

Enhancement of Visible Absorption by Multi-Modification of ZnO Nanorods

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ABSTRACT

ZnO NRs are multimodified by transition metals doping and noble metal decorating to enhance the visible absorption. Some transition metals as Cu, Ag, Co, and Mn are doped inside ZnO NRs to narrow the optical band gap leading to shift the absorbed edge toward visible region. The type as well as the concentration of metal doping is optimized to reach the narrowest optical band gap. More interestingly, the visible absorption is enhanced by decorating Ag NPs onto the optimized ZnO NRs doping through local surface plasmon resonance (LSPR) effect. The size of Ag NPs decorating is optimized by X-ray diffraction (XRD) pattern, absorbance spectra, the scan electron microscopy (SEM), and the transmission electron microscopy TEM images. Due to the enhancement of visible absorption, multi-modification ZnO can be applied in the development of optoelectronic devices using visible light, such as OLED, water splitting, solarcells.

Keywords: Doping, Decorating, Multimodification, ZnO NRs, Surface Plasmon Resonance

INTRODUCTION

Optoelectronic devices played an important role in the real life such as light-emitting diode (LED), fiber optic cables, photodetectors and solar cells [1]. Due to the light-matter interactions and electronic properties of matter to convert light into an electrical signal or vice versa of optoelectronic devices, it was used to apply for different fields such as medicine, telecommunications, and security systems, etc [2]. A main component in optoelectronic devices was an active material that was chosen based on some factors as optical, electrical properties as well as synthetically process [2,3]. One of the selected materials is group IV semiconductors that Si and Ge were used popular. However, these materials were expensive and exhausted. To overcome these challenges II-IV compounds were chosen to replace Si and Ge. ZnO was a group II-IV semiconductor with a wide bandgap (3.37 eV), large binding energy (60 meV), and easy synthesis [4,5]. There were many methods to synthesize ZnO NRs as radiation frequency (RF), magnetron sputtering, hydrothermal evaporation, thermal evaporation [6-8]. Thus, ZnO was a potential material for high-technology applications such as optoelectronic devices, solar cells, electronic devices, bio-devices and so on. ZnO is suitable for the active materials in optoelectronic devices due to its excellent advantages such as thermal stability, low cost,

environmental friendliness, abundance and direct band gap. However, ZnO can only react with the incident light in the ultraviolet (UV) region (the UV light accounted for only 4% solar energy) [9], which reduces the performance of devices due to the large band gap of ZnO. Many researches tried to narrow the optical band gap as well as enhance the visible absorption by doping with the transition metal or non-metal ions, decorating with metal, sensitizing with organic dyes, narrow band gap semiconductor quantum. Among them, doping with transition metals was an effective method to modify the properties of host materials, leading to widen the partial application in the real life. More interestingly, multi-modification of ZnO NRs by doping with transition metals (Cu, Ag, Co, Mn) and decorating with noble metals was a promising method to enhance the light absorption in the

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visible region, leading to the improvement in optoelectronic devices' performance [9,10]. Herein, multi-modification of ZnO NRs was carried out by doping Cu, Co, Mn, Ag and decorating Ag onto ZnO NRs to investigate their optical properties. Cu doped ZnO NRs presented the minimum optical band gap. 3% Cu concentration was optimized for reducing the optical band gap to the lowest value of 3.08 eV. Besides, Ag NPs were decorated onto ZnO NRs to investigate the LSPR effect. The size of Ag NRs was optimized to reach the highest LSPR effect with the absorption peak of 461.61 nm at around 9 nm diameter. In addition, the morphology of undoped ZnO NRs and Cu doped ZnO NRs was investigated by scanning electron

microscopy (SEM). The size and the distribution of AgNPs onto ZnO:Cu NRs were confirmed by transmission electron microscopy (TEM). Their structure was determined from energy-dispersive X-ray spectroscopy (XRD). The optical properties of multimodified ZnO NRs indicated that these materials enable the high performance of optoelectronic devices, especially, visible water-splitting devices.

EXPERIMENTAL METHODS

Growing pure ZnO NRs and doped ZnONRs

Pure ZnO NR and doped ZnO are grown on glass surface by hydrothermal method: A highly efficient method (**Figure 1**).

