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Habit-modifying additives and their morphological consequences on photoluminescence and glucose sensing properties of ZnO nanostructures, grown via aqueous chemical synthesis

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Abstract

Generally, the anisotropic shape of inorganic nano-crystal can be influenced by one or more of different parameters i.e. kinetic energy barrier, temperature, time, and the nature of the capping molecules. Here, different surfactants acting as capping molecules were used to assist the aqueous chemical growth of zinc oxide (ZnO) nanostructures on Au coated glass substrates. The morphology, crystal quality and the photoluminescence (PL) properties of the ZnO nanostructures were investigated. The PL properties of the prepared ZnO nanostructures at room temperature showed a dominant UV luminescence peak, while the “green-yellow” emissions were essentially suppressed. Moreover, the ZnO nanostructures were investigated for the development of a glucose biosensor. An adsorbed molecule has direct contribution on the glucose oxidase/ZnO/Au sensing properties. We show that the performance of a ZnO - based biosensor can be improved by tailoring the properties of the ZnO –biomolecule interface through engineering of the morphology, effective surface area, and adsorption capability.

Keyword: ZnO nanostructures; cationic and anionic molecules; PL spectra; and glucose sensitivity.

ZnO is an II–VI semiconductor and the electronic and optical properties of its nanocrystals depend on their size and morphology [1]. This can be attributed to surface-to-volume ratio, rather than to the quantum confinement [2]. ZnO nanostructures have received relatively high interest due to their potential for opto-electronics and sensor devices. The interest for optoelectronic application is due to the fact that, ZnO has a wide band gap of 3.37 eV and a relatively high exciton binding energy of 60 meV, in addition to the defect emissions that covers the whole visible region [2, 3]. ZnO exhibits remarkable properties for sensing applications due to its biocompatibility and high isoelectric point (IEP) ~ 9.5 [4]. These properties are suitable for the adsorption and immobilization of low IEP proteins or enzyme [5]. Due to these properties direct electron transfer between the enzyme's active sites and the electrode can be achieved [5]. It is worth mentioning that, the physical and chemical properties of metal oxides can be tuned through adjusting and controlling their structure and morphology [6-8] and therefore, the issues related to ZnO morphology have attracted extensive research interest for developing efficient nano-devices for various applications. The synthesis mechanisms are playing important role as the means to this end. Among the several chemical fabrication methods for the production of functional metal oxide nanostructures [7], is the aqueous chemical growth (ACG) [9]. In addition to the low cost, the ACG can be handled at low temperature $< 100^{\circ}$ C, organic molecules as an additive can also be used e.g., surfactants might be used in an ACG process to control the morphology of the nanostructures.

Earlier, the effect of organic surfactants like polyvinyl pyrrolidone, sodium dodecyl sulfate, polyethylene glycol, ethylene glycol and polyvinyl alcohol on the morphology of ZnO grown by the electrodeposition method have been studied [10]. Here, we report surfactant-assisted growth of the ZnO nanostructures with the ACG method by employing different organic additives such as sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), sodium *p*-toluenesulfonate (NaPTS), and cetyltrimethyl ammonium bromide (CTAB) into the growth solution. The last one is a well-known and common surfactant to grow ZnO [11]. However, different surfactants have been used here as the source of impurities and as habit-modifying additives that would yield a desired morphology of the ZnO nanostructures [12-14]. The optical properties of the different ZnO nanostructures were investigated. Furthermore, the ZnO nanostructures grown with different surfactants were used for the detection of glucose using the potentiometric method.

