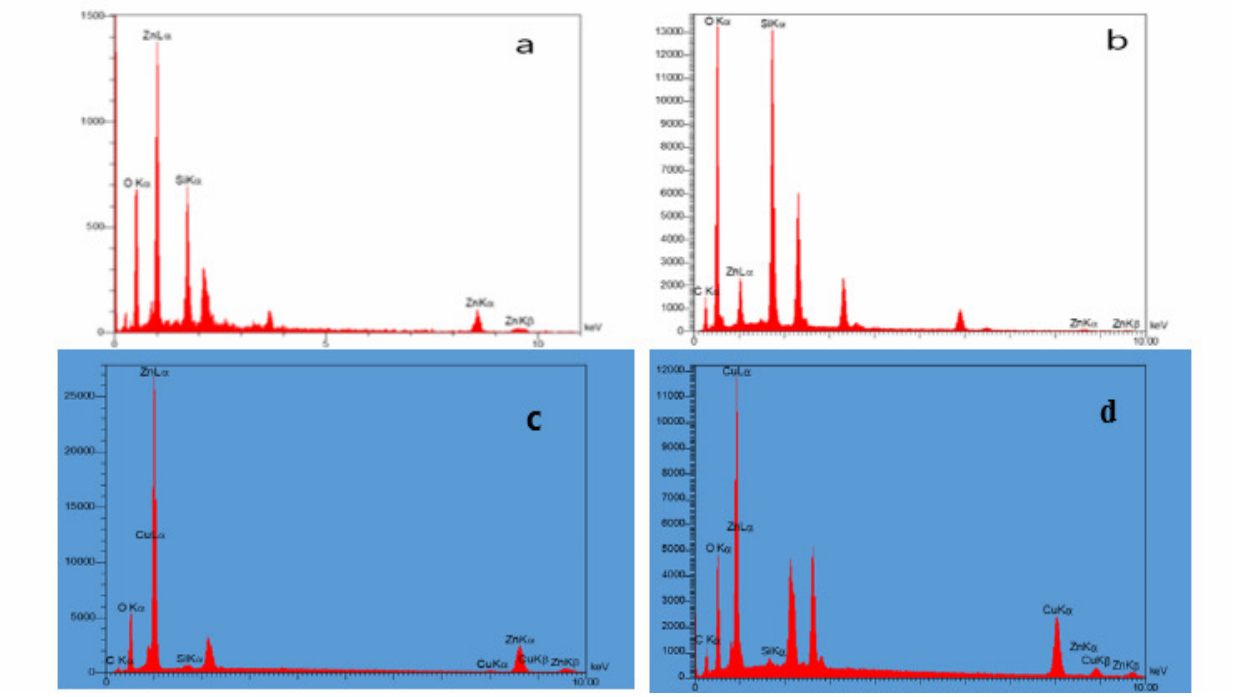

Fig. 2 : (EDX) for a. ZNR, b. ZNR@Gr, c. ZNR/Cu and d. ZNR@Gr/Cu

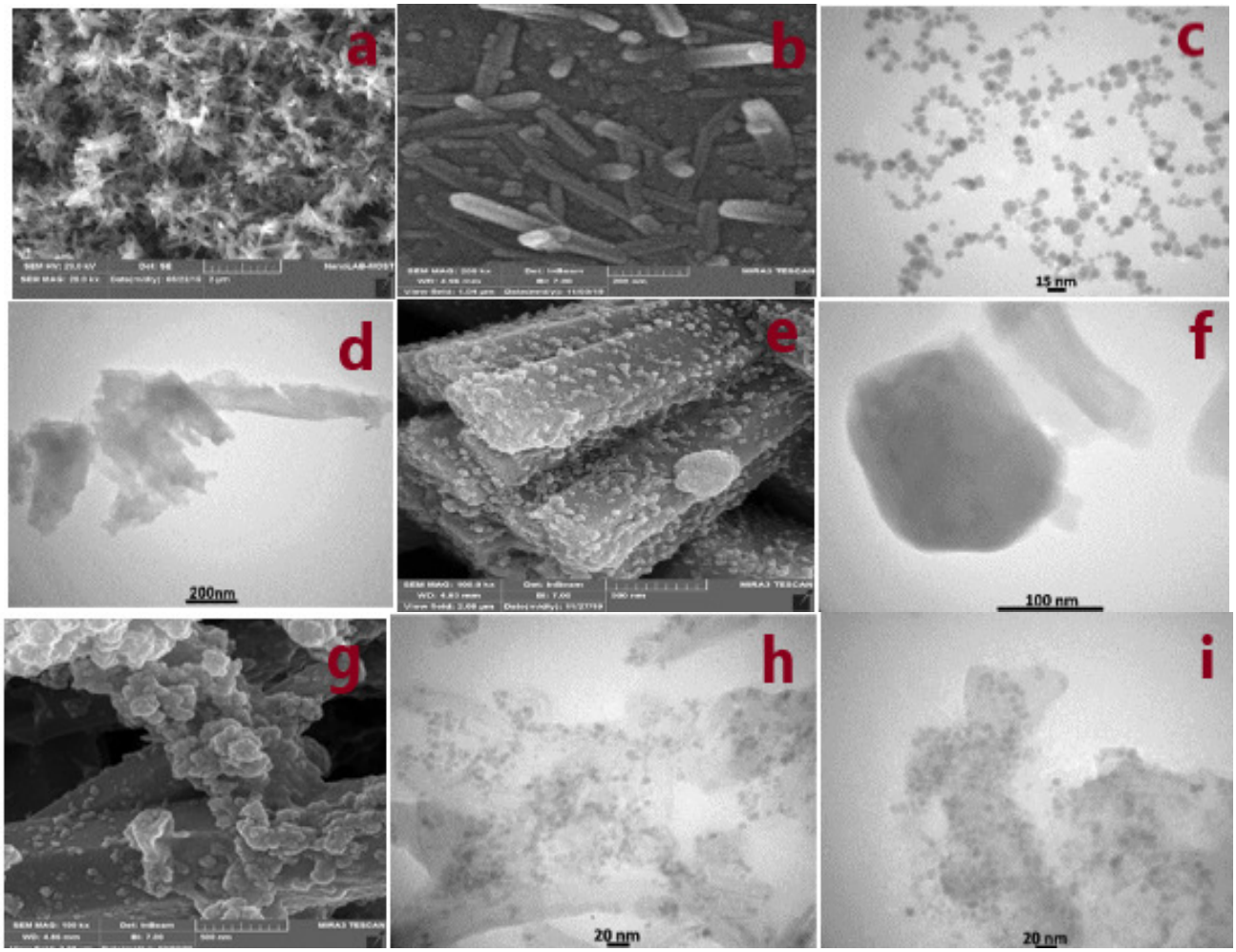

Fig. 3(a, b): SEM image of ZNR; ZNR@Gr (c,d) TEM image of