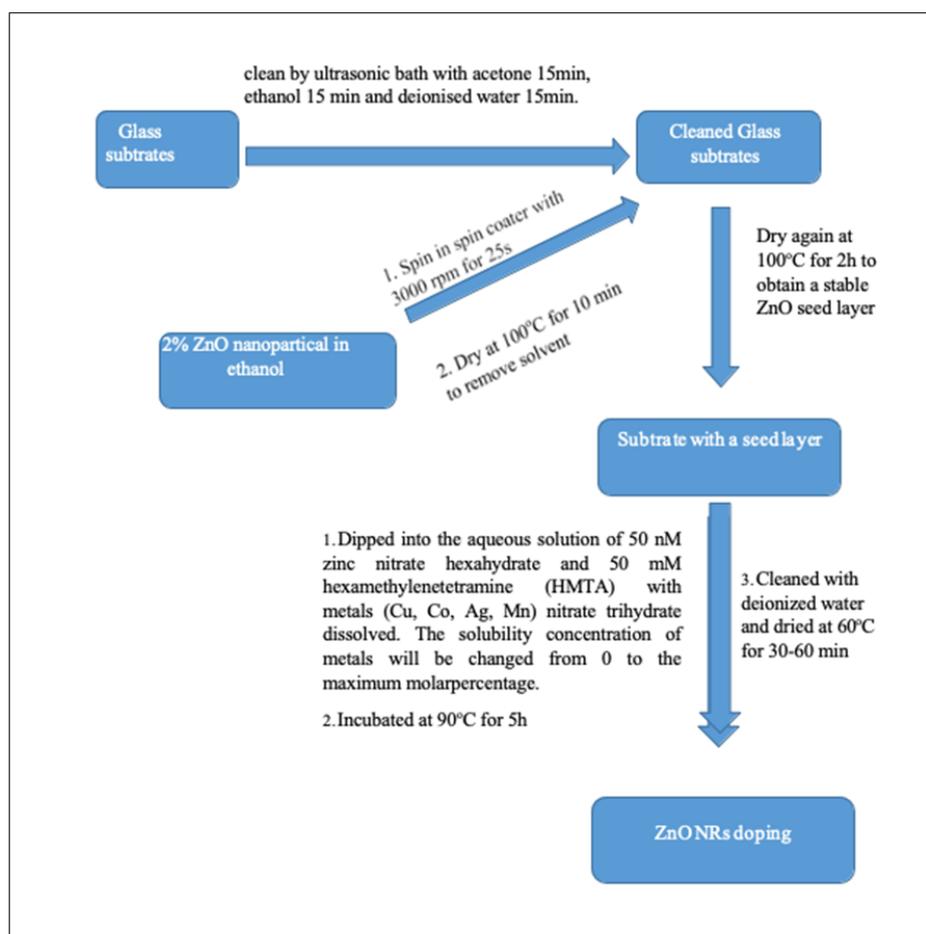


Figure 1. Hydrothermal method.

DECORATING AGNPS ON NANORODS

By sputtering and heat treatment method, Ag NRs were decorated onto ZnO NRs doping after finishing hydrothermal process. Firstly, the sputtering chamber had loaded samples with a working pressure in about 5×10^5 Pa. The silver target with diameter of 15 cm was attached on the target holder. The distance between target and samples was fixed at 7 cm. During pre-sputtering process, the samples

were covered by the movable shutter. Once the sputtering process began, the shutter would open to deposit Ag on the substrates. The thickness of Ag was controlled by changing the time from 5 to 20 s. Finally, samples were annealed in vacuum at 400°C in 3 h to form the nanoparticles.

MATERIAL CHARACTERISTICS

The surface morphologies and the density of nanorods were tested by scanning electron microscopy (SEM, Hitachi S-

4800). The size and the distribution of AgNPs were recorded using transmission electron microscopy system (TEM, JEOL, JEM-1400). The crystallographic structure of ZnO NRs and ZnO NRs doping was determined by the X-ray diffraction (XRD) which was performed on the D8 Advance- Bruker diffractometer operating at 40 kV, 100 mA with the Cu-K α radiation source ($\lambda = 0.154$ nm). The ultraviolet visible (UV-Vis) absorbance was recorded for all samples by UV-Vis-NIR spectrophotometer (JASCO V670) to study the optical properties of nanorods. The optical band gap was derived from absorbance spectra using Tauc's method. All measurements were carried out in the air at room temperature.