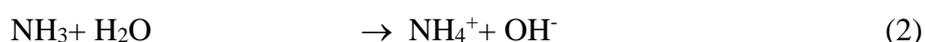
The ZnO nanorods on the gold coated glass substrates have been grown by the ACG method as follow: glass substrates were sonicated in ultrasonic bath for about 10 min in acetone, deionized water and isopropanol, respectively. The substrates were then fixed into vacuum chamber of an evaporator instrument. After this an adhesive layer of 20 nm of titanium was evaporated followed by a 100 nm thickness layer of gold. Then the substrates were seeded with zinc acetate dehydrate layer via spin coating technique at 1000 rpm for 20 s. The ZnO seed precursor was prepared from KOH in methanol (0.03 M). This solution was added slowly to a solution of 0.01 M zinc acetate dehydrates in methanol under vigorous stirring at 60 °C and for 2 hrs. This coating step was repeated three times to ensure uniform coverage of the ZnO seeds. The seed coated substrates were fixed horizontally upside-down in Teflon sample holder and kept in equimolar 0.075 M solution of hexamethylenetetramine (HMT) and zinc nitrate hexahydrate (ZNH)[13]. The samples containing growth solution was placed in preheated oven at 90 °C for 5 to 6 h. For other ZnO nanostructures the only difference in that, five different growth solutions were prepared separately then each growth solution an amount of about 160 mg of SDS, SDBS, NaPTS, or CTAB surfactants was added. Thus, these different surfactants might also be considered as habit-modifying additive that can tune the morphology [14]. The habit-modifying additives are usually selectively adsorbed on one face and hence inhibit growth of this face. After completion of the growth duration, the samples were washed with deionized water and dried at room temperature.

X-ray powder diffraction (XRD) measurements to examine the crystalline quality were performed using Phillips PW 1729 powder diffractometer. Figure 1 shows the XRD patterns of the ZnO with and without the surfactant- assisted growth of ZnO nanostructures. All the X-ray spectra show well-defined peak at 34.442° that corresponds to (002) plane and it is an indication that the growth orientation is along the c-axis (JCPDS-No 36-1451). All the other peaks can be assigned to hexagonal wurtzite structure of ZnO. Figure 1 suggests that there are no observable differences in the crystallographic orientation of the different ZnO grown nanostructures.

The morphology of the ZnO nanostructures was investigated by field emission scanning electron microscope (SEM: LEO 1550 Gemini). In Figure 2 (a) conventionally grown ZnO nanorods structure is shown [9, and 13]. The morphology of the ZnO nanostructures is sensitive to external conditions such as the solution pH value, the choices of the catalyst, and surfactant. It has been believed that the anisotropic shape of inorganic nanocrystal can be

influenced by one or more of different parameters i.e. kinetic energy barrier, temperature, time, and the nature of the capping molecules [15]. Here, the capping molecule is the only investigated parameter. However, the surfactant access with the existence of HMT might be producing a complex surrounding the nanostructures environment [16] and thus modulating kinetic energy is accompanied. The growth processes with CTAB and NaPTS have resulted in interconnected and stacked spiral nano-hexagonal-like structures as shown in Figure 2 (b) and Figure 2 (c), respectively. Meanwhile, a deviation to nano-wurtzite structures and nano-foam-like structures are shown in Figure 2 (d) and Figure 2 (e) when SDBS and SDS are incorporated in the growth solutions, respectively. The surfactant molecules are showing a crucial role in the growth process of ZnO nanocrystals and hence can be used to control the morphology. There are several interfacial phenomena that can be considered in the growth mechanism of these structures, e.g. adsorption, surface tension, and the critical micelle concentration [17]. This is because the surfactant molecules have both hydrophobic and hydrophilic portions in their structures. However, the adsorption phenomenon is more decisive factor for the capping molecules. The adsorption of surfactant molecules on the high-energy face of crystals is in the order NaPTS > CTAB > SDS > SDBS [18]. In the first two cases the capping molecules strongly inhibited the usual growth habit of ZnO nanorods i.e. along the c-axis which is a well-known to have a higher growth velocity compared to the other growth directions [19]. Whereas for the case of the SDBS, and from the SEM shown in Figure 2(d), it is clear that this surfactant has an equal dimensional contribution on the planes. While the SDS has the same contributions but has longer chain length of the hydrophobic part and this fact makes the morphology to have a foam shape like structure [20].

