Abstract

Electrochemical interface can be influenced by several factors such as the type of sensing electrode material, size, shape and orientation of the particles, crystal structure, ionic radius, surface area, and material composition. It is very important to understand the effect of these different factors on the electron transfer at the electrochemcial interface for a proper, cost effective, robust design and fabrication of electrochemical sensors for biomedical applications. Therefore this work focuses on the fundamental understanding of the effects of crystal structure, electrode material composition, and ionic size on electron transfer rate constant 'k'. To study the effect of one parameter on 'k', all the other parameters should be kept constant. In the literature it is reported that spinel crystal structure-based nanomaterials are always produced in spherical form therefore spinel crystal structure-based multi-metal oxides are chosen in this study to avoid the importance particle orientation. Spinel crystal structure based-nanomaterials are synthesized by using simple auto combustion dry synthesis and the materials are characterized by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), Raman, X-ray photoelectron (XPS), and ultra violet visible (UV-vis) spectroscopic techniques to understand the morphological and spectroscopic techniques to understand the morphological and structural properties of new materials. A single spinel phase for $Zn_xNi_{1-x}Fe_2O_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) and $ZnCr_xFe_{2-x}O_4$ (x = 0, 0.25, 0.5, 0.75, 1, 2) with spherical shaped nanoparticles of size varying between 20 and 70 nm is confirmed by XRD and FESEM images. While two separate spinel phases of $ZnFe_2O_4$ and $ZnBi_2O_4$ for $ZnBi_xFe_{2-x}O_4$ (x = 0, 0.25, 0.5, 0.75, 1, 2) are found with spherical and patch-like morphology particles at sub-micrometer scale. XRD also showed some secondary phases of ZnO, Fe_2O_3, and graphite for some materials. ZnO has hexagonal structure with pyramid shaped microparticles and ZnO/$ZnFe_2O_4$ has separate ZnO and $ZnFe_2O_4$ phases as expected with same morphology as $ZnFe_2O_4$ at nanoscale. Raman confirmed the molecular vibrations

with expected atomic bondings with respective Raman bands for each material. The elemental compositions and valence states of the elements in each material are verified by XPS full survey and high resolution spectra, respectively. The energy band gap (E_g) is estimated by diffuse reflectance UV-vis spectra and Tauc's plot method. E_g varies between 2 and 3 eV for different spinel nanomaterials, ZnO has an energy gap around 3.2 eV while $ZnO/ZnFe_2O_4$ has an E_g of 2.9 eV which is an average E_g of ZnO and $ZnFe_2O_4$. XPS valence band spectra are used to estimate the valence band maximum (E_V) and the conduction band minimum ($E_C = E_g + E_V$) is computed to construct energy band diagrams for each material.

Screen-printed carbon electrodes with carbon working electrode and counter electrode, and Ag/AgCl reference electrode are employed as reference electrochemical sensors. The carbon working electrode's surface is modified by spinel nanomaterials solution in 1-butanol by drop-casting. Cylic voltammetry is used to characterized the electrochemical sensors with paracetamol as a test molecule. It is found that all the surface-modified sensors with spinel nanomaterials have significantly enhanced the electrochemical sensing capability of the bare carbon sensor in detecting 1 mM paracetamol in 0.1 M phosphate buffer solution at pH 7. The kinetic rate constant of the sensors with three sets of spinel materials, no proper trend is observed but the rate constant of the bare carbon sensor is significantly enhanced. Among all the spinel-based sensors, $ZnFe_2O_4$ has the highest 'k' of 13.1 ± 2.8 ms^{-1} with a peak-to-peak separation of 386 ± 2 mV showing high electrochemical reversibility with faster reaction at the interface. The sensitivity of the normal spinel $ZnFe_2O_4$ is observed to be higher than the inverse spinel $NiFe_2O_4$. Zinc ferrite has improved the sensitivity of the bare carbon sensor by more than two times showing its excellent sensing capability towards paracetamol. The presence of Cr(III) in the composition of normal spinel zinc ferrite has degrading performance compared to $ZnFe_2O_4$. The inclusion of higher ionic sized Bi(III) in zinc ferrite has further decreased the sensitivity. The type of electron transfer mechanism is predicted by using the energy band edges of the nanomaterials and redox potentials of paracetamol. Only $ZnFe_2O_4$ has shown a possibility of direct electron transfer while the other materials are more prone to surface-mediated electron transfer. Since normal spinel $ZnFe_2O_4$ has shown the best performance, some of the potential applications are explored. $ZnFe_2O_4$, ZnO, and $ZnO/ZnFe_2O_4$ nanomaterials potential towards dissolved oxygen, and pH sensing is studied. Finally, $ZnFe_2O_4$ and $ZnCr_2O_4$ are used in the electrochemical sensing of anti-cancer drugs (5-Fluororacil and Etoposide).