ZNR@Gr; (e, f) SEM, TEM images of ZNR/Cu (g, h ,i) SEM and TEM image of ZNR@Gr/Cu.

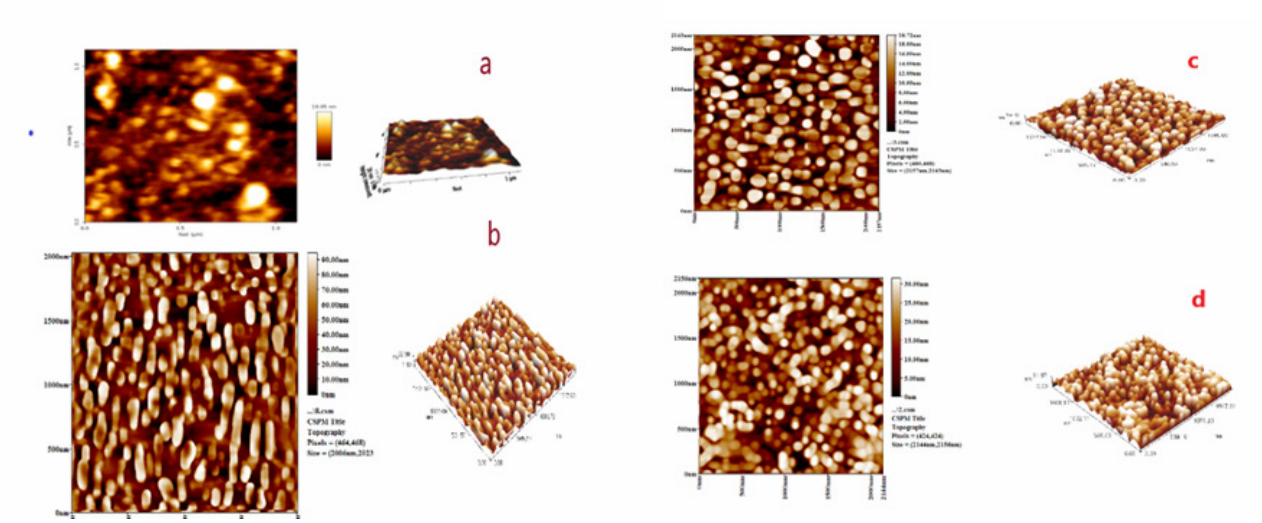

Fig. 4 : (a) AFM of ZNR., (b). AFM of ZNR@Gr, (c) AFM of ZNR/Cu, (d) AFM of ZNR@Gr/Cu

