

Synthesis and Properties of ZnO/Ag/Graphene Oxide Composites Photocatalyst

Nthambeleni Mukwevho, Elvis Fosso-Kankeu*, Frans Waanders, Neeraj Kumar, Suprakas Ray

Abstract—We report a simple approach to synthesize ZnO/Ag/graphene oxide composite using a facile low-temperature aqueous solution reaction. The corresponding optical properties were analyzed with photoluminescence spectroscopy (PL) and UV-vis spectrophotometer. The PL spectra of ZnO, ZnO/Ag, ZnO/Ag/graphene oxide were recorded at room temperature with excitation wavelength of 325 nm. The main advantage of the proposed ZnO/Ag/graphene oxide is that it delays the recombination process of the electron-hole pairs generated by the photon absorption which increases the photo catalyst performance. XRD results clearly showed the formation of ZnO/Ag/graphene oxide nanocomposite. PL spectra provided information about the separation and recombination of photo induced electrons and holes. The results showed that the doping of Ag nanoparticles induced visible light activity and facilitated efficient charge separation in the ZnO/Ag/graphene oxide nanocomposite.

Keywords—ZnO/Ag/graphene oxide, Chemical synthesis, Composites, UV-vis and PL.

I. INTRODUCTION

Some semiconductor materials modified by nanometre-sized metal clusters (Ag and Au) usually exhibit promising application in optics, catalysts etc. [1]. Previous studies have reported that TiO₂ deposited the noble metals can promote organic compound degradation under UV irradiation [2, 3, 4, 5]. Zinc oxide has been recognized as a potential semiconductor material for the degradation of various pollutants because of its higher quantum efficiency than that of TiO₂ [6-11]. When ZnO is irradiated by UV-light, the electrons are excited to the conduction Band (CB), leaving holes in the valence band (VB), and the as-formed electron-hole pairs are responsible for the photo catalytic activities of ZnO [12]. It has been reported that the slowing down of the electron-hole pair recombination is of great importance to

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improve the photo catalytic performances of ZnO. Previous studies were conducted where ZnO based composites were proposed to increase the photo catalytic performance and the authors reported that the recombination of electron-hole pairs could be retarded by hybridization ZnO with noble metallic particles such as Au, Ag and Pt [13]. Graphene, a monolayer of sp² bonded carbon atoms has superior electrical conductivity and mechanical properties, which makes it an outstanding electron-transport material in the process of photo catalysis [12, 13]. Many studies have been conducted by coupling semiconductor materials with graphene oxide as photo catalyst. The effect of individual Ag nanoparticles and graphene oxide have been considered for the enhancement of photo catalytic activity of ZnO, the authors realized that it was a meaningful research to combine these different materials into a hetero structure for the performance improvement of semiconductor photo catalysts [14]. In this study, we report the facile low-temperature aqueous solution reaction synthesis method of ZnO/Ag/graphene oxide composites. The results of this study showed that the silver and ZnO nanoparticles can be coated uniformly on the surface of graphene oxide and the composites have a better UV emission performance than pure ZnO. The current study aims to determine the optical properties of ZnO/Ag/graphene oxide composites.

II. MATERIALS AND METHODS

A. Preparations of ZnO/Ag/Graphene Oxide Nanocomposites

Graphene oxide (GO) was prepared through the Hummer's method with slight modifications [13, 15]. In a typical procedure, 50 mL of H₂SO₄ and 5.5 mL of phosphoric acid (H₃PO₄) were added into a flask containing 2 g graphite in ice bath under stirring. After that, 6g potassium permanganate (KMnO₄) was added slowly to the above mixture, and the ice bath was removed after several minutes. The colour of the solution turned to dark green while keep stirring for 2 h at 35 °C. Then, 100 mL water was added slowly to the reaction mixture and the conical flask was bathed in boiling water, the reaction mixture was kept at this temperature for another 30 min. After that, the flask was cooled in an ice bath, and 350 mL distilled water was added to stop the reaction. 20 mL H₂O₂ (30%) was added to reduce the residual permanganate to soluble manganese ions. Eventually, the precipitation was centrifuged and washed with 1 M HCl and distilled water for several times, and then was vacuum dried at 60°C for 24 h. ZnO nanoparticles were prepared by adding 25 mL NaOH