To understand the observed behaviors of ZnO nanostructures, it is necessary to recall the growth mechanism of ZnO nanorods. The possible reactions involved in the synthesis of ZnO nanorods are summarized below [12]:

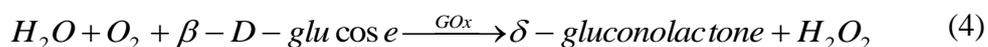


The HMT plays a role as a buffer medium and also supplies the ammonia (NH₃) during the growth. NH₃ reacts with water and generates hydroxide (OH⁻) ions and finally OH⁻ ions react

with Zn^{2+} ion and yields $Zn(OH)_2$. During growth the expected pH value might be between 6.5 and 7 [11]. $Zn(OH)_2$ is thermodynamically unstable and it would be dehydrated when they are incorporated into the crystal, therefore could be referred as growth unit [14]. Marino et al., have shown that the crystal structure of ZnO is a hexagonal closed packing for Zn which surrounded by four oxygen atoms and consequently has two polar surfaces [21]. Smith et. al., reported that the complex growth units possesses a characteristic of polaron due to the structural feature of a tetrahedron, i.e., asymmetrical position of central Zn atom in a tetrahedron [22]. Wang et. al., have reported that equation 3 plays an important role in the growth process [14]. The (0001) plane (terminated with zinc) of ZnO has the maximum surface energy, while the $(000\bar{1})$ plane (terminated with oxygen) has the minimum surface energy. As a result, the growth along the [0001] direction has a faster rate than that along other directions [14, 19]. In our work, with a certain amount of the head group (cationic or anionic) of the surfactant e.g., CTAB would be dissociated in water into CTA^+ and Br^- [23]. The electrostatic attraction between CTA^+ and $Zn(OH)_2$ endows the surfactant the capability to act as an ionic carrier resulting in a kinetic inhibition of growth on [0001] direction.

The photoluminescence (PL) properties of the prepared ZnO nanostructures were studied at room temperature. Generally, ZnO have two pronounced peaks of luminescence. The UV emission peak is so called near band edge (NBE) emission due to free excitonic emission, and possibly assisted remaining donor bound excitonic emission [24]. The other peak is called the “green-yellow” band in the visible region, and is also called the deep level emission (DLE) band. Our grown ZnO nanorods have demonstrated these two peaks clearly. Figure 3 shows the PL spectra of all the grown ZnO nanostructures. Table I shows the PL peak position in the UV region and the full width at half maxima (FWHM). The NBE intensity and shape depends strongly on various parameters such as the dimension of the nanostructures, impurities and defects concentrations [25]. However, in the case of the surfactants molecules assisted growth, the NBE appears as the predominant contribution with relatively position shift and intensity variation. This is attributed to the effect of the surfactants that are absorbed by the surface of the ZnO and might be considered as impurities. Although bare ZnO has drawn the narrowest FWHM as is shown in Table I. These adsorbed molecules have suppressed the DLE which is an obstacle for obtaining an intense NBE that is expected from ZnO [26].

A glucose oxidase (GOx) solution was prepared by dissolving 30 mg of enzyme in 3 mL of 10 mM Phosphate buffered saline (PBS) of pH = 7.3 and 300 μ L of Glutaraldehyde. Then later, using drop casting, the GOx was physically adsorbed on the ZnO nanostructures surfaces through electrostatic attraction and the samples were left to dry in a fume hood at room temperature for 3 hours. The electrochemical response of the enzyme immobilized ZnO electrodes was measured against a silver-silver chloride reference electrode at room temperature using electrical instrument (Keithley 2400 model). A stock solution containing 1.89g of glucose in 100 ml PBS was prepared. Figure 4 (a-e) represents the primarily sensing performance of the as grown ZnO, ZnO:CTAB, ZnO:NaPTS, ZnO:SDBS, and ZnO:SDS immobilized GOx/Au electrodes, with sensitivity of 71, 66, 32, 35, and -42 mV/decade respectively. Each electrode has been examined by changing the glucose concentration from 1×10^{-6} to 1×10^{-2} M and the electromotive voltage is recorded accordingly. During the interaction of the immobilized GOx with glucose molecules, the δ -gluconolactone and hydrogen peroxide are produced as a result of this reaction. The glucose concentration can be determined through these two products and also through the consumption of oxygen. Due to the presence of water, gluconolactone undergoes spontaneous conversion into gluconic acid, at a pH of 7.3 some charged species such as gluconate and hydronium ions are generated as shown in the following equations [27]:



This is the mechanism behind the generation of potentiometric response of the fabricated GOx/ZnO/Au electrodes. Because of the generation of charge environment in the reaction vessel and flow of these charges on the surface of a compound semiconductor nanomaterial which provide a solid platform for the production of strong electrical signals in an output potential [28]. The different morphology of the ZnO nanostructures was realized by incorporation of a small amount of surfactant as impurities in the growth solution. The impurities act as extrinsic donors (or acceptors), thus these impurities would significantly change the conductivity of the sensor electrodes [29].

