

Synthesis of Ag Nanoparticle-Decorated ZnO Nanorods Adopting the Low-Temperature Hydrothermal Method

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Vertically aligned and highly dense Zinc oxide (ZnO) nanorods (NRs) have been successfully synthesized by a two-step hydrothermal method and decorated by silver (Ag) nanoparticles (NPs) via a dip coating technique. Absorption spectra indicate the presence of metal Ag NPs. The photoluminescence (PL) spectrum of as-grown ZnO nanorods shows ultra violet (UV) emission centered around 390 nm and a sharp defect-related emission peak around 580 nm. The presence of Ag NPs on the ZnO NRs shows a significant red shift in PL peak position in the visible region and a complete quenching of UV emission. The changes in UV–Vis and PL spectra of ZnO NRs decorated with Ag metal NPs are studied and discussed.

Key words: ZnO nanorods, hydrothermal, dip coating, surface plasmon, photoluminescence

INTRODUCTION

ZnO (Zinc Oxide) is a II-VI wide band gap oxide semiconductor. It has excellent material properties such as large surface-to-volume ratio, direct wide band gap (3.37 eV) and high excitonic binding energy (60 meV), which make this material very promising for optoelectronic applications.^{1–5} Onedimensional ZnO nanostructures such as nanorods, nanobelts, nanotubes, nanoribbons, nanowires and nanocables⁶⁻¹² have been synthesized by various methods. ZnO nanowires and nanorods have attracted researchers due to their easy preparation and potential use in various nano-devices. ZnO NRs have been manufactured by different means, such as vapor-liquid-solid (VLS),13 spray pyrolysis,¹⁴ metal organic chemical vapor deposition (MOCVD),¹⁵ pulsed laser deposition¹⁶ and hydrothermal method.¹⁷ The hydrothermal process (MOCVD),¹⁵ pulsed \mathbf{is} а low temperature, cost-effective and

straightforward technique that requires very few steps for NR preparation. ZnO NRs are very useful in nanoelectronic devices due to their unique properties and large surface-to-volume ratio. This sizeable surface-to-volume ratio in ZnO NRs plays a crucial role in their optical and electronic properties.^{18–20} Using suitable external materials, one can modify the optical properties of ZnO NRs according to requirements.^{21–24} Decoration of ZnO nanorod surfaces with metal nanoparticles is an effective way to alter the properties of ZnO NRs.

In recent years, various researchers such as Cheng et al.,²⁵ Bera et al.,²¹ Dhara et al.,²⁶ and Chauhan et al.²⁷ decorated ZnO NRs with various metals, such as Au, Pd, Ti, Pt, Al, Ag and Au-Pd, using various methods. Silver (Ag) is the most favorable metal for decoration of ZnO nanorods because of its high efficiency, low cost and ease of fabrication, and its unique electrical, optical, and thermal properties.

Several fabrication techniques, such as photoreduction,²⁸ microwave-assisted deposition-precipitation,²⁹ electro-deposition,³⁰ thermal evaporation and sputtering,²⁷ have been employed by researchers for the preparation of Ag-decorated ZnO NRs. In

⁽Received May 2, 2019; accepted October 25, 2019)

the present work, a low-cost and straightforward hydrothermal method followed by dip coating method was used to synthesize Ag-decorated ZnO NRs. Three samples of Ag-decorated ZnO NRs with different Ag concentrations and a pure ZnO NRs as reference material were prepared. The effect of the quantity of Ag on the structural, morphological, optical performance of Ag-decorated ZnO nanorods is analyzed here.

MATERIALS AND METHODS

Seed Layer Coating

ZnO nanorod arrays were grown on an ITO coated glass substrate by a two-step low-temperature hydrothermal method.³¹ For the hydrothermal growth of ZnO NRs, first ZnO nanocrystal seeds were coated on the ITO coated glass substrate by a sol-gel spin coating method. To prepare the solution for seed layer growth, 0.01 M NaOH solution in methanol (0.03 m) was added dropwise to a solution of 0.01 M zinc acetate dihydrate in methanol at 60°C and stirred for 2 h. The solution was uniformly spin coated on the ITO coated glass substrate at the rate of 2500 rpm for 30 s. After the coating, the film was annealed at 110°C for 10 min to ensure particle adhesion to the substrate surface. The coated substrate was then heated at 150°C for 1 h in the oven to get the ZnO seed layer.