solution (4 M) into 25 mL of 0.2 M ZnSO₄ solution at an approximate rate of 5 mL/min. Then, the mixture was kept at 60°C for 2 h. The Ag/ZnO nanocomposites were prepared by adding 10mL of 0.01M AgNO₃ into the mixture solution of C₆H₁₂N₄ and Zn (NO₃)₂·6H₂O, and the mixture was also kept at 90°C for 2 h and sonicated for 30 min. To prepare Ag/ZnO/graphene oxide nanocomposites, 50 mg of GO was dispersed in 40mL of water and kept in a bath type ultrasonicator for 30 min and then 25mL 0.1M Zn (NO₃)₂·6H₂O solution, 10mL of 0.01M AgNO₃, 25mL 0.2M C₆H₁₂N₄ were dropped into the mixture and the mixture was kept at 90°C for 2 h, then sonicated for 30 min. All of the samples prepared above were centrifuged and washed by distilled water for several times and were dried at 45°C in vacuum for 24 h.

B. Characterization of The Composites

XRD analysis was used to determine the composition of the particles; the diffractometer used was the Philips model X'Pert pro MPD, at a power of 1.6 kW used at 40 kV; Programmable divergence and anti-scatter slits; primary Soller slits: 0.04 Rad; 2θ range: 4-79.98; step size: 0.017° [16-20]. Room temperature photoluminescence (PL) spectra were recorded using a fluorescence spectrometer. The excitation source was a Xe lamp and the excitation wavelength was 325 nm. UV-vis absorbance spectra of the samples were recorded by using a Shimadzu UV-2401PC spectrophotometer

III. RESULTS AND DISCUSSION

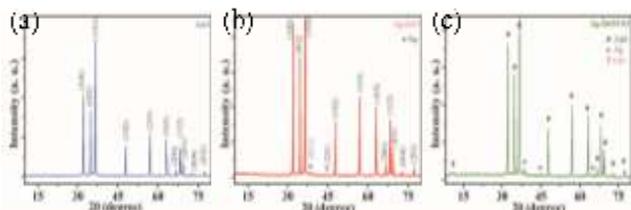


Fig.1. XRD patterns of (a) ZnO, (b) ZnO/Ag and (c) ZnO/Ag/graphene

XRD is an important analysis to determine the phase and purity of the synthesized samples [21-25]. Figure 1. Represents the XRD patterns of (a) ZnO, (b) ZnO/Ag and ZnO/Ag/graphene nano composites. The phase and structure of the prepared material were confirmed through XRD analysis, figure 1 exhibits (100), (002), (101), (102), indicating hexagonal structure. The diffraction peak that labelled with # could be readily indexed to the hexagonal Wurtzite ZnO (JCPDS card NO. 04-0783), while those marked with * could indexed to the cubic structure of Ag (JCPDS file NO. 79-0208). The addition of silver and graphene did not affect the structure of pure ZnO as the binary and ternary nano composites shows broad peaks which indicate the sizes of the nano composite are small, whereas the pure material shows sharp peaks big of big size compared to composites ZnO/Ag and ZnO/Ag/graphene. From the XRD pattern of the ZnO/Ag sample which is shown in Figure 1 (b), It can be seen that there are two sets of diffraction peaks, one for ZnO and the other for Ag which is represented by blue dot, which indicate that the synthesized sample are well-constructed. In Figure 1(c), the

observed diffraction peak of graphene oxide is very smaller which may be related to the low amount of graphite oxide added and low diffraction intensity of graphene oxide. In figure 1(b), the intensity of the peak (002) of ZnO from ZnO/Ag sample is higher than that of ZnO only sample, this result tells us that Ag helps the ZnO to grow with high orientation. The diffraction peak of graphene oxide in figure 1(c) is detected in a short peak, It is also confirmed in the literature [26] that graphene oxide can hardly be detected in the XRD pattern of ZnO/Ag/graphene oxide due to the insertion of nanoparticles between the adjacent graphene oxide sheets which cause the disorder of layer spacing. In Figure 1(c) the data showed a main peak in the (111) intensity for Ag nanoparticle, which may result to the enhanced photo catalytic activity of our synthesized ZnO/Ag/graphene oxide composite.