This also could be deduced from Table I i.e. the energy band gap have been affect by the different surfactants where are varied from 3.253 eV for bare ZnO to the maximum value of 3.269 eV belonging to ZnO:CTAB . The surfactants are believed to be localized at the surface [19] and therefore could be considered as impurities. The increased sensitivity and selectivity of the sensors for exposure to glucose molecules have been realized by incorporation CTAB. CTAB is a cationic surfactantwhile the rest are to some extent anionic surfactants.ZnO has been screened with more holes since the adsorbed mechanism is suggested to be on the surface of the ZnO. According to Eq.(5) the target analytes have a positive “H” and negative “gluconate” charge, consequently the CTA⁺ molecules would communicated with the negative ions and at the same time the ZnO would detect the positive ions thus the overall signal that reach the Au electrode is propagated. This is also consentient with the results reported in [30], where the enhancement in the sensitivity realized using CTAB was demonstrated. On the other hand, Br⁻after dissociating in water possibly canbe incorporated at oxygen site and could serve as ashallow donor level [31]; therefore the ZnO conductivity is increased. While the lowest sensitivity towards glucose molecules is attributed to the fact that theNaPTS in water would be dissociated into PTS and Na⁺ that might act as a p-type doping and the conductivity will bedecreased.Therefore, one could ascribe that effect of the surfactants into the band gap (see the inset in Figure 4).These effects along with the large volume to surface ratio tailoring the properties of the ZnO–GO_x interface through engineering of morphology and effective surface area.

In summary, different ZnO nanostructures were grown by surfactant-assisted ACG method on Au coated glass substrates. The morphology was observed to be altered by the use of the different surfactants. The crystal quality was found be the same for all the samples. The PL properties of the prepared ZnO nanostructures at room temperature showed a paramount UV peak and the “green-yellow” is to some extent suppressed. The UV intensity and shape are depending on the surfactants that are absorbed by the surface of the ZnO and might be considered as impurities. These adsorbed molecules have direct contributions on the optical band gap of ZnO. Consequently, the sensing properties towards glucose molecules have been affected. ZnO:CTAB has shown wider range of detection “ $1 \times 10^{-6} - 1 \times 10^{-2}$ M” as compared to the others surfactants. The sensor sensitivity was 66 mV/decade. This sensing property is attributed to the fact that CTAB is cationic surfactant while the rest vary between anionic surfactants and neutral molecules.

Acknowledgement

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Figure captions

Figure 1: XRD spectra of the ZnO nanostructures, grown with and without the different surfactants.

Figure 2: SEM images of as-grown ZnO nanostructures before and after adding surfactants: (a) ZnO nanorods-like structures; (b) ZnO:CTAB interconnected nanodisk-like structures; (c) ZnO:NaTPSnanohexagonal-like structures; (d) ZnO:SDBSnanowurtzite structures; (e) ZnO:SDSnanof foam-like structures, and (f) growth habit under standard conditions.

Figure 3: Room temperature PL spectra of the ZnO nanostructures, grown with and without the different surfactants.

Figure 4: Calibration curve for enzymatic glucose sensors where the ZnO nanostructures grown with assistance of: (a) CTAB, (b) NaPTS, (c) SDBS, (d) SDS, and (e) ZnO nanorods with the standard growth condition i.e. without surfactants. The insets proposed Fermi level position at ZnO surfaces.

Table I: Summary of the PL properties of ZnO nanostructures grown with and without surfactants.