ZnO Nanorod Growth

To get vertically aligned ZnO NRs, the seed-layercoated substrate was dipped into the solution of equimolar (25 mM) concentration of hexamethylenetetramine (HMT) $[(CH_2)_6N_4]$ and zinc nitrate hexahydrate $[Zn(NO_3)_2 \cdot GH_2O]$ in double distilled water. The sample was kept in the oven, and the process was carried out at 80°C for 5 h, and later on, the ZnO NRs samples were dried in air at room temperature.

Ag Nanoparticle Decoration

A dip coating method was used to modify the surface of ZnO NRs with Ag NPs. Three solutions of different molar concentrations, 5 mM, 10 mM, and 15 mM, of Silver nitrate (AgNO₃) were added to a solution of 10 ml distilled water and 0.5 ml ethanol at room temperature. To decorate the ZnO NRs, the hydrothermally grown ZnO NR sample was merged into the AgNO₃ solutions for 120 s at room temperature. The specimens deposited with different concentrations of Ag are named as A5, A10, and A15, respectively. The growth conditions were identical for all the samples.

CHARACTERIZATION

The as-grown ZnO NRs and Ag decorated ZnO NRs were studied by different characterization techniques. The morphology and crystal structure

of samples were characterized using scanning electron microscopy (SEM) high-resolution transmission electron microscopy (HRTEM) and x-ray diffraction (XRD). The formation of ZnO NRs/Ag heterostructure was confirmed by high-resolution transmission electron microscopy (HRTEM). The compositional analysis of the samples was done by using energy dispersive x-ray spectroscopy (EDX). The optical properties of ZnO NRs were studied by using ultraviolet-visible (UV-Vis) spectroscopy and photoluminescence (PL). The PL measurement was recorded at room temperature using a 325 nm He-Cd laser as an excitation source. The UV-Vis absorption spectra were recorded in the range of 200-800 nm.

RESULTS AND DISCUSSION

ZnO NWs Structural and Morphological Properties

SEM and TEM

Figure 1 shows the SEM image of ZnO NRs decorated by Ag nanoparticles prepared by the hydrothermal method followed by dip coating deposition of Ag. The average diameter of ZnO NRs was estimated to be in the range of 70–90 nm with lengths of 2 μ m.

The detailed microstructures and compositional information of Ag decorated ZnO nanorods were analysed by TEM and TEM-EDS. Figures 2a and b show the TEM images taken on ZnO nanorods decorated with Ag nanoparticles. These figures reveal that all the prepared nanoparticles are spherical with the size range of 6–9 nm. TEM images confirm that the Ag NPs are attached with ZnO NRs. The EDX analysis of Ag decorated ZnO nanorods for the selected area also confirms the presence of Zn, O, and Ag, which is shown in Fig. 3.

The EDX spectrum is given in Fig. 3 shows peaks corresponding to Zn, O, and Ag. EDX confirms the presence of Ag in the sample.



Fig. 1. FESEM image of the hydrothermally grown ZnO NRs on the ITO substrate.

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Fig. 2. (a, b) The TEM images of ZnO nanorods after Ag nanoparticles decoration.



Fig. 3. Energy-dispersive x-ray spectroscopy (EDX) spectrum of Ag NPs decorated ZnO NRs.

XRD Pattern

The XRD pattern shown in Fig. 4 indicates that the hydrothermally grown ZnO NRs on a glass substrate are highly crystalline. The figure shows several diffraction peaks at $2\theta = 31.83^{\circ}$, 34.60° , 36.28° , 47.59° , 56.63° , 62.90° , 68.15° and 69.01° , which correspond to ZnO (100), (002), (101), (102), (110), (103), (112) and (201) planes, respectively. All the peaks of the XRD pattern confirm the hexagonal wurtzite structure of ZnO NRs with lattice parameter a = 3.25 Å and c = 5.181 Å, which are very close to the standard values (JCPDS Card No.—36-1451). The highly intense peak at 34.40° corresponds to (002) plane, indicating the growth orientation of ZnO NRs along c axis.

For ZnO NWs sensitized with Ag NPs, there are two small peaks at 66.38° and 73.1° , which can be indexed to (220), (311) in XRD patterns, confirming the formation of Ag NPs. Perhaps due to small quantity of Ag NPs, other Ag peaks were not observable. Compared to the XRD pattern of asgrown ZnO NWs, no shift in the peak position for



Ag-decorated ZnO NWs indicates Ag nanoparticles are positioned only on the surfaces of ZnO nanowires, without disturbing their crystal nature.²⁹ XRD data clearly indicate the synthesis of Ag metal nanoparticles on ZnO surface. Ag particle sizes were calculated using the Debye–Scherrer formula, which represents ~ 8 nm Ag nanoparticles, in good agreement with the Ag particle size calculated from TEM analysis.

