



ZnO nanoparticles decorated with organic anion receptor: Selective recognition of sulfate anion

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ABSTRACT

A new monopodal thiourea based sensor has been synthesized and same sensor was decorated on ZnO by a chemical precipitation technique. Burning of ZnO coated sample at 500 °C for 30 min provided the sample free of organic part and this annealing also destroys the fern like structure of the compound. The anion binding abilities of both parent monopodal sensor and ZnO coated sensor were investigated in the DMSO/H₂O (9.5/0.5, v/v) solvent system. The ZnO decorated sensor exhibits selective recognition of sulfate ion, whereas the monopodal sensor does not. This selectivity is attributed to the unique binding mode for sulfate ion, in which tetrahedral anion forms hydrogen bonds to sensor through both hydrogen bond donor and hydrogen bond acceptor sites.

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1. Introduction

The development of sensors capable of selective recognition of anionic species is a research area of current interest [1]. These artificial sensors generally consist of hydrogen bond donor functionalities comprised of urea/thiourea moieties, which may offer two parallel hydrogen bond donors to bind an anion [2,3]. These receptors are generally found to be more selective for spherical anion especially fluoride [4]. The tripodal frameworks having three units of thiourea have exhibited selectivity for tetrahedral anion over other spherical and trigonal planar anions [5,6]. However, sometimes these receptors are difficult to synthesize, thus there is always a need to develop a sensor system through easy synthetic schemes. One strategy is based upon simple synthesis of monopodal receptor and then to decorate it on some nanoparticles so that the resultant sensor may offer coordination sphere as is expected from the tripodal receptors [7]. The strategy is explored for cation recognition [8] and to the best of our knowledge the concept is not extended much for anion recognition [9]. In this manuscript a simple receptor is synthesized and then it is decorated on the surface of ZnO nanoparticles. ZnO itself shows some significant properties due to very less toxicity and efficient excitonic emission at room temperature, which makes it an excellent candidate for several applications [10]. Grain boundaries and other surface defects of ZnO sample affect its physical properties to an appreciable extent [11]. Oxygen vacancies or other surface defects formed in

between the grain boundaries and interfaces are claimed to be responsible for the room temperature ferromagnetism in nano-grained ZnO. For the occurrence of this ferromagnetism, it is necessary that specific grain boundary area (ratio of the grain boundary area to grain volume) is greater than a certain threshold value. Besides room temperature ferromagnetism, high temperature ferromagnetism can be attributed to amorphous nature of intergranular layers in ZnO [12]. Due to ferromagnetic properties of nanostructured ZnO; it finds applications in spintronics, which in turn depends upon the grain boundaries in doped ZnO [13]. Many other physical phenomena like plasticity, strength, resistivity, etc. are also controlled by these grain boundaries [14]. So, in the light of above explanation, behavior of the ZnO compound can be attributed to the grain boundaries and other surface defects of ZnO.

2. Result and discussion

Receptor **1** was synthesized by series of steps including the imine linkage synthesis through the condensation reaction between salicylaldehyde and propylamine. The imine linkage was reduced with NaBH₄ and the resultant compound (with reduced imine linkage product) was subjected to react with 4-nitrophenyl isothiocyanate (Fig. S1). This product was characterized with spectroscopic methods (Fig. S2–4) and purity was established with elemental analysis. The IR spectrum of compound **1** showing a band at 1768 cm⁻¹, is attributed to the stretching in –C=S bond. The ¹H NMR (400 MHz, DMSO-d₆) was found to be according to the structure of compound **1**: δ 9.93(br, 1H, –OH), 9.72(s, 1H, –NH), 8.1(d, 2H, Ar H), 7.6(d, 2H, Ar H), 7.13(m, 2H, –CH₂), 6.86(d, 1H,

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Ar H), 6.81(t, 1H, Ar H), 4.9(s, 2H, Ar -CH₂), 3.7(t, 2H, -N-CH₂), and 0.86(t, 3H, -CH₃). The ¹³C NMR (400 MHz, DMSO-*d*₆) was also found to be according to the expected signals of compound **1**: δ 178.34, 154.90, 152.28, 149.82, 147.80, 142.22, 128.35, 123.75, 123.25, 119.12, 115.08, 39.70, 39.28, 39.08, and 11.01. Receptor **1** was coated on the surface of ZnO through in-situ synthesis of ZnO in the presence of compound **1**. The resultant product **2** was characterized by the shift in the ¹H NMR signal assigned for -OH, showing that compound **1** is attached to ZnO through -OH group. The -OH signal of pure compound **1** at 9.93 ppm specify that these protons are under the influence of strong hydrogen bonding; however after decoration of **1** on ZnO, the -OH signal shifted downfield and broaden (Fig. S6). The morphology of **2** was realized with SEM, showing that there might be a possibility of non-covalent supramolecular interactions to generate a self-assembled fern like structure due to the structure directing nature of compound **1** (Fig. 1C). Compound **2** was heated at 500 °C for 2 h to burn the organic part of compound **2** and resultant material is designated as **2** (annealed). This heat treatment leads to destruction of the fern like structure of compound **2** due to the dearth of supramolecular interactions prevailed in compound **2** (Fig. S7). The

