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Band gap engineering and photoluminescence studies of imine linked ZnO nanoparticles synthesized by direct precipitation route

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ABSTRACT

An imine linked dipodal organic receptor **1** is synthesized using condensation reaction between 2-aminothiophenol and 4-diethylaminosalicylaldehyde which is used as a capping agent over ZnO resulting in surface modified ZnO nanoparticles **1.ZnO**. The conjugate **1.ZnO** shows emission at 420 nm. The emission spectra obtained from surface modified ZnO nanoparticles is pure and sharp with full width half maximum (FWHM) 60 nm in comparison to emission spectra of pure ZnO which shows emission at 434 nm, 456 nm and 520 nm. It is demonstrated that organic receptor **1** acted as a capping monolayer over ZnO semiconductor as the surface defects that otherwise resulted in electronic transitions has not shown emission at various wavelengths in visible range. Thus the capping agent has successfully passivated the ZnO nanoparticles. The synthesized **1.ZnO** nanoparticles can be used in active layer of light emitting diode providing blue emission at 420 nm.

1. Introduction

Semiconductor industry is the building blocks for the future technology development especially in the field of electronic based systems. The CMOS technology is rapidly growing towards large scale integration on a single chip leading to smaller size consuming smaller area, lower power consumption, faster speed etc. [1]. Further, reducing the size also leads to various challenges especially short channel effects [2–4]. The preferable option is the use of nanomaterials instead of bulk materials. So, the world is moving towards material characterization due to increasing demand for lower chip area [5–6]. The size dependent properties of the materials have gained momentum nowadays. When compared to bulk phase materials, nanomaterials exhibit unusual and outstanding properties [7]. As a result, we are moving towards era of nanomaterials. The benefit of using nanomaterials is their ability to change their key properties without any change in their chemical composition. Due to reduced dimensions of the materials, their several attributes such as optical, electronic, physical, chemical and magnetic properties exhibit remarkable uniqueness. The family of semiconductors is dominated by silicon and germanium. But, the high speed technology requires a material with higher effective carrier velocity that can be achieved with gallium arsenide (GaAs) also [8–10]. Some electronics properties of GaAs are better to those of silicon as it has higher electron velocity and electron mobility [11–12]. Contrary to silicon junctions, GaAs devices are relatively insensitive to heat owing to their wider band gap and less noise at high frequencies. But, high temperature and high power operation devices require a material with higher breakdown field strength too and that material is ZnO. ZnO, the wurtzite structured semiconductor is blessed with a bandgap of 3.3 eV and high exciton binding energy of 60 meV. The high excitonic binding energy ensures efficient excitonic emissions at room temperature [13–14]. Metal oxide semiconductor ZnO finds applications in electronic devices which includes solar cell, light emitting diodes, transparent electrodes, photodetectors and many more [15]. Nanoscale components have high surface area to volume ratio that makes them ideal for their use in composite materials, drug delivery and chemical storage. However, high surface to volume ratio also results in high density of surface defects, which are needed to be passivated as it finally controls the luminescence properties. Capping agents bearing carboxylic acid (—COOH), thiol (—SH), and amine ($—NH_2$) function groups may be used to stabilize the ZnO nanoparticles by avoiding agglomeration among ZnO nanoparticles. The agglomeration can be evaded by passivating the surface of pure ZnO nanoparticles as the capping agent controls the growth of nanoparticles immediately after the nucleation stage [16–18]. The Al_2O_3 coating and hydrogen plasma treatment was carried

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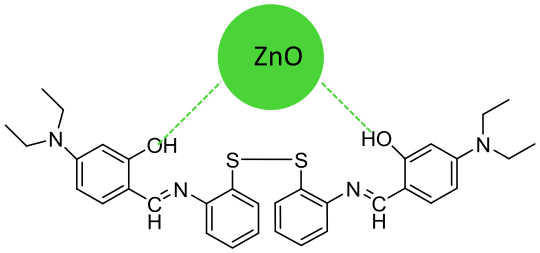

Scheme 1. Organic receptor capped ZnO (1.ZnO).

out to passivate the surface effects resulting in deep level emissions was carried out by Chen et al [19–20]. The surface states of ZnO contribute majorly to green and orange emissions. The presence of defects on the surface of ZnO nanoparticles is considerable for light emitting diodes resulting in white light emission [21–24]. However, the electronic transitions due to the existence of surface defects resulting in the red, orange, yellow and green emission needs to be evaded in order to get narrow spectral line width in LEDs. To achieve this purpose, imine linked organic receptor is used as a capping agent to passivate the surface of ZnO forming core-shell structure. Wet chemical precipitation route is used to modify the ZnO surface using organic receptor. The Physiochemical interactions that occur at the surface of ZnO caused by organic receptor resulted in the quenching of deep level emissions. The passivation effect is confirmed from the Photoluminescence studies of surface passivated ZnO nanoparticles. Surface decorated ZnO nanoparticles are synthesized, characterized and its application in Cu(II) determination is also discussed.