RESULTS AND DISCUSSION

To shift the absorbing edge of the ZnO NRs toward the visible light region, ZnO NRs were doped with transition metals as Cu, Ag, Co, Mn at different concentrations. Among them, the absorbed edge of Cu doped ZnO NRs exhibited the highest shift toward visible light (Figure 1a). To confirm the visible shift absorbed edge under transition metals doping, the optical band gap of Co, Ag, Mn, and Cu doped ZnO NRs was calculated from the absorbance spectra using the Tauc's method with the values of 3.22, 3.20, 3.12, and 3.08 eV, respectively (Figure 1b). Therefore, Cu was selected to dope inside ZnO NRs to enhance the absorption in visible region. The structure as well as optical properties of ZnO: Cu NRs was optimized at the different Cu concentration through XRD and UV-Vis and PL. The crystal structure of ZnO: Cu NRs at different Cu concentration was determined through XRD analysis method. Undoped and Cu doped ZnO NRs owned six peaks [12] observed at $2\theta = 31.76, 34.39, 36.21, 47.59, 62.85$ and 67.98° , which correspond to (100), (002), (101), (102),

(103) and (112) peaks in (Figure 2a). At further doping concentration (over 3%), there was occurrence of the new diffraction peak at 69.3° characterizing Cu phase, as seen in (Figure 2a) inset. The formation of peak was attributed to the agglomeration of Cu that enabled the new phase in lattice. The highest intensity of the XRD peak belonged to (002) plane, which was shifted for higher dopant concentration (pure ZnO NRs: 34.4° , 3% Cu doped ZnO NRs: 34.3°) (Figure 2b). Because the radius of Zn $^{2+}$ and Cu $^{+}$ is 0.72 Å and 0.96 Å, respectively [13], Cu ion well replaced Zn ion in the crystal lattice. However, the XRD peaks shift to lower angle which was explained by the tensile deformation of crystal lattice. According to theory, the bonding in ZnO was largely ionic (Zn $^{2+}$ - O $^{2-}$), which favours doping with Cu so no change in crystalline structures was detected [13].

The optical band gap decreases with the increase of Cu concentration inside ZnO NRs from 1% to 3% due to the new ion Cu energy level forming in the band gap. However, with the further increase of Cu concentration, the optical band gap went up (Figure 2c). According to Burstein-Moss effect, the Fermi level of p-type (n-type) semiconductors lied within the valence band (conduction band) and their position depends on the concentration of holes (electrons) [14]. Thus, besides the actual band gap which was attributed to excitation of the electron from top of valence band to bottom of conduction band, the excitation of electrons from Fermi level in the valence band to the conduction band (or from valence band to Fermi level in the conduction band (n-type)) was related to optical band gap. The minimum optical band gap was reached at 3% Cu concentration with the value of 3.08 eV. Both red shift and back shift demonstrated that Cu ions were successfully incorporated into the Zn site of the ZnO matrix.