the average size disruption of ZNR/Cu less than19.72 with roughness (4.92) nm and image d. of ZNR@Gr/Cu with (30) nm roughness and the average size distribution less than (7.12) nm. The average size disruption of graphene oxide was not large than 90 nm, which matches very good with ZNR thin film to prepare the ZNR@Gr structure. The thickness of graphene oxide was about 2.63 nm, which coincides to 5 layers of GO agree with (Yuzhi Zhang *et al.*, 2019). The uniformly method to synthesize sprinkled Cu NP with the average size (10-15) nm it was well-covered ZNR@Gr structure to obtain the ZNR@Gr/Cu and ZNR/Cu composite thin films.

Optical properties characterization

The UV-Vis absorption spectrometer (SP8001 Taiwan) and (PL) (Hitachi F-4600 and Shimadzu) spectra of ZNR, ZNR/Cu, ZNR@Gr, and ZNR@Gr/Cu could be got within ranges (300 –1000) nm and (300 – 800) nm of the wavelength. The UV-Vis spectra (Fig. 5(a)) exhibit that for all products, there shows an intensive absorption in the UV region as a result the energy of light was more than the ZnO band gap (3.37 e. v). Raising in the light intensity of absorption in the range of 300 –1000 nm, were exhibited at ZNR/Cu, ZNR@Gr and ZNR@Gr/Cu, which could be enhanced effect of thin film absorption agree with (Yuzhi Zhang *et al.*, 2019) and that effect is very useful for many photonic applications like improved the photo electrode of water splitting, sensors, antibacterial etc. The optical band gaps of the thin film were obtained when $(\alpha h\nu)^2$ is plotted against photon energy ($h\nu$) at Fig. 5(b) straight line, which mention that the absorption edge is lead to a direct transition between valence and conduction bands. The intercept of the straight line on $h\nu$ axis matches to the optical band gap (Eg). The band gap of ZNR was 3.2 e. v, but the energy gap degreased at the ZNR/Cu 2.9 e. v, 2.7 e.v of ZNR@Gr and 2.2 e. v at ZNR@Gr/Cu. When Eg of thin films reduced that mean the absorption were double increased at ZNR to ZNR@Gr/Cu thin film. Energy band gap decreases as particle size of the semiconductor nano materials increased agree with (Madan Singh *et al.*, 2018) PL spectra reflect the recombination efficiency of photo-excited electron–hole pairs of semiconductors materials (Fig. 5(c)).

