

View Article Online View Journal

RSC Advances

This article can be cited before page numbers have been issued, to do this please use: M. M. Rahman and A. M. Asiri, *RSC Adv.*, 2015, DOI: 10.1039/C5RA08224B.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

Journal Name

ARTICLE

CROYAL SOCIETY OF CHEMISTRY

Fabrication of highly sensitive ethanol sensor based on doped nanostructure materials using tiny chips

Mohammed M. Rahman, Abdullah M. Asiri

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Doped CuO-Fe₂O₃ nanocubes (NCs) are prepared by facile wet-chemical process using active reactant precursors with reducing agents at higher pH medium (pH>10). NCs are totally characterized in details using various methods, such as FTIR spectroscopy, X-ray photoelectron spectroscopy's (XPS), transmission electron microscope (TEM), dynamic light scattering (DLS), powder XRD, UV-vis. spectroscopy, FESEM coupled XEDS, and FE-SEM etc. The thin-layer of NCs onto tiny chips (surface area, ~0.02217 cm²) is deposited for fabricating a selective ethanol sensor in short response time in liquid-phase medium. The fabricated chemi-sensor is also exhibited higher sensitivity, large-dynamic concentration ranges, long-term stability, and improved electrochemical performances towards ethanol. The calibration plot is linear ($r^2 = 0.9937$) over the large ethanol concentration ranges (0.1 nM to 0.1 mM). The sensitivity and detection limit is ~7.258 μ Acm⁻²mM⁻¹ and ~0.08±0.02 mM (signal-to-noise ratio, at a SNR of 3) respectively. This novel effort is initiated a well-organize way of efficient nanomaterials-based-sensor development for toxic pollutants in environmental and health-care fields in large scales.

Key words: CuO-Fe₂O₃ nanocubes; Wet-chemical method, I-V technique; Selectivity; Sensitivity; Ethanol

Introduction

The significance of safety for lives as well as ecological plants has been studied with great attention in semiconductor sensors for toxic chemical detection by reliable methods [1]. Semiconductor nanostructure materials are very sensitive and efficient due to their smaller spherical-size and high active surface to volume ratio as contrasted to the conventional nanomaterials in micro- or nano-meter ranges. Nanostructure metal oxides have demonstrated an enormous deal of consideration due to their outstanding properties occurring of huge active surface area, high stability, quantum confinement consequence, and high porosity as well as permeability (mesoporous nature), which are reliant on the shape and size of the nanocrystal [2,3]. Nanomaterials have attracted a wide interest owing to their unique properties and potential application in chemical sensors fabrication [4,5]. Semiconductor material has been recognized as a promising host nanomaterial for doping transition metal at room temperature. It is revealed a stable morphology and composed of a number of disorder phases with geometricallycoordinated metal and oxide atoms, piled alternately along the axes [6]. Transition metals co-doped in semiconductor materials have concerned profound research effort for its exceptional and outstanding properties as well as versatile applications [7]. Recently, an extensive development has been made on the research leading of metal-oxides co-doped ZnO-based nanomaterials actuated by both fundamental sciences and potential advanced technologies [8]. The doped semiconductor nanostructures exhibit promising uses as fieldeffect transistors [9], UV photo-detectors [10], gas sensors [11], field emission electron sources [12], nanomaterials [13], nanoscale power

generators [14], and many other functional devices [15]. Transition metal doping semiconductor nanostructure is also an competent method to regulate the energy level surface states of ZnO, which can further progress by the changes of doping concentrations into semiconductor materials. The doped nanostructure materials have achieved substantial attention due to their catalysis, opto-electronics, bio-chemicals, magnetic, photo-catalysis, electronics, mechanical properties and their prospective applications in various fields. Doped nanostructure materials would be good candidates due to their higher & specific surface-area, higher-aspect-ratio & active surface area, lower-potentials, lower-resistances, higher-catalytic activity, and smart electrochemical as well as optical characteristics. Transition material has been recognized as an attractive guest-objects for doping into semiconductor materials (as host-object), which exhibits a stable and controlled morphology contained a significant amount of repeated crystal-phases coordinated with cationic and anionic parts [16]. Nanostructure materials have potential characteristics for their outstanding and excellent electro-catalytic properties towards chemical, physico-chemical, and chemical-sensor various applications [17]. In last decade, a widespread progress has been introduced by transition-metal doped semiconductor materials in advanced-sciences with sophisticated-technologies [18,19]. The lowdimensional nanomaterial displays exciting uses in the field significance electronics (i.e., diode, LED, transistors) [20], ultraviolate photo-detectors [21], chemi- or immuno-sensors (bio-assays) [22,23], magnetic-filed (i.e., para-magnetic) [24], doped-materials [25], energy-generator [26], and various bio-chips, and microdevices [27,28]. The doped nanomaterial is prepared by an effective thermal-method to control the surface-energy of metallic states that can promote/growth by the changing in doping concentration in semiconductor nanostructure materials. Undoped copper oxide nanomaterials have significant characteristic behaviours due to the potential applications in fabrication of nano-electronics, optoelectronics, bio-sensors, bio-chemical-chips, field-emission displays, and surface-active properties [29-31]. Guest (CuO) and host nanostructure materials (Fe₂O₃) were exhibited a major-function in improvement of accurate, higher-reproducibility, highly electrosensitive & reliable toxic chemical chemi-sensors using tiny

Center of Excellence for Advanced Material Research (CEAMR) and Chemistry department, Faculty of Science, King Abdulaziz University, Jeddah 21589, P.O. Box 80203, Saudi Arabia

^{*}Corresponding author (Prof. M.M. Rahman)

Center of Excellence for Advanced Material Research (CEAMR) and Chemistry department, Faculty of Science, King Abdulaziz University, Jeddah 21589, P.O. Box 80203, Saudi Arabia