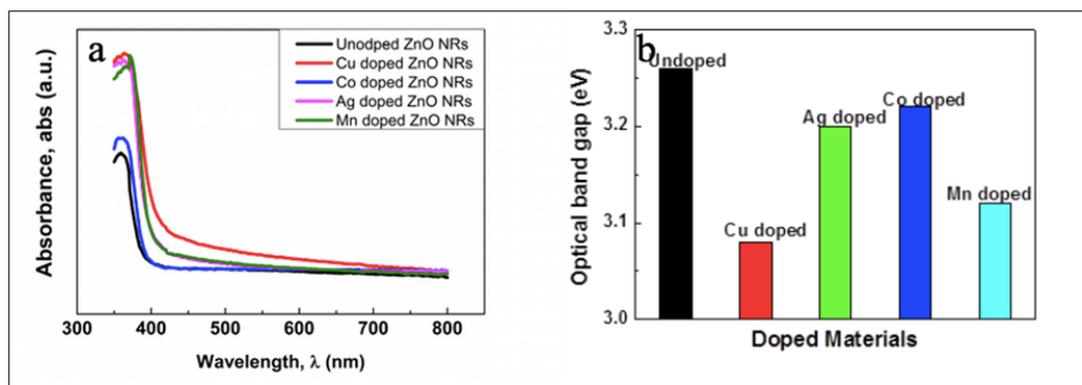


Figure 1. a) The absorbance spectra of ZnO NRs doped with Co, Ag Mn and Cu at optimised metal concentration. b) The optical band gap was derived from the absorbance spectra by Tauc's method [11].

Figure 2d showed two different photoluminescence (PL) spectra of pure ZnO NRs and 3% Cu doped ZnO NRs. A sharp UV emission band at about 385 nm was attributed to the near-band-edge (NBE) emission corresponding to the

recombination of the free excitons through an exciton-exciton collision process [15,16] and another broad green-red emission band ranging from 480 to 700 nm was assigned to deep level visible emission (DLE) region originating

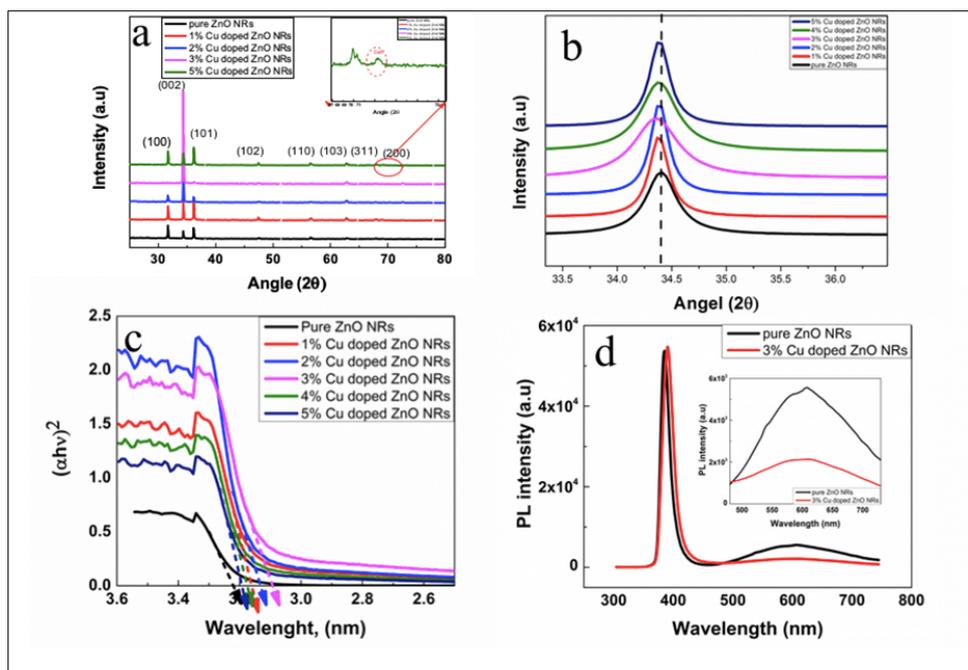


Figure 2. a) XRD patterns of the undoped and Cu doped ZnO nanorods at different concentrations and the large scale at 5% Cu doping (inset). b) Comparison of the (002) peaks taken for undoped and Cu doped ZnO NRs. c) Tauc's plot from absorbance spectra of Cu doped ZnO NRs for different Cu concentrations. d) Room temperature PL spectra of pure ZnO NRs and 3% Cu doped ZnONRs [11].