XRD pattern of **2** (annealed) shows scattering analogs (2θ) of 31.8, 34.5, 36.3, 47.5, 56.6, 62.9, and 67.9 corresponding to the reflection from 100, 002, 101, 102, 110, 103 and 112 crystal planes, respectively (Fig. 1D). The distribution of particle size of compound **2** (showing average particle size of 7.5 nm) was measured with DLS based particle size analyzer by dissolving the compound in DMSO:H₂O (70:30; v/v). The EDAX analysis of **2** shows the presence of organic compounds along with ZnO, while compound **2** (annealed) shows the presence of only ZnO and no remnant of any organic compound (Fig. 1E,F). To understand the properties of compound **2**, another material of ZnO (pure) was prepared by using the same procedure as that was used for the synthesis of compound **2** except no capping reagent was used. A comparison of solid state UV-vis absorption spectra of ZnO (pure), and compound **2** (ZnO coated with **1**) is shown in Fig. 2A. The ZnO (pure) exhibited peak at 380 nm corresponding to the exciton state of ZnO. The absorption spectra of ZnO coated with **1** showed a band at 360 nm. The fluorescence spectrum of ZnO (pure) exhibited a green emission band at 576 nm; however the intensity of this band was quenched upon capping of ZnO with receptor **1** (Fig. 2B). The noticed effect can be explained on the basis of model offered

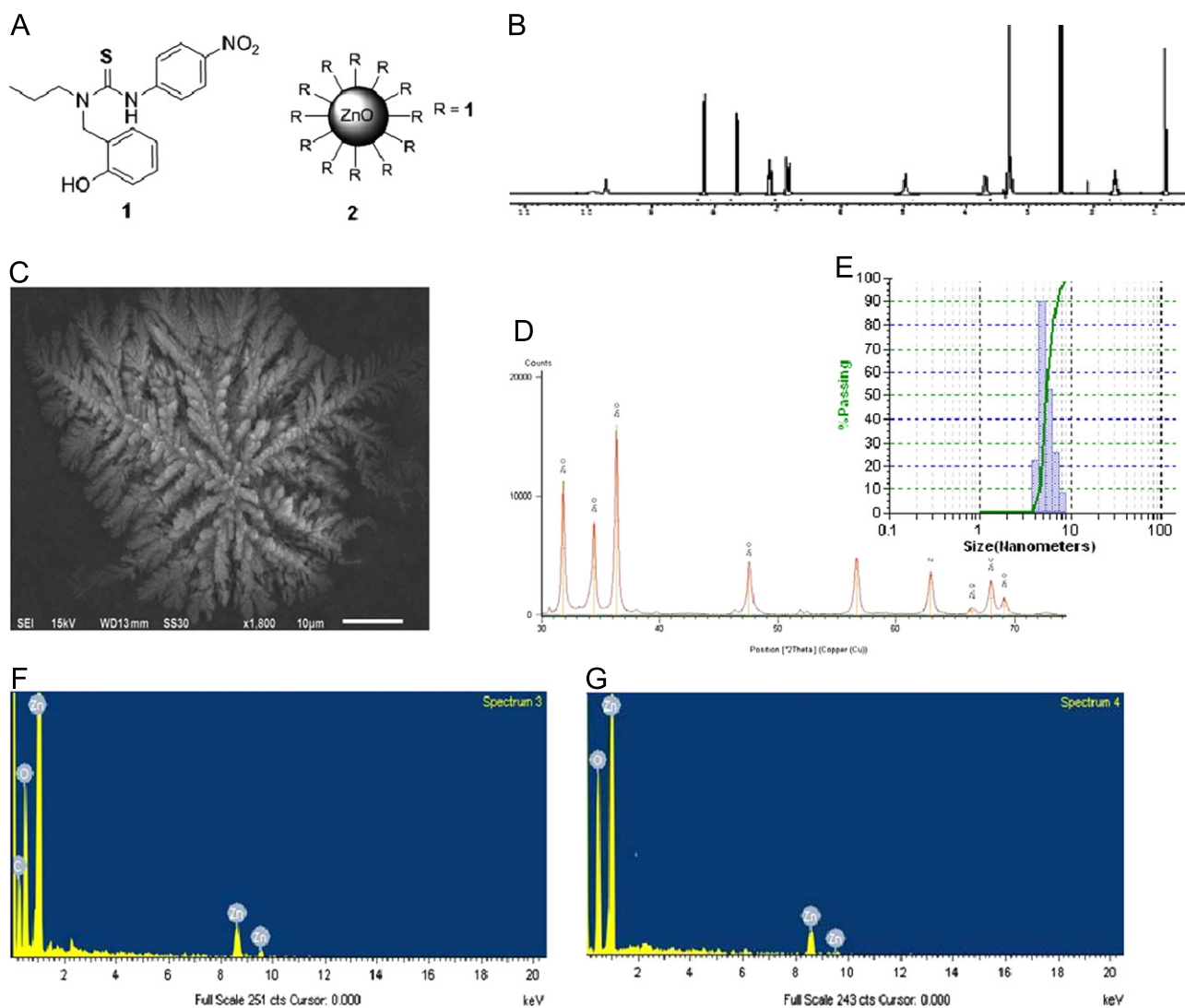


Fig. 1. (A) Chemical structures of compounds **1** and **2**; (B) ¹H NMR spectrum of compound **1** (400 MHz, DMSO-*d*₆); (C) SEM image of compound **2**, showing a fern like self assembled structure due to the structure directing nature of compound **1**; (D) X-ray powder diffractogram of ZnO (obtained by heating compound **2** at 500 °C for 2 h; (E) distribution of particle size of compound **2** (showing average particle size of 7.5 nm); measured with DLS based particle size analyzer by dissolving the compound in DMSO:H₂O (70:30; v/v); (F) EDX analysis of compound **2** (as prepared) showing the coatings of organic molecules on ZnO; and (G) EDX analysis of compound **2** (obtained by heating compound **2** at 500 °C for 2 h) showing the burning of organic molecules from the surface of ZnO.

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