Email: mmrahman@kau.edu.sa, Phone/Fax (b): +966-59-642-1830

COMMUNICATION

chips. Doped nanostructure materials have been also attracted the considerable attention for the researchers, generally to control growth monitoring owing to the increasing demand in healthcare and bio-medical fields [32-34]. Semiconductor nanomaterials are being comprehensively investigated owing to their exclusive surface behaviours communed by large-active surfaces, which can construct them perfect chemical recognizing elements as iono-sensor or chemo-sensors. Lately, development of chemi-sensors using doped nanostructure metal-oxides, active conducting polymers and nanocomposites are the key motive for the detection of determination carcinogenic elements and hazardous-chemicals [35-38]. Ethanol detection is important in different technological scientific areas i.e., ecological & environmental monitoring, clinicaldiagnosis, & various practical industrial applications [39-41]. It has been also increasing the attention for toxicity analysis in recent years, particularly hazardous and carcinogenic chemicals, owing to concerns about eco-environmental protection and health-care fields. Ethanol is a toxic analytes, which is generally applied in various research resolution and industrial laboratories for R&D purposes. Long-time revelations to ethanol can consequences in various infections, such as health-troubles and nerval-diseases, and probably cell damages. Therefore, the determination and recognition of ethanol in liquid phase is a significant task using doped CuO-Fe₂O₃ nanocubes coupled onto tiny chips. The doped CuO-Fe2O3 NC has interesting behaviours i.e., large and active-surface area, nontoxicity, chemical-instability, elemental activities, and good-conductivity, which offered good-electron communication characteristics that encouraged electron transfer to the target analytes. Typically, it is also demonstrated that transition metal doped semiconductor nanomaterials (such as meso-porous nanomaterials) can propose huge surface-area, higher-stability, nano-porosity, and consistency, which could develop the potential chemical sensors.

Ethanol is extremely toxic and usually serious to health and environment, it is immediately required the detection by using a reliable sensing method with prepared doped CuO-Fe₂O₃ NCs using tiny chips. The investigation of ethanol by doped CuO-Fe₂O₃ NCs films on chips is prepared and studied in details of the chemical sensors. The easy-coating method for the construction of CuO-Fe₂O₃ NCs thin-film within conductor binding-agents is developed in preparation of nanomaterial films onto smart chips. In this approach, doped CuO-Fe₂O₃ NCs fabricated films with conducting binders is utilized towards the target carcinogenic analytes using reliable Current-vs-Voltage (I-V) method. It is confirmed that the fabricated chemical sensor by I-V method is the unique and efficient approach for ultra-sensitive recognition of ethanol with CuO-Fe₂O₃ NCs onto tiny chips in short response-time.

Experimental

Materials and Methods:

Copper chloride, binders (butyl carbitol acetate and ethyl acetate), iron chloride, sodium hydroxide, and all other chemicals were in analytical grade and purchased from Sigma-Aldrich Company. They were used without further purification. The absorption maxima (λ_{max}) of CuO-Fe₂O₃ NCs was investigated by UV-vis spectrometer, where the band-gap energy (E_{bg}) calculated based on this study. A FT-IR spectrum of CuO-Fe₂O₃ NCs was investigated using FT-IR spectrophotometer, which used for the metals-oxygen bonds (Cu-O and Fe-O) confirmation. The XPS measurement of doped CuO-Fe₂O₃ NCs was measured with Thermo-Scientific K-Alpha spectrometer (Germany), for the calculation of binding energy (KeV) of Cu, Fe, and O. Morphology, particle-size, and arrangement of CuO-Fe₂O₃ NCs was recorded by using a FESEM instrument from JEOL (JSM-7600F, Japan). The crystallinity and crystal-patterns of CuO-Fe₂O₃ NCs was measured

by powder X-ray diffractometer at room conditions. Raman-shift was employed to determine the band-shift of CuO-Fe₂O₃ NCs by Raman spectrometer in different radiation sources. The size of CuO-Fe₂O₃ nanocubes was performed by transmission electron microscope (TEM; JEM-2100F, Japan). TEM sample was prepared as follows: the synthesized CuO-Fe2O3 NCs were dispersed into ethanol under ultrasonic vibration for 2 min, and then the TEM film is dipped in the solution and dried for investigation. The particle size was determined by DLS (photon correlation spectroscopy) with Zetasizer NanoZS (Zetatrac NPA 152-31A, USA) at 25.0 °C. The CuO-Fe₂O₃ nanocubes were dispersed with 3.0 mL distilled water in order to obtain accurate scattering intensity before the measurement. Equivalent amount of sample was dispersed into 3.0 ml distilled water at 25.0 °C before analysis. All the samples were analyzed in triplicate (n=3). Current-vs-voltage (I-V) method (two electrodes composed onto fabricated micro-chip) was measured for ethanol ions by using Keithley-Electrometer from USA.

Preparation and growth mechanism of CuO-Fe₂O₃NCs:

The term "wet chemical methods" emerged in contrast to conventional and solid-state synthesis methods of nanostructural materials widely used in preparation of doped or undoped nanomaterials. The term refers to a group of methods of powder and material production using liquid phase at one of the preliminary process stages. The wet chemical products of solids in liquid-phase synthesis are much smaller grains (crystallites) and, usually, lower temperature and shorter duration of phase formation. Here, Facile and low-temperature synthesis of CuO-Fe2O3 NCs was prepared by a wet-chemical process using active reactant precursors such as copper chloride (CuCl₂), iron chloride (FeCl₃), and sodium hydroxide (NaOH). In a usual reaction procedure, 0.1 M CuCl₂ was dissolved in 50.0 ml deionized (DI) water mixed with 50.0 ml FeCl₃ solution (0.1 M) under continuous stirring. pH of resultant solution was adjusted over 10.0 by the addition of NaOH and resulting mixture was shaken and stirred continuously for 10.0 minutes at room conditions. After stirring, the solution mixture was then put into conical flux and heat-up at 120.0 °C for 6.0 hours. The temperature of solution was controlled manually throughout the reaction process at 90.0 °C. After heating the reactant mixtures, the flux was kept for cooling at room conditions until reached the room temperature. The final CuO-Fe₂O₃ doped products were prepared, which was washed with DI water, ethanol, and acetone for several times subsequently and dried at room-temperature. The as-grown product was kept for air dry for few hours and then used for structural, elemental, morphological, and optical characterizations. The growth mechanism of the CuO-Fe₂O₃ nanocube materials can be explained on the basis of chemical reactions and nucleation, as well as growth of doped nanocrystals. The probable reaction mechanisms (i-iv) are presented here for obtaining the CuO-Fe₂O₃ nanomaterials in below.

$NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$	(i)
$\operatorname{CuCl}_2 + \operatorname{NaOH}_{(aq)} \rightarrow \operatorname{Cu}^{2+}_{(aq)} + \operatorname{OH}^+_{(aq)} + \operatorname{Na}^+_{(aq)} + 2\operatorname{Cl}^{(aq)}$	(ii)
$\operatorname{FeCl}_{3(s)} + 2\operatorname{NaOH}_{(aq)} \rightarrow \operatorname{Fe}^{3+}_{(aq)} + 2\operatorname{OH}^{-}_{(aq)} + 2\operatorname{Na}^{+}_{(aq)} + 3\operatorname{Cl}^{-}_{(aq)}$	(iii)
$\operatorname{Cu}^{2+}_{(aq)} + 2\operatorname{Fe}^{3+}_{(aq)} + 6\operatorname{NaOH}_{(aq)} \rightarrow \operatorname{CuO.Fe}_{2}\operatorname{O}_{3}_{(s)} \downarrow + 6\operatorname{Na}^{+} + 2\operatorname{H}_{2}\operatorname{O}$	(iv)

The reaction is forwarded slowly according to the equation (i) to equation (iii). During preparation, the pH value of the reaction medium plays an important role in the doped nano-material oxide formation. Over pH 10, when CuCl₂ is hydrolyzed with NaOH solution, copper hydroxide is formed instantly according to the equation (ii). During the whole synthesis route, NaOH operates a pH buffer to control the pH value of the solution and slow contribute of hydroxyl ions (OH⁻). When the concentrations of the Cu²⁺ and OH⁻ ions are achieved above in critical value, the precipitation of CuO nuclei begin to start. As there is high concentration of Fe³⁺ ions [according to the reactions (iii)] in the solution, the nucleation of Fe₂O₃ crystals become slower due to the lower activation energy barrier of heterogeneous nucleation. Hence, as the concentration of

Journal Name

Cu²⁺ existences, a number of larger CuO-Fe₂O₃ crystals with aggregated cube-like morphology form after the reactions [equation (iv)]. The shape of as-prepared CuO-Fe₂O₃ NCs is approximately reliable with the growth pattern of copper oxide doped iron oxides nanocrystals [42,43]. Then the solution was washed thoroughly with acetone, ethanol, and water successively and kept for drying at room condition. In NCs growth technique, initially CuO and Fe₂O₃ nucleus growth takes place by self-aggregation, which then reaggregates and produced CuO-Fe₂O₃ nanocrystal according to the Ostwald ripening method. Nanostructure material crystallizes and reaggregates with each other through Vander-Waals forces and forms doped CuO-Fe₂O₃ nanocubes morphology, which is presented in Scheme 1. Finally, the as-grown CuO-Fe₂O₃ NCs were fully characterized in detail of their morphological, structural, elemental, and optical properties, and applied for detection of ethanol chemical sensor for the first time. The phases of the dried in air and doped powder materials were examined using XRD. The morphology and cross section of the powders were observed with SEM equipped with XEDS. The evaluation of band-gap energy and metal-oxygen bond formation (Cu-O and Fe-O) was examined by using UV/vis. and FTIR Spectroscopy.



Scheme 1: Probable growth mechanism of doped CuO-Fe₂O₃ NCs at low-temperature by wet-chemical process

Construction of *µ*-Chips using photolithography method:

Electrochemical u-chips were fabricated by conventional photolithographic technique, where electrodes and passivation layers are developed on silicon wafer followed by dicing and packaging [44,45]. Nitrogen-doped silicon wafers are prepared and overflowed by extra-pure water. In this step, all contaminations on the surface and native SiO₂ layer are removed perfectly. At first, the wet oxidation is employed and then dry oxidation is executed, where, wafers are annealed in the nitrogen environment. Aluminum is sputtered with aluminum-1% Si target. Then the photolithograph processes are applied. Resist coating, baking, exposure, and development are employed by Kanto chemicals, and then it is rinsed thoroughly by ionic water. Aluminum is etched by etching solution and resistance layer is removed perfectly by plasma etching instrument. Then silicon wafers are cleaned by acetone, methanol, and finally by plasma simultaneously. Silicon nitride (SiN) layer is deposited by chemical vapor deposition and then pad electrode surfaces are etched by reactive ion etching. Finally residual resist layer is removed by plasma etching. After photolithographic process, platinum is sputtered by SP150-HTS. Then it is patterned by lift-off method, in which wafers are immersed into the remover, and then washed with isopropyl alcohol. Photolithographic process is again investigated, where titanium is sputtered as a binding layer, and then gold is evaporated by deposition method. Finally, gold layer is patterned by lift-off method. Parylene passivation layer is formed for the protection of the µ-chip from water. Photolithographic process is performed again for pad protection. Then parylene-dimer is evaporated by deposition apparatus. Photolithography process is done again for patterning. Parylene layer is patterned by etching. Finally, un-necessary resists are removed by acetone and then wafer is cleaned by isopropyl alcohol (IPA). Resist is coated on a whole surface of the silicon wafer for protection during dicing process is executed. Silicon wafer is diced into pieces by dicing apparatus and stored into the desiccators, when not in use. Resist on µ-chip surface is removed by acetone and cleaned with isopropyl alcohol (IPA). The opposite side of the chip is roughed by a sandpaper sheet for better adhesion and electrical stability. The µ-chip is bonded with die and packaged by silver paste. It is dried in a drying oven. Pads on chip are connected to the package through gold wire with bonding machine. Finally, silicon-based adhesive is put on the periphery of the chip to protect pads and gold wire from sample solution. Adhesive is dried for 24 hours at room temperature. The semiconductor smart µ-chips were fabricated on silicon wafer. Aluminum was sputtered to fabricate as wiring and bonding pads. Pt-Ti-TiN was sputtered on thermal oxide of silicon and patterned by photolithography to fabricate counter electrode (CE). Ti-TiN layers were used for strong adhesion. Au-Ti were sputtered and lithographed, which made circular working electrode (WE) with a diameter of 1.68 mm in the centre of the µ-chip. After electrodes fabrication, palylene layer was fabricated by evaporation method as a passivation layer. The wafer was diced to 5.0 mm square µ-chips. This µ-chip was bonded to a package by silver paste. Aluminum pads were connected to the package by gold wire. Finally, adhesive (Araldite, Hantsman, Japan) was put on the periphery of the chip, which prevents target solution from contacting pads.