Fig. 1:

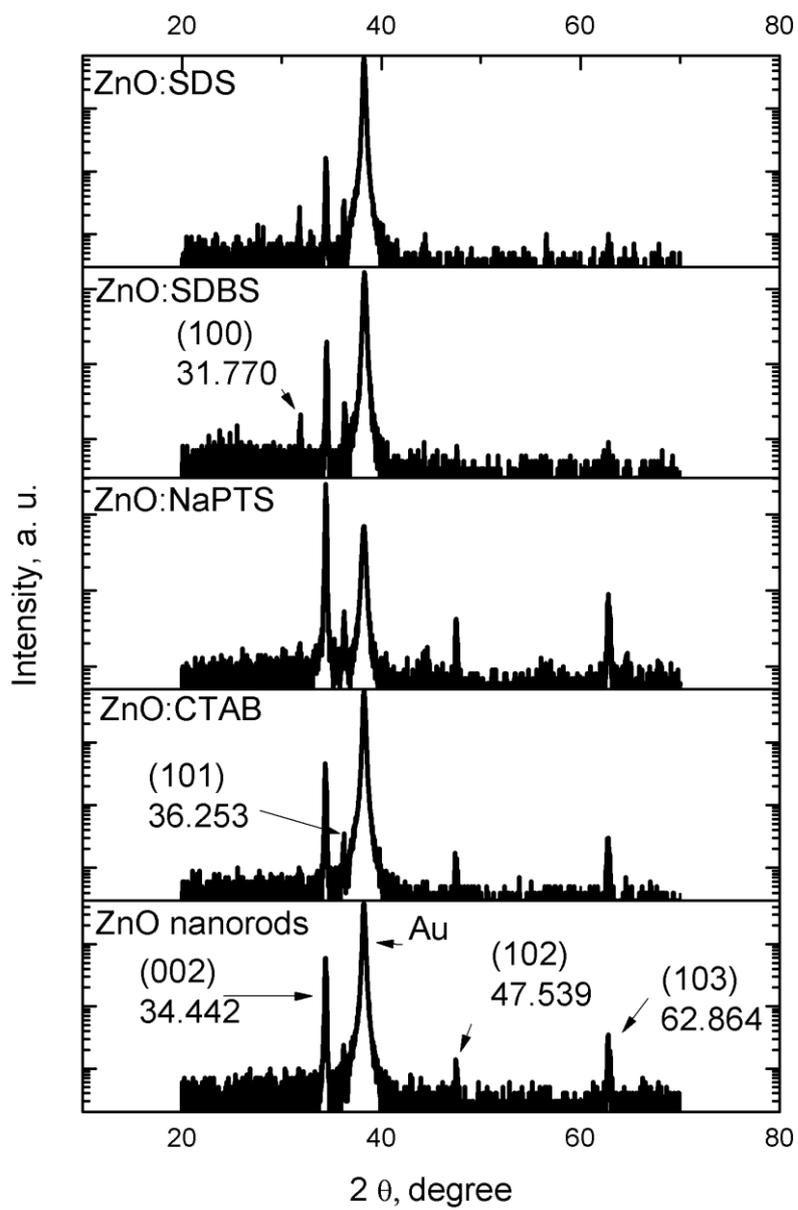


Fig. 2:

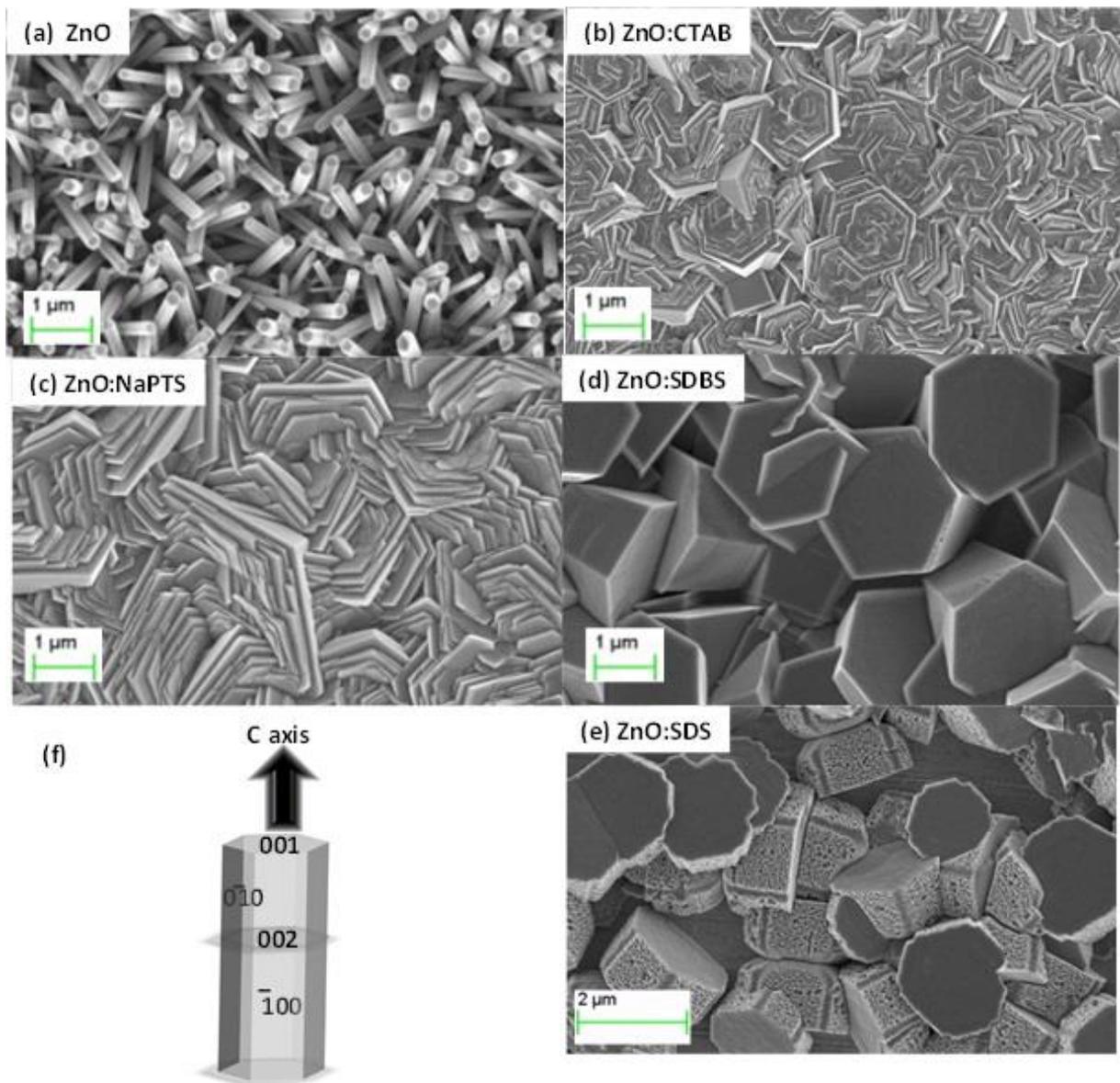


Fig. 3:

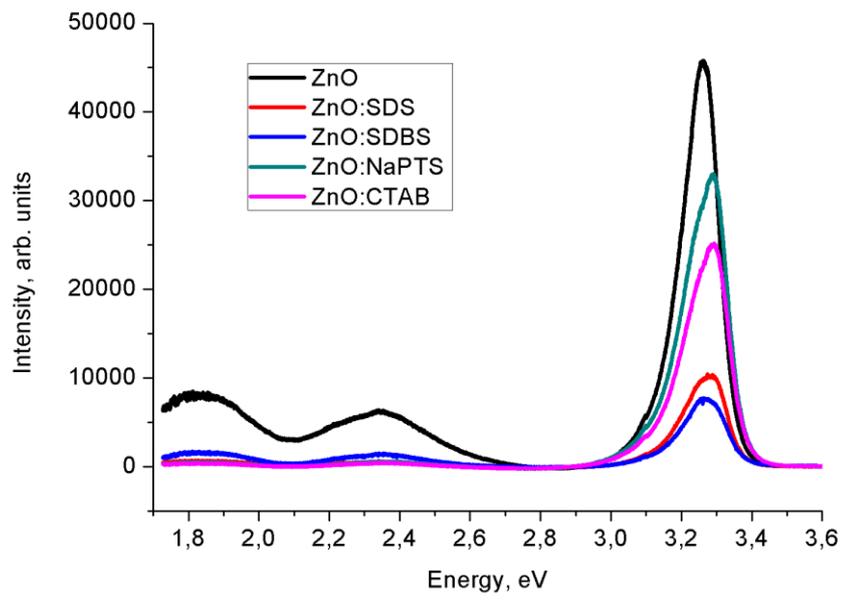


Fig. 4:

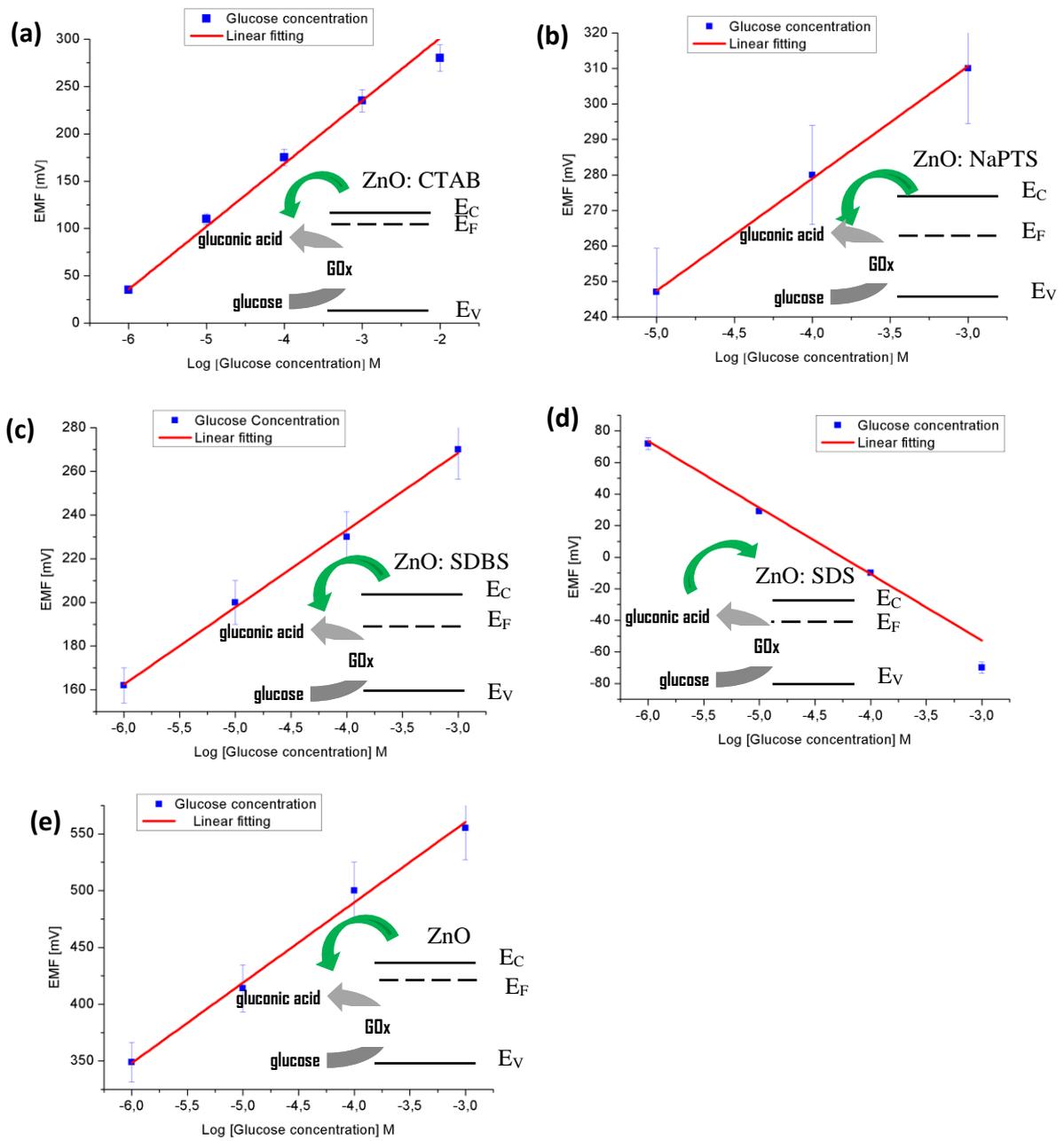


Table I:

Type of Materials	UV peak position (nm)	FWHM (nm)	UV peak position (eV)	FWHM (eV)
ZnO	381.35428	13.87826	3.253	0.11888
ZnO:CTAB	379.51713	17.97788	3.269	0.15564
ZnO:NaPTS	379.82675	17.68345	3.266	0.15282
ZnO:SDBS	380.20532	15.58057	3.263	0.13436
ZnO:SDS	380.09711	16.83327	3.264	0.14519