UV-Vis and PL Spectra Analysis

The optical properties of pure ZnO nanorods and Ag NP-decorated ZnO NRs (A5, A10, and A15) were investigated using UV-Vis and photoluminescence (PL) spectroscopy. Figure 5 shows the UV-Visible optical absorption spectra taken in the range of 300-800 nm for different concentrations (5 mM, 10 mM, 15 mM) of Ag decorated upon ZnO nanorods. It is clear that all the spectra show low absorption in the visible region. Maximum absorbance was achieved when the 15 mM concentration solution of Ag was used for ZnO nanorod decoration. No significant variations in UV region absorption were observed. Since the Ag nanoparticles attached



Fig. 5. UV–Vis absorption spectra of Ag decorated ZnO nanorods for various concentrations.

to the ZnO NR surfaces is less dense, as evident from the TEM images, the surface plasmon resonance peak corresponding to Ag nanoparticles could not be observed in the absorption spectra of the Ag/ ZnO nanoparticles.

Figure 6 shows room temperature PL spectra of the ZnO NRs (A) and ZnO NRs decorated with Ag NPs (5–15% Ag@ZnO) at an excitation wavelength of 325 nm. Figure 6 (A) exhibits two peaks: one broad peak around 350 nm and another sharp peak around 450 nm. The UV peak is attributed to near band edge free exciton emission. The second blue emission intense peak centered around 450 nm originates from deep level defects, such as oxygen vacancies.³²

It is observed that the UV emission peak for all the Ag NPs/decorated ZnO NRs is wholly removed in comparison to that of as-grown ZnO NRs. In addition, there is a significant red shift towards the green region as the concentration of Ag increases. The Ag NP-decorated ZnO NRs samples exhibit a splitting (called Rabi splitting) of PL peak in the range of 645–665 nm, which has been commonly related with red luminescence. As a result of the decoration of Ag NPs, the PL intensity of ZnO NRs emission peak is decreased in the UV region. It is clear from TEM images that the Ag NPs are in direct contact and attached to the surfaces of the ZnO NRs. Electron transfer may have occurred between the energy levels of these two materials, where Ag NPs act as electron sinks, which trap electrons from ZnO NRs, inhibiting the recombination of photogenerated excitons in Ag NPs/ZnO NR heterostructure.³³⁻³⁵ This process is known as direct electron transfer from the semiconductor to the plasmonic nanostructures.³⁶ Luminescence of Ag-decorated ZnO nanorods has been increased in



Fig. 6. PL spectra of (a) as-grown ZnO nanorods and (b) ZnO Nanorods decorated with Ag nanoparticles for various concentrations.

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visible region, which indicates enhancement in the number of defects and oxygen vacancies in the decorated nanorods.

Ag NPs can interact with surface defects of the ZnO during the deposition process of Ag NPs on ZnO NRs. This interaction will change the defect states. The red luminescence has originated from the doubly ionized oxygen vacancies due to lattice disorder or imperfections arising due to the attachment of Ag nanoparticles on ZnO NRs.^{37,38} When metal NPs are directly in contact with a semiconductor, the electron transfer takes place between them. The light emission will be enhanced in the case of electron transfer from metal NPs to semiconductor.³⁹

In ZnO, generally several singly ionized charge states of intrinsic native defects such as zinc interstitial and oxygen vacancies, etc. exist. When a photo-excited electron trapped in these defects recombines with a hole, visible emission takes place. In the Ag NPs/ZnO NRs heterostructure most of the photo-excited electrons are trapped in these deep levels defects, instead of the conduction band of ZnO NRs.^{33,40} Since the native defect energy level is higher than the Fermi energy level of Ag NPs, so all the photoelectrons migrate to the Ag nanoparticles.

Further, the deep level emission of ZnO NRs is coupled with the surface plasmon (SP) of the Ag NPs on the ZnO NWs surface. Energy transfer can be possible between the semiconductor and metal NPs due to exciton-SP interaction.²⁵ When the energy of excitons becomes more significant than the SP energy, the energy transfer takes place from excitons to SPs, resulting in a red shift of the emission peak.³⁹ This exciton-SP coupling also improves the recombination rate of deep level emission, which results in enhancement of visible emission.⁴¹

In PL spectra, a doublet of Rabi splitting is observed when Ag nanoparticles are attached with ZnO NRs.⁴² The strongly coupled SPs and excitons at the metal/semiconductor interface demonstrate Rabi splitting.^{43–45} The interaction between photons and excitons produces upper- and lower-polariton branches. In a system with stronger coupling between excitons and photons, the splitting between the two polariton branches is large.⁴⁵

It is clear that, for 5 mM concentration, there is almost no splitting. By increasing the concentration from 5 mM to 10 mM, a clear and sharp Rabi splitting occurs, which indicate a robust coupling regime. The Rabi splitting is decreased as the concentration further increases up to 15 mM.