Fabrication of doped CuO-Fe₂O₃NCs/µ-chip assembly:

Construction of µ-chip by conventional photolithography method has been already explained in previous section. Here, a tiny µ-chip is fabricated by as-grown CuO-Fe₂O₃ NCs with conducting coating agents (ethyl cellulose powder, EC & butyl carbitol acetate solvent, BCA). After that, CuO-Fe₂O₃ NCs fabricated µ-chip assembly is moved into heating-oven at 65.0 °C intended for 2 hours to make complete drying and uniform-film formation. Fabricated NCs/micro-chip and Pt micro-line (onto micro-chip) are worked a working and counter electrode respectively. As purchased ethanol is used to make target solution to formulate different concentration (1.0 $nM \sim 1.0$ mM) in 0.1M phosphate buffer solution with deionised system (0.1M PBS is made in deionised water) and use as a selective target toxic-analyte. 15.0 µL of target analyte solution (in phosphate buffer solution, 0.1M PBS) is dropped onto the NCs/chip during investigation. The Current/Voltage (I-V, slope of calibration-curve) is utilized to calculate of target NCs sensitivity. Limit of detection (LOD) is manipulated from the 3N/S ratio vs. sensitivity (~3×Noise vs. Sens.) in linear portion of total concentration range of calibration-plot. Current-Voltage technique is evaluated as a potential-sources by electrometer in two (working-counter) electrodes assembly. CuO-Fe₂O₃ NCs is made and exhibited for the detection of target ethanol in solution-phase system.

Results and discussion

Evaluation of Morphological and Elemental property:

FESEM images of as-grown CuO-Fe₂O₃ NCs are presented in Figure 1(a-c). It exhibits the images of the NCs with nano-dimensional sizes of as-grown CuO-Fe₂O₃ NCs. The dimension of NC is calculated as ~0.11 μ m. It is clearly exposed from the FESEM images that the facile synthesized CuO-Fe₂O₃ NCs is nanostructures in cubic-shape, which grown in very high-density and possessing almost uniform cubes. When the size of doped material decreases into nanometer-sized scale, the surface area is increased significantly, this improved the energy of the system and made re-distribution of Cu and Fe ions possible. The nanometer-sized cube could have tightly packed into the lattice, which is an agreement with the publish reports [46,47].

Journal Name



COMMUNICATION

Figure 1. (a-c) FESEM images and (d) elemental analysis of asgrown CuO-Fe₂O₃ NCs at room conditions.

The X-ray electron dispersive spectroscopy (XEDS) analysis of these CuO-Fe₂O₃ NCs are indicated the presence of copper (Cu), iron (Fe), and oxygen (O) composition in the pure as-grown nanostructure material, which is presented in Figure 1d. It is clearly displayed that the prepared nanomaterials contained only Cu, Fe, and O elements with the 4.99, 90.75, 4.26 wt% respectively, which is presented in Figure 4d (inset). No other peak related with any impurity has been detected in the FESEM coupled XEDS, which confirms that the nanocubes are composed only with Cu, Fe, and O.

Evaluation of Optical and Structural property:

The as-grown CuO-Fe₂O₃ NCs is also investigated in terms of the atomic and molecular vibrations. To predict the functional-recognition, FTIR spectra fundamentally in the region of 400~4000 cm⁻¹ is investigated at room conditions. Figure 2a displays the FTIR spectrum of NCs, which represents band at 532 cm⁻¹. These observed broad vibration bands (at 532 cm⁻¹) could be assigned as metal-oxygen (Cu-O and Fe-O mode) stretching vibrations, which demonstrated the configuration of CuO-Fe₂O₃ NCs materials.

The optical property of the as-grown CuO-Fe₂O₃ NCs is one of the significant characteristics for the assessment of its photocatalytic activity. UV/visible absorption are a technique in which the outer electrons of atoms or molecules absorb radiant energy and undergo transitions to high energy levels. In this phenomenon, the spectrum obtained due to optical absorption can be analyzed to acquire the energy band-gap of the doped metal oxides. For UV/visible spectroscopy, the absorption spectrum of CuO-Fe₂O₃ NCs solution is measured as a function of wavelength, which is presented in Figure 2b. It presents a broad absorption band around 648.0 nm in the visible-range between 200.0 to 800.0 nm wavelengths indicating the formation of CuO-Fe₂O₃ NCs. Band-gap energy (E_{bg}) is calculated on the basis of the maximum absorption band of CuO-Fe₂O₃ NCs and found to be ~1.9135 eV, according to following equation (v). 1040

$$E_{\rm bg} = \frac{1240}{\lambda} (\rm eV)$$
 (v)

Where E_{bg} is the band-gap energy and λ_{max} is the wavelength (648.0 nm) of the CuO-Fe₂O₃ NCs. No extra peak associated with impurities and structural defects are observed in the spectra, which proved that the synthesized microstructure controlled crystallinity of as-grown CuO-Fe₂O₃ NCs [48].



Figure 2. (a) FT-IR, (b) UV/visible, and (c) X-ray powder diffraction of as-grown CuO-Fe $_2O_3$ NCs at room conditions

Crystallinity and crystal phase of as-prepared CuO-Fe₂O₃ NCs were investigated. Powder X-ray diffraction patterns of doped nanocubes are represented in Figure 2c. The CuO-Fe₂O₃ NCs sample were investigated and exhibited as face-centered cubic shapes. Figure 2c reveals characteristic crystallinity of the CuO-Fe₂O₃ NCs and their crystalline arrangement, which is investigated by powder X-ray crystallography. The peaks were found to match with CuO phase (Tenorite) having face-centered monoclinic geometry [Joint Committee on Powder Diffraction Standards, JCPDS#073-6234]. The major phases are indicated the characteristic peaks (Hash symbol, #) with indices for 2θ values at 35.5(110), 38.2(111), 53.1(020), 57.1(202), 67.8(113), 74.1(221), and 76.1(-222) degrees. The monoclinic lattice parameters are a=4.662, b=3.417, c=5.118, β =99.48, Point group: C2/c, and Radiation: CuKa1 (λ = 1.5406). These indicate that there is significant amount of crystalline CuO present in semiconductor nanomaterials. The reflection peak is found to match with iron oxide phase (Hematite, α -Fe₂O₃) having Rhombohedral geometry [JCPDS#080-2377]. In Fig 2c, the phases (with indices) are represented to the major characteristic peaks (star symbol, *) for as-grown crystalline iron oxide at 20 values of 24.1(012), 32.5(104), 39.4(006), 40.7(113), 43.4(202), 49.3(024), 54.1(116), 57.6(018), 62.3(214), 64.1(300), 69.2(208), 71.6(1010), and 75.5(220) degrees. The lattice parameters are a=5.03521; c=13.7508, Z=6, point group: R-3c(167), and radiation: CuK_a1 (λ = 1.5406). These indicate that there is considerable amount of crystalline iron oxide present in doped nanostructure materials. These confirmed that there is major number and amount of crystalline doped CuO-Fe₂O₃ NCs present in NCs [49]. Crystallite size was calculated by Debye-Scherrer's formula given by equation (vi)