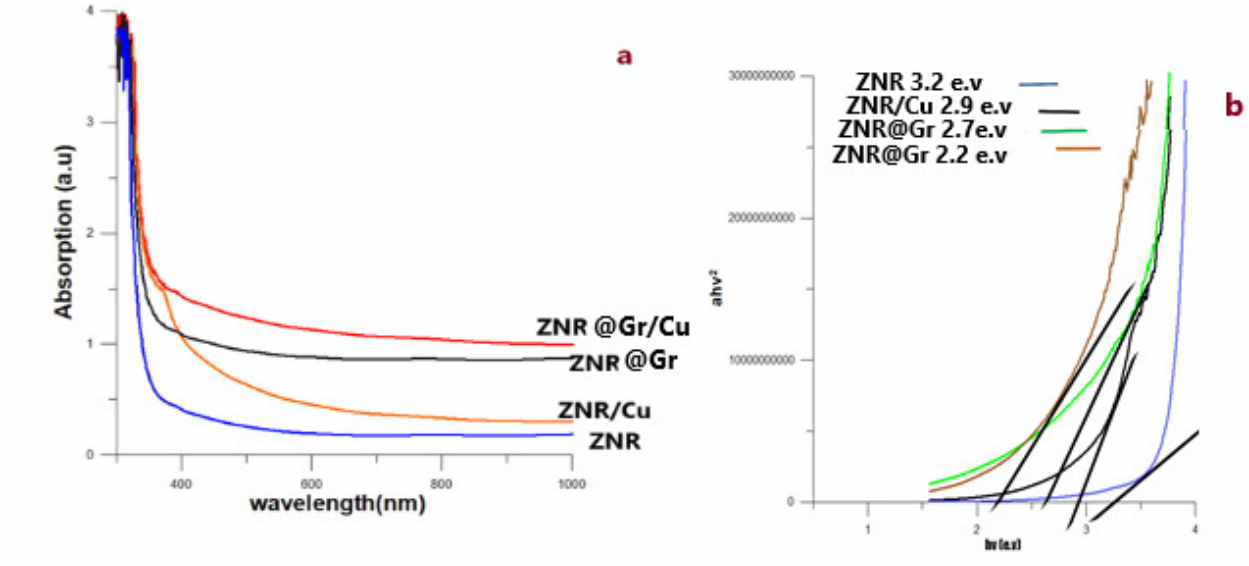

Fig. 5 a, b

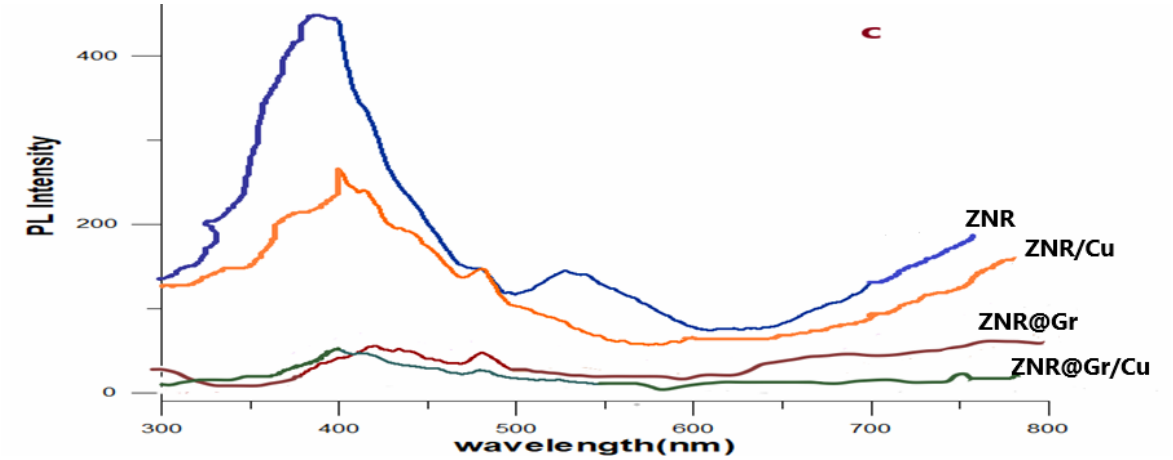

Fig. 5 : (a) UV-visible spectra of all thin films (b)direct optical energy plotted all thin films (c) PL spectra of all thin films.

An emission peak can be noted at 300 nm, which could be referred to the band-edge emission resulting from the recombination of excitonic centers, agree with (Peng Hu *et al*., 2011). The intensity of the peaks reduced after forming with Cu or graphene, which reflected reduced in the recombination efficiency of photo electron–hole pairs of the semiconductor. Graphene or Cu NP obtained excited electrons in the conduction band (CB) to split up the electron–hole pairs effectively and the energy gap of ZNR was reduced when combining with Cu or graphene. agree with (Dongying Fu *et al*., 2012). ZNR@Gr/Cu displayed the weakest UV emission. The surface of the samples ZNR@Gr could be mixed with Cu NP, which were more greatly reduced the recombination efficiency of photo electron–hole pairs. ZNR displayed strong emission at wavelength of Vis light regain, however the intensity of emission decreases after incorporating with graphene and Cu NP. The results fixed that the mixed with graphene and Cu NP could be canceled the ZNR surface blemish, agree with (Lu Y *et al.,* 2016).

Conclusions

Electrostatic self-assembly and solution reduction method could be improved to form ZNR@Gr/Cu thin film with good physical absorption properties and low cost. The SEM and TEM images fixed that ZNR was good-covered with 5 layers of graphene, and Cu NP with average size (10-15) nm were graced uniformly outside ZNR@Gr. Doubling increase in absorption accrued at Vis-IR region. It was observed due to the presence of GO&Cu (ZNR@Gr/Cu). The composite material displayed improved absorption of light and reduced PL intensity, which decreased recombination of photogenerated electron–hole pairs within reason the coated of graphene and garnished with Cu NP the electron transmission ability of the semiconductor was increased, and that was very useful for many photonic applications.

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