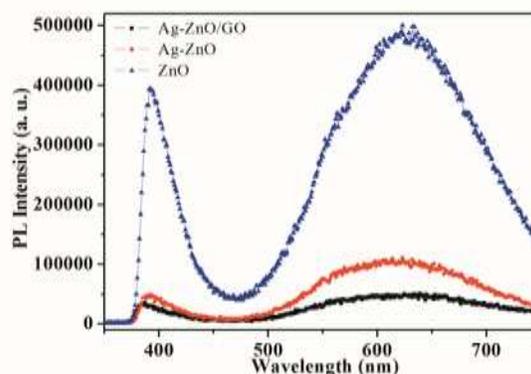


Fig.2. Room temperature photoluminescence spectra of ZnO, ZnO/Ag and ZnO/Ag/graphene

Figure 2 shows the PL spectra taken from the ZnO, ZnO/Ag and ZnO/Ag/graphene oxide composite at room temperature from 350nm emission. According to the literature Guoqing et al., 2014 [1], ZnO usually exhibits two strong emission peaks, which is near near-band-edge and a green broad-band, respectively. It is also reported by Fang et al., 2013 [13] that green broad-band emission peak originated from the single ionized oxygen vacancies whereas the near-band-edge peak is from the direct recombination of the exciton-exciton collision process. It could be seen from figure 2 that all individual curves show similarly two emission bands: a near-band-edge at 375 nm and a green broad-band at 626nm. These support the literature [8] that there might be a great number of surface deep traps such as oxygen vacancies. It could be seen in the spectra that the PL intensities of the synthesized samples increases in the following order: ZnO/Ag/graphene, ZnO/Ag and ZnO. It is proven that the prepared sample with the low PL intensity, the higher the separation rate of photo induced charge carriers [27-29]. From figure 2, as the sample ZnO/Ag/graphene oxide is the weakest among others, it indicates that the photoluminescence of ZnO/Ag/graphene oxide is more efficiently than that of ZnO/Ag by the doping of graphene, same applies to the prepared sample ZnO/Ag its fluorescence is more efficiently than that of pure ZnO by the doping of Ag. The work function of the element Ag is about -4.26eV and from ZnO is about -5.2eV [12]. This phenomenon suggests that, with the incorporation of Ag and graphene oxide

in ZnO it increases the separation of photo induced electrons and holes.

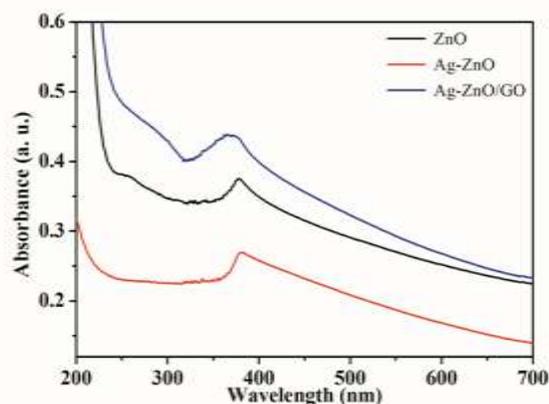


Fig.3. UV-vis absorption spectra

UV-vis spectroscopy is an effective tool to investigate the light absorbing behaviour of prepared powder samples. Figure.3. shows the UV-vis absorbance spectra of prepared samples ZnO, ZnO/Ag and ZnO/Ag/graphene. The absorption edges values were calculated to be 370nm ZnO, 380nm ZnO/Ag and 398 ZnO/Ag/graphene oxide by using the method reported by Provenzano et al., 2001 [30]. The absorption of all samples were at <400nm that indicates the absorption edge active at ultra violet (UV) region. Band gaps (E_g) of the samples above were calculated [31] from the equation: $E_g = hc/\lambda = 1240/\lambda$

Where h is plank constant/ c is speed of light, λ is cut off wavelength at 370nm ZnO, 380nm ZnO/Ag and 398nm ZnO/Ag/graphene oxide corresponding to the band gaps of 3.351eV, 3.263eV and 3.11eV. These results obtained were in good agreement with the analysis of PL observation.

IV. CONCLUSION

In summary, a simple facile low temperature aqueous solution reaction method was found to prepare ZnO/Ag/graphene oxide composites. The PL spectra indicates that the green broad-band emission of the ZnO/Ag/graphene oxide composites was weakened because of the doping of silver and graphite oxide. This method has a great potential for the synthesis of the multicomponent graphene-based Nano composites with high photo catalytic efficiency.

ACKNOWLEDGMENT

The authors are grateful to the sponsor from the North-West University and the National Research Foundation (NRF) in South Africa. Any opinion, findings and conclusions or recommendations expressed in this material are those of the authors and therefore the NRF does not accept any liability in regard thereto.

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