Journal Name

Where D is the crystal size; λ is the wavelength of the X-ray radiation (λ =0.15406 nm) for CuK α ; K is usually taken as 0.9; and β is the line width at half-maximum height (FWHM) [50]. The average cross sectional diameter of CuO-Fe₂O₃ NCs is close to ~0.11 μ m.

Evaluation of Binding energy:

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic method that determines the chemical-states of the elements that present within doped materials. XPS spectra are acquired by irradiating on a nanomaterial with a beam of Xrays, while simultaneously determining the kinetic energy and number of electrons that get-away from the top one to ten nm of the material being analyzed. Here, XPS measurements were measured for CuO-Fe₂O₃ NCs semiconductor nanomaterials to investigate the chemical states of Fe₂O₃ and CuO. The XPS spectra of O1s, Fe2p, and Cu2p are presented in Fig. 3a. The O1s spectrum shows a main peak at 531.3 eV in Fig. 3b. The peak at 531.3 eV is assigned to lattice oxygen may be indicated to oxygen (ie, O_2^{-}) presence in the CuO-Fe₂O₃ NCs [51]. XPS was also used to resolve the chemical state of the doped Fe₂O₃ nanomaterial and their depth. Here, the spin orbit peaks of the $Fe2p_{(3/2)}$ and $Fe2p_{(1/2)}$ binding energy for all the samples appeared at around 713.2 eV and 724.1 eV respectively, which is in good agreement with the reference data for Fe_2O_3 [52]. In Figure 3d, the spin orbit peaks of the $Cu2p_{(3/2)}$ and $Cu2p_{(1/2)}$ binding energy for all the samples appeared at around 932.5 eV and 953.1 eV respectively, which is in good agreement with the reference data for CuO [53]. XPS compositional analyses evidenced the co-existence of the two single-phase of CuO and Fe₂O₃ nanomaterials. Therefore, it is concluded that the wet-chemically prepared doped CuO-Fe₂O₃ NC materials have NCs phase contained two materials. Also, this conclusion is reliable with the XRD data noticeably.



Figure 3. XPS of (a) doped CuO-Fe₂O₃ NCs, (b) O1s level, (b) Fe2p level, and (d) Cu2p level acquired with MgKα1 radiation.

Particle size analysis by TEM and DLS:

Further structural characterization of CuO-Fe₂O₃ materials was investigated and found in cube-shaped morphology by TEM analysis. As shown in Figure 4a, the TEM images of CuO-Fe₂O₃ nanomaterials had a cubic-shape with an average diameter of 0.11 μ m. The TEM observation shows the exact

DOI: 10.1039/C5RA08224B

COMMUNICATION

full consistency in terms of shape and dimension. The size distribution of CuO-Fe₂O₃ nanocubes was measured by DLS at 25.0 °C. Before investigation, NCs were well-dispersed into 3.0 mL distilled water in order to obtain the accurate scattering intensity. The dispersed solution of NCs were analyzed in triplicate (n=3). The size distribution was measured by DLS showed approximately normal distribution (Fig 4b). The hydrodynamic sizes of CuO-Fe₂O₃ NCs were 0.1274 µm in the 0.1001~0.1558 µm ranges. SEM, TEM, and XRD could determine the morphous and original diameter of the particles. DLS mainly reflects the hydrodynamic size in dispersion media. The hydrodynamic size of CuO-Fe₂O₃ NCs was measured in distilled water as stock media. The observation showed that owing to the Van der Waals force and hydrophobic interaction with surrounding media the hydrodynamic size is generally larger (~0.1274 µm) than original (~0.11 µm). The zeta potential (particle charge) was also measured by determining the nanocubes electrophoretic mobility using the same instrument Zetasizer NanoZS at 25.0 °C. The values were calculated using Helmholtz-Smoluchowski equation. The CuO-Fe₂O₃ NCs were diluted 10 times with filtered deionized water to obtain ideal concentration range for optimal measurement. (Viscosity values of the dispersion media were made less than equivalent to water [1.0 mPas] at 25.0 °C). Here, it was also measured the zeta potential, mobility, conductivity, charge, and dielectric constant as 5.7 mM, 0.44 u/s/V/cm, 415.0 uS/cm, 0.056 fC, and 79 respectively.



Figure 4. Particle size analysis of $CuO-Fe_2O_3$ NCs by (a) TEM and (b) DLS.

Application: Chemical sensor with NCs/µ-Chips assembly

The potential application of CuO-Fe₂O₃ NCs assembled onto μ -chip as chemical sensors (especially ethanol analyte) has been monitored for detecting hazardous chemicals, which are not environmental affable. Improvement of doping of these