from intrinsic defect such as zinc vacancies (V_{Zn}), interstitial zinc (Zn_i), oxygen vacancies (V_O) or interstitial oxygen (O_i) [15,17,18]. Interestingly, **Figure 2d** in set exhibited the decrease of the PL emission intensity in DLE region. This reduction of PL band intensity was explained by the non-radiative recombination involving Auger recombination and multi photon recombination. Moreover, there was a slight shift toward lower wavelength in DLE region that was related to the recombination between photoinduced carrier and Cu impurity. Under doping, the existence of electron energy level of impurity (Cu^+ and Cu^{2+} states) in the band gap of ZnO NRs contributed to narrowing the optical band gap. As a result, the optical band gap changed from 3.26 to 3.08 eV with the increase of Cu concentration from 0 to 3% leading to shift in the absorbance edge toward visible region. However, the narrowest optical band gap of ZnO:Cu NRs was 3.08 eV, corresponding to 400 nm wavelength. Therefore, the visible absorption was still limited. To overcome this challenge, Ag NPs were decorated onto ZnO:Cu NRs to enhance the absorption in the visible region. **Figure 3a** showed the XRD pattern of Cu doped ZnO NRs decorated by AgNPs. Besides the characteristic peak of ZnO NRs, the presence of Ag peak at 38° demonstrated that an Ag phase occurred in the XRD pattern, which means that Ag NPs covered around the nanorod. **Figure 3b** presented the SEM image of Cu doped ZnO NRs decorated with AgNPs. The nanorods have high area density with the large

coverage on the sample surface. The length and diameter of nanorods are 1.5 μm and 500 nm, respectively. It was clearly seen that AgNPs covered Cu doped ZnO NRs in TEM image. **Figure 3c** exhibited that small AgNPs with uniform spherical shape was distributed around nanorods. It confirmed that a large amount of nanoparticles was successfully decorated on the nanorods' surface. The average diameter of AgNPs was approximately 9 nm. **Figure 3d** presented the absorbance spectra of ZnO:Cu NRs and ZnO:Cu NRs decorating with Ag NPs. The absorbance spectrum of Cu doped ZnO NRs (black line) showed a sharp absorption peak in the UV region at 371.24 nm, and along with a small absorption tail in the visible area. For Ag NPs decorating sample, beside the characteristic peak of ZnO NRs doping, we can see clearly the new peak at 461.61 nm (green line). The appearance of peak in the visible region was attributed to SPR effect which is explained more detail (**Figure 4**).

Figure 4 presented a mechanism of enhancement absorbance in the visible region by LSPR effect using AgNPs decorated ZnO:Cu NRs. There were two reasons to extend visible absorbance. At first, this enhancement was attributed to the LSPR effect between AgNPs and semiconductor that is featured in strong light absorbance. It was demonstrated that the interaction between the incident photon and AgNPs with the size of a few nanometers gave rise to a very efficient