The PL revealed that the coupling is strong when the ZnO NRs is decorated with Ag of concentration of 10 mM, which may be the maximum limit, after which the coupling becomes weak.

CONCLUSION

Ag nanoparticles have been successfully decorated on the surface of ZnO nanorods through a cost-effective and simple hydrothermal method, followed by dip coating. The decoration of silver nanoparticles on the surface of ZnO nanorods greatly enhances and redshifts the visible emission peak in PL spectra, along with quenching in UV emission. The enhancement and red shifting of visible emission and quenching of UV emission might be due to a combination of carrier transfer from the ZnO NRs defect level to the Fermi level of Ag nanoparticles and coupling of surface plasmonexcitons. The experimental results indicate that the Ag NP-decorated ZnO NRs have good potential for optoelectronic device applications.

ACKNOWLEDGMENTS

A portion of this research was performed using facilities at CeNSE/INUP/PE26/2018-2019, funded by Ministry of Electronics and Information Technology (MeitY), Govt. of India, and located at the Indian Institute of Science, Bengaluru.

REFERENCES

- 1. A. Janotti and C.G. Van de Walle, *Rep. Prog. Phys.* 72, 126501 (2009).
- M. Willander, O. Nur, Q.X. Zhao, L.L. Yang, M. Lorenz, B.Q. Cao, J.Z. Perez, C. Czekalla, G. Zimmermann, M. Grundmann, A. Bakin, A. Behrends, M. Al-Suleiman, A. El-Shaer, A. Che Mofor, B. Postels, A. Waag, N. Boukos, A. Travlos, H.S. Kwack, J. Guinard, and D.L.S. Dang, *Nanotechnology* 20, 332001 (2009).
- 3. Z.L. Wang, Mater. Today 7, 26 (2004).
- U. Ozgur, Ya.I. Alivov, C. Liu, M.A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho, and H. Morkpv, J. Appl. Phys. 98, 1 (2005).
- J.W.P. Hsu, D.R. Tallant, R.L. Simpson, N.A. Missert, and R.G. Copeland, *Appl. Phys. Lett.* 88, 252103 (2006).
- K.N. Hui, K.S. Hui, Q. Xia, T.V. Cuong, Y.R. Cho, J. Singh, P. Kumar, and E.J. Kim, ECS Solid State Lett.2, (2013).
- 7. X. Wang, J. Song, and Z.L. Wang, J. Mater. Chem. 17, 711 (2007).
- C. Wang, B. Mao, E. Wang, Z. Kang, and C. Tian, Solid State Commun. 11, 141 (2007).
- 9. L. Wang, K. Chen, and L. Dong, J. Phys. Chem. C 114, 41 (2010).
- J. Singh, R.S. Tiwari, and O.N. Srivastava, J. Nanosci. Nanotechnol. 7, 1783 (2007).
- J. Liu, Y.H. Ahn, J.Y. Park, K.H. Koh, and S. Lee, *Nanotechnology* 20, 445203 (2009).
- J.J. Wu, S.C. Liu, C.T. Wu, and K.H. Chen, *Appl. Phys. Lett.* 81, 1312 (2002).
- 13. X. Wang, C.J. Summers, and Z.L. Wang, *Nano Lett.* 4, 423 (2004).
- E. Kärber, T. Raadik, T. Dedova, J. Krustok, A. Mere, V. Mikli, and M. Krunks, *Nanoscale Res. Lett.* 6, 359 (2011).
- W. Lee, H.G. Sohn, and J.M. Myoung, *Mater. Sci. Forum* 449, 1245 (2004).
- J. Singh, P.K. Srivastava, P.K. Siwach, H.K. Singh, R.S. Tiwari, and O.N. Srivastava, *Sci. Adv. Mater.* 4, 467 (2012).
- Z.H. Ibupoto, K. Khun, M. Eriksson, M. AlSalhi, M. Atif, A. Ansari, and M. Willander, *Materials* 6, 3584 (2013).
- V.A. Fonoberov, K.A. Alim, A.A. Balandin, F. Xiu, and J. Liu, *Phys. Rev. B* 73, 165317 (2006).
- J.V. Foreman, J. Li, H. Peng, S. Choi, H.O. Everitt, and J. Liu, *Nano Lett.* 6, 1126 (2006).
- Y.L. Wu, A.I.Y. Tok, F.Y.C. Boey, X.T. Zeng, and X.H. Zhang, Appl. Surf. Sci. 253, 5473 (2007).
- A. Bera and D. Basak, ACS Appl. Mater. Interfaces 2, 408 (2009).
- J.P. Richters, T. Voss, L. Wischmeier, I. Rückmann, and J. Gutowski, Appl. Phys. Lett. 92, 011103 (2008).