CuO-Fe₂O₃ NCs on μ -chip as chemical sensors is in the initial stage and no other reports are available. The NCs sensors have advantages such as stability in air, non-toxicity, chemical inertness, electrochemical activity, simplicity to assemble or fabrication, and bio-safe characteristics. As in the case of toxic ethanol sensors, the phenomenon of reason is that the current response in I-V method of CuO-Fe2O3 NCs considerably changes when aqueous ethanol are adsorbed. The calcined CuO-Fe₂O₃ NCs were applied for modification of chemical sensor, where ethanol was measured as target analyte. The magnified construction view of internal µ-chip center (sensing area) is presented in the Figure 5(a-c). Figure 5(a-c), platinum line (PtE) and gold-central-circle onto micro-chip is employed as CE and WE electrodes (potential sources on 2-electrodes system) respectively. Figure 5d, the probable detection mechanism of NCs/chips is presented with fabricated ethanolsensors using I-V methods. Figure 4e, expected experimental I-V responses with NCs/chips by reliable conducting coating agents are developed. The fabricated-surface of CuO-Fe₂O₃ NCs sensor was made with conducting binders on the µ-chip surface, which is presented in the Figure 5(c-d). The fabricated µ-chip electrode was placed into the oven at low temperature (60.0 °C) for two hours to make it dry, stable, and uniform the surface totally. I-V signals of chemical sensor are anticipated having NCs doped thin film as a function of current versus potential for hazardous ethanol. The real electrical responses of target ethanol are investigated by simple and reliable I-V technique using CuO-Fe₂O₃ NCs fabricated µ-chip, which is presented in Figure 4e. The time holding of electrometer was set for 1.0 sec. A significant amplification in the current response with applied potential is noticeably confirmed. The simple, reliable, possible reaction mechanism is generalized in Figure 4d in presence of ethanol on NCs sensor surfaces by I-V technique. The ethanol is converted to water and carbon dioxide in presence of doped nanomaterials by releasing electrons (-6e) to the reaction system (conduction band, C.B.), which improved and enhanced the current responses against potential during the I-V measurement at room conditions.



Figure 5. Schematic diagram of (a) real camera-view from top of bared chips, (b) expected magnified-view of $CuO-Fe_2O_3$ NCs fabrication onto chips, (c) expected magnified view of $CuO-Fe_2O_3$ NCs /chips assembly with conducting coating binders onto sensing-area of tiny chips, (d) probable reaction mechanism of target-ethanol ions in presence of doped NCs, and (e) expected responses of I-V methods in the experimental results.

Page 6 of 10

uncoated NCs/µ-chip surfaces, which indicates the surface is slightly inhibited with CuO-Fe₂O₃ NCs during the measurement of I-V curve. The current changes for the without target (dark-dotted) and with target analyte (blue-dotted) injecting of towards target ethanol (~15.0 μ L) ethanol (~0.1 μ M) onto with CuO-Fe₂O₃ NCs modified u-chips is showed in Figure 6b. A significant current enhancement is exhibited with the CuO-Fe2O3 NCs modified µ-chips compared with uncoated µ-chips due to the presence of nanostructures, which has higher-specific surface area, larger-surface coverage, excellent absorption and adsorption capability into the porous NCs surface towards the target ethanol. A control experiment is performed for the comparison of current response in various compositions of NCs, such as CuO NCs, Fe2O3 NCs, and CuO-Fe2O3 NCs embedded µchips. Here, I-V responses of undoped CuO NC coating u-chip, undoped Fe₂O₃ coating NC u-chip and doped CuO-Fe₂O₃ NC coating u-chip are measured by deducting the background current (0.001mM analyte). In this control experiment, the doped CuO-Fe₂O₃ NC coating u-chip exhibits the highest current response compared to un-doped CuO or Fe₂O₃ NCs, which is presented in Electronic Supplemental section (S1). This significant change of surface current is monitored in every injection of the target ethanol onto the CuO-Fe₂O₃ NCs modified µ-chips by electrometer. I-V responses with CuO-Fe₂O₃ NCs modified µ-chip surface are investigated from the various concentrations (0.1 nM to 1.0 mM) of ethanol, which is showed in Figure 6c. It shows the current changes of fabricated µ-chip films as a function of ethanol concentration in room condition. It was also found that at low to high concentration of target analyte, the current responses were enhanced regularly. The potential current changes at lower to higher potential range (potential, +0.1 V to +1.3 V) based on various analyte concentration are observed, which is clearly presented in Figure 5c. A large range of analyte concentration is measured the probable analytical limit, which is calculated in 0.1 nM to 0.1mM. The calibration (at +0.5V) and magnified-calibration curves are plotted from the various ethanol concentrations, which are presented in the Figure 6d. The sensitivity is estimated from the calibration curve, which is close to $\sim 7.258 \ \mu \text{Acm}^{-2}\text{mM}^{-1}$. The linear dynamic range of this sensor displays from 0.1nM to 0.1mM (linearity, R= 0.9937) and the detection limit was considered as 0.11±0.02 nM [3×noise (N)/slope(S)]. 1e-4 1e-4 b 9e-5 а 9e-5

In Figure 6a shows the current responses of un-coated

(gray-dotted) and coated (dark-dotted) µ-chip working electrodes

with CuO-Fe₂O₃ NCs in absence of target ethanol. With NCs

fabricating surface, the current signal is slightly reduced compared to



Journal Name

Fig. 6. I-V responses of (a) uncoated and coated µ-chip with CuO-Fe₂O₃ NCs; (b) in absence and presence with 0.1µM ethanol with CuO-Fe₂O₃ NCs/chip; (c) concentration variations (0.1 nM to 0.1mM) of analyte; and (d) calibration plot of with CuO-Fe₂O₃ NCs fabricated on µ-chip surfaces. Potential was chosen in +0.1 to +1.5 V ranges. Error limit of I-V measurement was \pm 0.01. There are three trial has been done in same experimental concentration at similar condition

The resistance value of doped semiconductor materials are decreased (current increased) with increasing surrounding active oxygen, which are the fundamental characteristics of nanomaterials [54]. Actually, oxygen adsorption demonstrates a significant responsibility in the electrical properties of the CuO-Fe₂O₃ NCs onto tiny µ-chip. The oxygen ion adsorption is removed the conduction electrons and increased the resistance of CuO-Fe₂O₃ NCs. Unstable oxygen species (i.e., O₂⁻ & O⁻) are adsorbed on the doped NC surface at room temperature, and the quantity of such chemisorbed oxygen species is directly depended on morphological and structural properties. At room condition, O2- is chemisorbed, while on nanocubes morphology, O_2^- and O^- are chemisorbed significantly. For this reason, the active O_2^- is disappeared quickly [55]. Here, ethanol sensing mechanism on CuO-Fe₂O₃ NCs/µ-chip sensor is executed due to the presence of semiconductors oxides. The oxidation or reduction of the semiconductor NCs is held, according to the dissolved O₂ in bulk-solution or surface-air of the neighbouring atmosphere according to the following equations (viiix).