2. Experimental section

Organic receptor **1** was synthesized by condensation reaction between 2-aminothiophenol (1.07 ml, 10 mM) and 4-diethylaminosalicylaldehyde (1.93 gm, 10 mM) (Scheme1). The organic receptor was characterized by mass spectroscopic technique ESI-MS, which shows m/z = 599.4 $[M + H]^+$, where M = $C_{34}H_{38}N_4O_2S_2$. The presence of imine linkage in organic receptor was also confirmed by getting a signal at 8.44 ppm in ^{1}H NMR spectra (Fig. 1a). The ZnO nanoparticles were synthesized by in-situ reaction of organic receptor with zinc nitrate hexahydrate. Drop wise alcoholic solution of sodium hydroxide was then added to the solution, which lead to the formation of surface passivated ZnO nanoparticles **(1.ZnO)**. The exact nature of binding sites of **1** responsible for coordination with ZnO were determined from the changes in the ^{1}H NMR spectrum of **1** upon interaction with ZnO. The synthesized ZnO nanoparticles capped with imine linked organic receptor was then characterized with ^{1}H NMR spectra, where shift in the signal due to —CH═N— was observed (Fig. 1b). Broadening of all signals also confirmed the binding of organic receptor **1** on the surface of ZnO (Fig. 2.).

3. Results and discussion

The IR spectrum was recorded for **1** and **(1.ZnO)**, where up field shift in the bands was observed. The band shift in the IR spectra observed clearly demonstrated the influence of capping agent on ZnO nanoparticles and thus, electronic environment has been modified. The confirmation of surface modification of ZnO

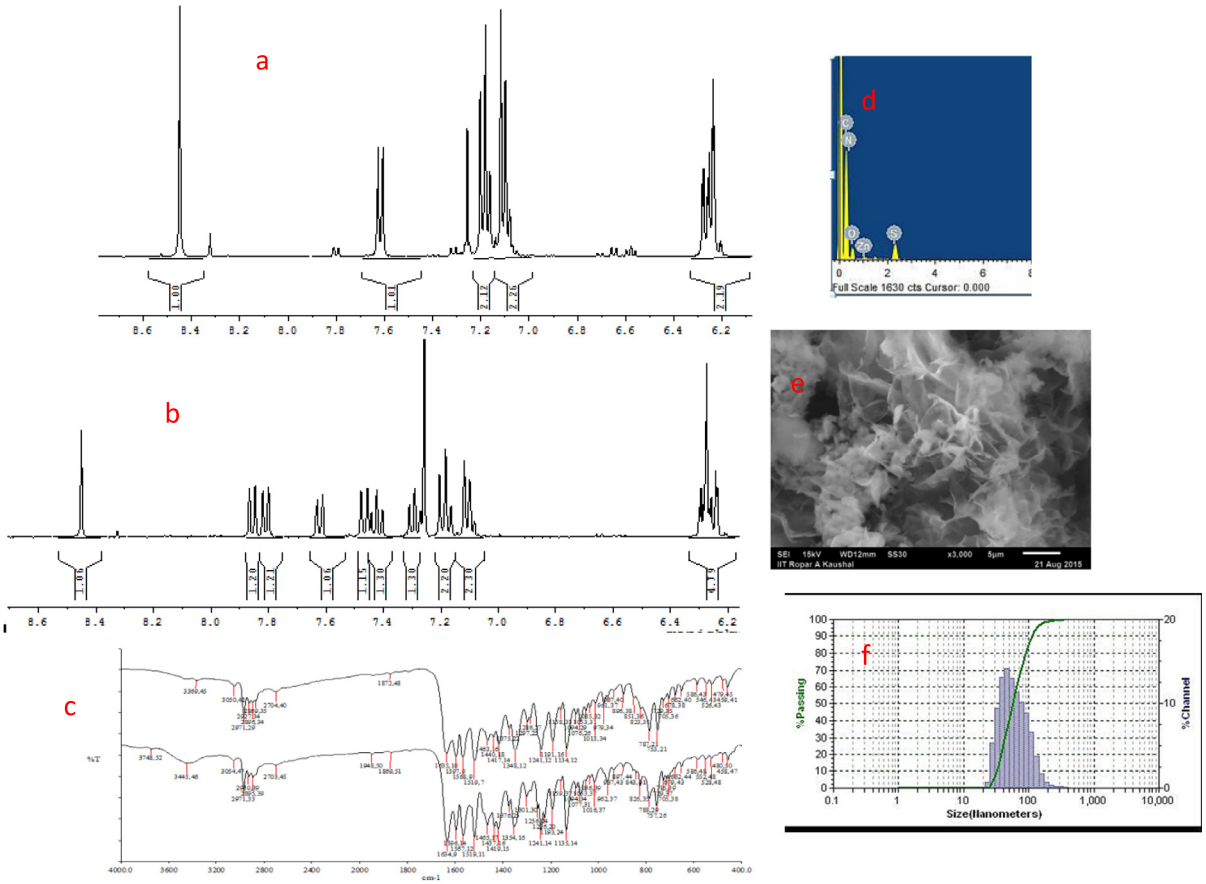

Fig. 1. a. ^{1}H NMR of organic receptor **1** b. ^{1}H NMR of receptor capped ZnO (**1.ZnO**) c. IR spectra of **1** (above) and **1. ZnO** (below) d. EDX image of **1.ZnO** showing the presence of organic compound together with Zn and O e. SEM image of **1.ZnO** showing supramolecular assembly forming sheet like structure. f. DLS based particle size analyzer showing particle size of 56 nm.