- J. Chang, C.K. Najeeb, J.-H. Lee, M. Lee, and J.-H. Kim, J. Phys. D Appl. Phys. 44, 095101 (2011).
- K. Shahi, R.S. Singh, A.K. Singh, M. Aleksandrova, and R. Khenata, Appl. Phys. A 124, 277 (2018).
- C.W. Cheng, E.J. Sie, B. Liu, C.H.A. Huan, T.C. Sum, H.D. Sun, and H.J. Fan, *Appl. Phys. Lett.* 96, 071107 (2010).
- 26. S. Dhara and P.K. Giri, J. Appl. Phys. 110, 124317 (2011).
- P.S. Chauhan, A. Rai, A. Gupta, and S. Bhattacharya, Mater. Res. Express 4, 055004 (2017).
- Y. Chen, W.H. Tse, L. Chen, J. Zhang, and Chen, *Nanoscale Res. Lett.* 10, 106 (2015).
- K. Saoud, R. Alsoubaihi, N. Bensalah, T. Bora, M. Bertino, and J. Dutta, *Mater. Res. Bull.* 63, 134 (2015).
- B. Slimi, I.B. Assaker, A. Kriaa, B. Mari, and R. Chtourou, J. Solid State Electrochem 21, 1253 (2017).
- L.E. Greene, M. Law, J. Goldberger, F. Kim, J.C. Johnson, Y. Zhang, R.J. Saykally, and P. Yang, *Angew. Chem. Int. Ed.* 42, 3031 (2003).
- P. Fageria, S. Gangopadhyay, and S. Pande, RSC Adv. 4, 24962 (2014).
- M.D.L. Ruiz-Peralta, U. Pal, and R.S. Zeferino, ACS Appl. Mater. Interfaces 4, 4807 (2012).
- A.J. Cheah, W.S. Chiu, P.S. Khiew, H. Nakajima, T. Sarasota, P. Songsiriritthigul, S. Radiman, and M.A.A. Hamid, *Catal. Sci. Technol.* 5, 4133 (2015).
- 35. S. Kandula and P. Jeevanandam, RSC Adv. 5, 76150 (2015).
- S. Kuriakose, V. Choudhary, B. Satpati, S. Mohapatra, and Beilstein, J. Nanotechnol. 5, 639 (2014).

- S.N.H. Daud, C.Y. Haw, W.S. Chiu, Z. Aspanut, M.Y. Chia, N.H. Khanis, P.S. Khiew, and M.A.A. Hamid, *Mater. Sci.* Semicond. Process. 56, 228 (2016).
- M.Y. Chia, W.S. Chiu, S.N.H. Daud, P.S. Khiew, S. Radiman, R. Abd-Shukor, and M.A.A. Hamid, *Mater. Charact.* 106, 185 (2015).
- X.D. Zhou, X.H. Xiao, J.X. Xu, G.X. Cai, F. Ren, and C.Z. Jiang, *Europhys. Lett. Assoc.* 93, 5 (2011).
- X. Zhang, J. Qin, Y. Xue, P. Yu, B. Zhang, L. Wang, and R. Liu, Sci. Rep. 4, 1 (2014).
- H.H. Park, X. Zhang, K.W. Lee, A. Sohn, D.W. Kim, J. Kim, J.W. Song, Y.S. Choi, H.K. Lee, S.H. Jung, I.G. Lee, Y.D. Cho, H.B. Shin, H.K. Sung, K.H. Park, H.K. Kang, W.K. Park, and H.H. Park, *Nanoscale* 7, 20717 (2015).
- 42. Y. Arakawa, M. Nomura, S. Iwamoto, *SPIE Newsroom*, (2010).
- A. Christ, S.G. Tikhodeev, N.A. Gippius, J. Kuhl, and H. Giessen, *Phys. Rev. Lett.* 91, 183901 (2003).
- D.E. Gomez, K.C. Vernon, P. Mulvaney, and T.J. Davis, Nano Lett. 10, 274 (2009).
- B. Piccione, C.O. Aspetti, C.H. Cho, and R. Agarwal, Rep. Prog. Phys. 77, 8 (2014).

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