Published on 09 July 2015. Downloaded by Yale University Library on 11/07/2015 12:32:24

 $O_{2(diss)}$ (CuO-Fe₂O₃ NCs/ μ -chip) $\rightarrow O_{2(ads)}$ (vii) e^{-} (CuO-Fe₂O₃ NCs/ μ -chip) + $O_2 \rightarrow O_2^{-}$ (viii) e^{-} (CuO-Fe₂O₃ NCs / μ -chip) + $O_2^{-} \rightarrow 2O^{-}$ (ix)

These reactions are held in bulk-system or air/liquid interface or adjacent atmosphere due to the small carrier concentration which enhanced the resistances. The ethanol sensitivity could be attributed to the high oxygen deficiency on CuO- $Fe_2O_3 NCs/\mu$ -chip (eg. MO_x) and higher density conducts to increase oxygen adsorption. Larger the quantity of oxygen adsorbed on the fabricated sensor surface, larger would be the oxidizing potential as well as faster would be the oxidation of ethanol. The reactivity of ethanol would have been very large as compared to other fabricated material surfaces surface under identical condition [56,57]. When ethanol reacts with the adsorbed oxygen on the exterior/interior of the CuO-Fe₂O₃ NCs/µ-chip layer, it oxidized to carbon dioxide and water by releasing free electrons (6e) in the conduction band, which is expressed through the following reactions (x).

$CH_3CH_2OH_{(ads)} + 6O_{(ads)} \rightarrow 2CO_2 + 3H_2O + 6e(C.B.)(x)$

In the reaction system, these reactions referred to oxidation of the reducing carriers. This method is enhanced the carrier concentration and consequently decreased the resistance on adjacent reducing analytes. The elimination of ionosorbed oxygen amplified the electron concentration onto CuO-Fe₂O₃ NCs/µ-chip and hence the surface conductance is increased in the film [58]. The reducing analyte (ethanol) gives electrons to CuO-Fe2O3 NCs/µ-chip surface. Consequently, resistance is reduced, and hence the conductance is increased. This is the cause why the analyte response (current) amplifies with increasing potential. Thus produced electrons contribute to rapid increase in conductance of the thick CuO-Fe₂O₃ NCs/µ-chip film. The CuO-Fe2O3 NCs unusual regions dispersed on the surface would progress the capability of nanomaterial to absorb more oxygen species giving high resistance in air ambient, which is presented in Figure 7.



Figure 7. Mechanism of ethanol detection with active CuO-Fe₂O₃ NCs/u-chip is presented at ambient conditions.

The sensor response time was ~10.0 sec for the CuO-Fe₂O₃ NCs coated µ-chip sensor to achieve saturated steady state current in I-V plots. The major sensitivity of u-chip sensor can be attributed to the good absorption (porous surfaces NCs fabricated with binders), adsorption ability, high-catalytic activity, and good bio-compatibility of the CuO-Fe2O3 NCs/µ-chip. The expected sensitivity of the NC fabricated sensor is relatively better than previously reported ethanol sensors based on other composites or materials modified electrodes [59]. Due to perceptive surface area, here the doped nano-materials developed a beneficial microenvironment for the toxic chemical detection (by adsorption) and recognition with excellent quantity. The prominent sensitivity of CuO-Fe₂O₃ NCs affords high electron communication features which improved the direct electron communication between the active sites of nano-sheets composed microstructures and µ-chips. The modified thin CuO-Fe₂O₃ NCs/µ-chip sensor film had a better reliability as well as stability in ambient conditions. CuO-Fe₂O₃ NCs/µ-chip exhibits several approaching in providing ethanol chemical based sensors, and encouraging improvement has been accomplished in the research section.

It was also investigated the sensing selectivity performances (interferences) with other chemicals like acetone, dichloromethane, methanol, chloroform, ethanol, 4-nitrophenol, methanol, propanol, and butanol (Figure 8a). Ethanol exhibited the maximum current response by I-V system using CuO-Fe₂O₃ NCs fabricated micro-chip electrodes. Therefore, it was specific towards ethanol compared to all other chemicals. Current responses (at +0.5V) of all inferring analytes converted into percentile (% responses) by deducting the blank current (reading only in PBS system) are calculated and presented in Figure 8b. By deducting the current value of blank solution, it was found the current value less than 10% for all chemicals (acetone 4.1%; dichloromethane 3.7%; chloroform 4.3%; 4-nitrophenol 2.7%; methanol 3.5%, propyl alcohol 8.6%, butanol 7.4%, and iso-propyl alcohol 5.4%, and blank 0%) compared to target ethanol (90.0%). Therefore, it is clearly demonstrated the sensor is most selective towards ethanol compared with other chemicals.



Figure 8. I-V responses of CuO-Fe₂O₃ NCs coated μ -chip are presented for ethanol sensors (a) selectivity, (b) Current responses of analytes at +0.5V (Presented in percentage), (c) control experiment, and (d) reproducibility study. Ethanol and other chemicals concentration are taken as 0.1µM for selectivity study. Delay time: 1.0s. Potential range: 0 to +1.5V.

A control experiment was performed with the various nanomaterial fabricated microchip using individually Fe₂O₃ CuO, and CuO-Fe₂O₃ NCs at 0.001mM analytes concentration by I-V method (Figure 8c). A significant enhancement of current responses was observed by CuO-Fe₂O₃ NCs/chip compared to undoped Fe₂O₃ and CuO individually. To investigate the reproducibly and storage stabilities, I-V response for CuO-Fe₂O₃ NCs coated µ-chip sensor was examined (up to 2 weeks). After each experiment, the fabricated CuO-Fe₂O₃ NCs/µ-chip substrate was washed gently and observed that the current response was not significantly decreased (Figure 8d). The sensitivity was retained almost same of initial sensitivity up to week (1st to 2nd week), after that the response of the fabricated electrode gradually decreased. A series of six successive measurements of 0.1µM ethanol in solution yielded a good reproducible signal at CuO-Fe₂O₃ NCs/µ-chip sensor in different conditions with a relative standard deviation (RSD) of 3.1%. The sensor-to-sensor and run-to-run repeatability for 0.1µM ethanol detection were found to be 1.8% using CuO-Fe₂O₃ NCs/µ-chip. To investigate the long-term storage stabilities, the response for the NCs sensor was determined with the respect to the storing time. The longterm storing stability of the CuO-Fe2O3 NCs/µ-chip sensor was investigated significantly at room conditions. The sensitivity retained 92% of initial sensitivity for several days. The above results clearly suggested that the fabricated sensor can be used for several weeks without any significant loss in sensitivity. The dynamic response (0.1 nM to 0.1 mM) of the sensor was investigated from the practical concentration variation curve. The sensor response time is mentioned and investigated using this sensor system at room conditions. In Table 1, it is compared the performances for ethanol chemical detection based various modified electrode materials [60-69]. It exhibits the higher sensitivity using CuO-Fe₂O₃ NCs/chip compared other nanomaterials fabricated electrodes with the similar target analytes.