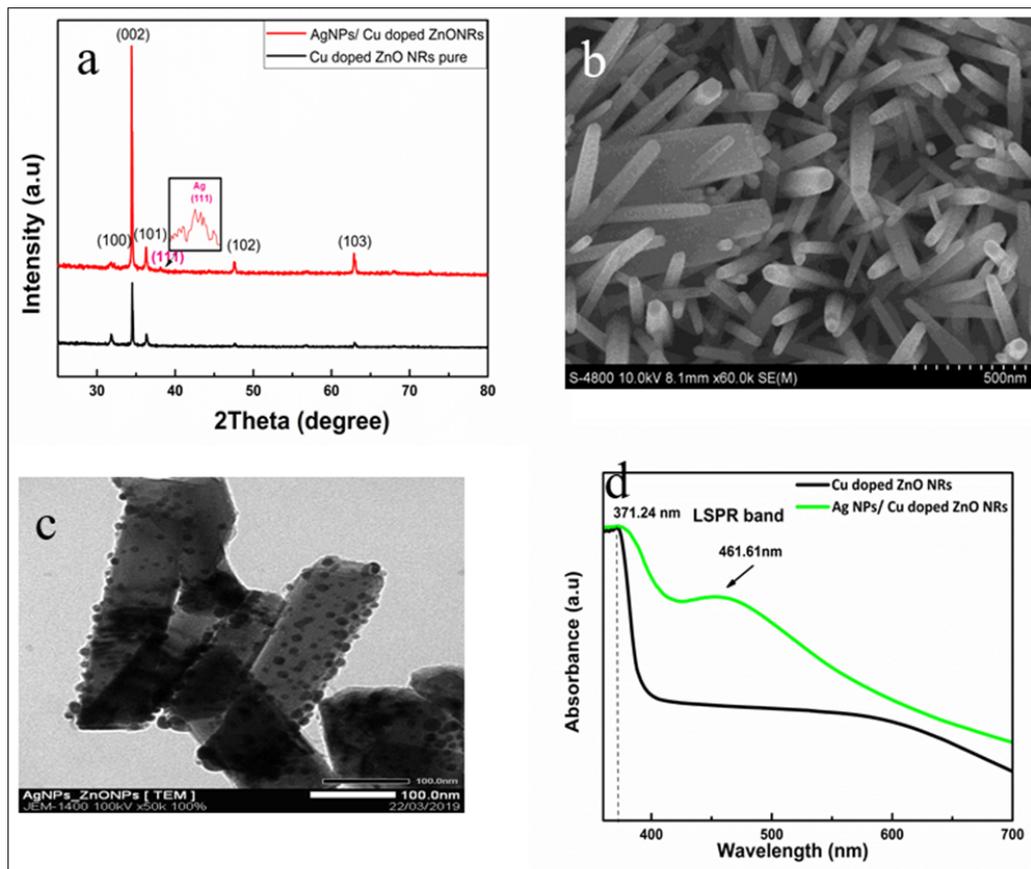


Figure 3. a) The XRD pattern of Cu doped ZnO NRs with and without decorating with Ag NPs. b) SEM and c) TEM image of Ag NPs decorated Cu doped ZnO NRs d) The SPR effect through the absorbance spectra of Cu doped ZnO NRs with and without decorating with Ag NPs [11].

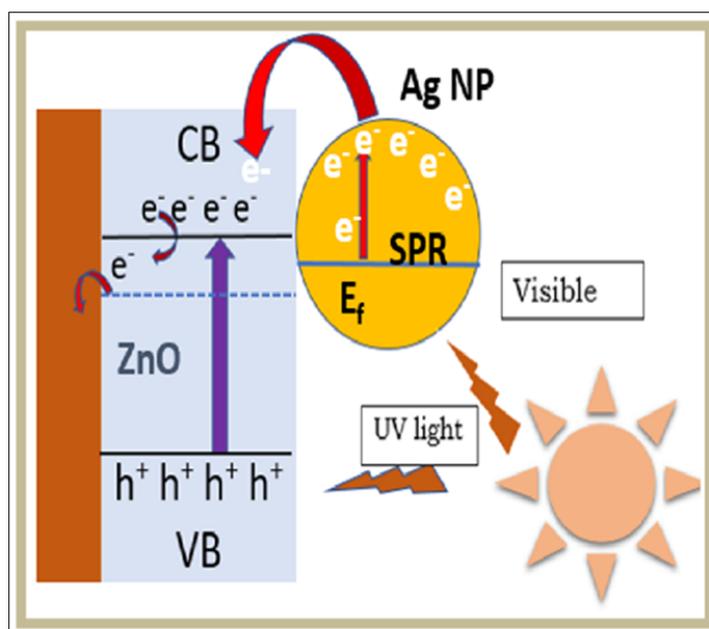


Figure 4. Mechanism of LSPR effect by Ag NPs decorated ZnO NRs doping [11].

resonant light scattering that increased the direct light absorption of host materials. Secondly, the strong light scattering was induced from interaction of the incident light and AgNPs, lengthening the optical path and further reducing the light energy loss. The extended absorbance of the AgNPs decorated NRs in the visible region confirmed that AgZnO: Cu samples were of considerable practical importance due to the efficient utilization of sunlight or visible light. Multimodification of ZnO NRs was a potential method to synthesise the optical materials leading to improvement in the efficiency of optoelectronic devices using the solar light, especially, solar water splitting devices.

CONCLUSION

ZnO NRs were multi-modified to shift the absorbance edge toward long wavelength light and enhance the absorption in the visible region. ZnO NRs doped 3% Cu concentration showed the best results when optimized to achieve a minimum bandwidth of 3.08 eV. The AgNPs are uniformly decorated on ZnO: Cu NRs by sputtering and heat treatment. The size of AgNPs is optimized with an average diameter of 9nm through which the SPR effect is clearly observed at the absorption peak at 461.61 nm.

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