 Table 1: Comparison the performances for ethanol detection based on various nanomaterials fabricated sensor.

		Range . LDR			LOD	e	
Ni/Pt/Ti	Pote ntial ampe rome try		$3.08 \ \mu Am \ M^{-1} \ cm^{-2}$				[60]
Ni-doped SnO ₂ nanostru cture	I-V	1.0nM ~1.0m M	$2.3148 \\ \mu A \\ cm^{-2}m \\ M^{-1}$	0.84 40	0.6 nM	10.0 s	[61]
Pd– Ni/SiNW s electrode	Pote ntial ampe rome try		$\begin{array}{c} 0.76\\ \text{mAm}\\ \text{M}^{-1}\text{cm}\\ ^{-2}\end{array}$	0.99 70	10.0 μM		[62]
ZnO- CeO ₂ Nanopart icles	I-V	1.7m M~1.7 M	2.1949 μA cm-2 mM-1	0.94 63	0.6±0.0 5 mM	10.0 s	[63]
RuO- modified Ni electrode	Cycli c volta mme try	100~1 000 ppm	4.92 μApp m ⁻¹ cm ⁻²			13.0 s	[64]
CeO2 nanopart icles	I-V	0.17m M~0.1 7M	0.92 µAcm ⁻² mM ⁻ 1	0.74 58	0.124± 0.010 mM	10.0 s	[65]
Al-doped ZnO nanomat erial	I-V meth od	Up to 3000p pm	1000 ppm ethano l			~8.0 s	[66]
CuO nanoshee ts	I-V	up to 1.7M	~ 0.972 2 $\mu A cm^{-1}$	0.78 06	0.143 mM	10.0 s	[67]
Sm- Doped Co ₃ O ₄ Nanoker nels	I-V	1.0nM ~10.0 mM	2.1991 ±0.10 μAcm ⁻ ² mM ⁻¹	0.90 65	0.63±0. 02 nM	10.0 s	[68]
Sb ₂ O ₃ - ZnO MFs	I-V	0.17m M~0.8 5M	5.845 uA cm ⁻ ² mM ⁻¹	0.99 89	0.11±0. 02 mM	10.0 s	[69]
CuO- Fe ₂ O ₃ NCs	I-V	0.1nM ~0.1m M	7.258 uA cm ⁻ ² mM ⁻¹	0.99 37	0.087 nM	10.0 s	This wor k

Conclusions

CuO-Fe₂O₃ NCs were synthesized by easy, simple, efficient, reliable, and economical approaches using active reducing agents. The optical, elemental, structural, and morphological properties were investigated by FTIR, XRD, XEDS, XPS, FESEM, TEM, DLS, and UV-visible techniques. CuO-Fe₂O₃ NCs/µ-chip was prepared by simple fabrication technique and displayed higher sensitivity for chemical sensing. NCs/µ-chips were efficiently prepared for sensitive and selective ethanol sensor based on doped CuO-Fe₂O₃ NCs embedded chips with conducting coating binders. The analytical performances of fabricated ethanol NCs sensors were excellent in terms of sensitivity, detection limit, linear dynamic ranges, and in short response time. CuO-Fe2O3 NCs/µ-chips were exhibited higher-sensitivity (~7.258 uAcm⁻²mM⁻¹) and lowerdetection limit (~0.087±0.02 nM) with good linearity in short response time, which efficiently utilized as chemical sensor for ethanol onto tiny µ-chips. This novel approach is introduced a well-

Please do not adjust margins RSC Advances

organized route of efficient chemical sensor development for environmental pollutants and health-care fields in broad scale.

Acknowledgements

This work was supported by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under grant no. (130-520-D1435). The authors, therefore, gratefully acknowledge the DSR technical and financial support.

References

- 1.N.M. Shaalan, T. Yamazaki, T. Kikuta, Sens. Actuator B 153(2011)11–16.
- D.J. Díaz. Book Review of Nanostructure Materials in Electrochemistry. J. Am. Chem. Soc., 130(2008)10033– 10034.
- Sinkó, N. Hüsing, G. Goerigk, H. Peterlik. Nanostructure of Gel-Derived Aluminosilicate Materials. Langmuir, 24(2008)949–956.
- 4.X. Wang, J. Song, J. Liu, Z.L. Wang, Science, 316(2007)102.
- K. Keren, R.S. Berman, E. Buchstab, U. Sivan, E. Braun, Science, 302(2003)1380.
- Chakraborti, J. Narayan, J.T. Prater, Appl. Phys. Lett. 90(2007)062504.
- 7.Hara, K.; Horiguchi, T.; Kinoshita, T.; Sayama, K.; Sugihara, H.; Arakawa, H. Sol. Energy Mater. Sol. Cells 64(2000)115.
- 8.Wang, Z. L. J. Phys.: Conden. Matt. 16(2004)R829.
- 9.Ng, H. T.; Han, J.; Yamada, T.; Nguyen, P.; Chen, Y. P.; Meyyappan, M. Nano Lett.4(2004)1247.
- 10.Soci, C.; Zhang, A.; Xiang, B.; Dayeh, S. A.; Aplin, D. P. R.; Park, J.; Bao, X. Y.; Lo, Y. H.; Wang, D. Nano Lett. 7(2007)1003.
- 11.Li, Q. H.; Liang, Y. X.; Wan, Q.; Wang, T. H. Appl. Phys. Lett. 85(2004)6389.
- 12.Lee, C. J.; Lee, T. J.; Lyu, S. C.; Zhang, Y.; Ruh, H.; Lee, H. J. Appl. Phys. Lett. 81(2002)3648.
- 13.Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. Science 292(2001)1897.
- 14.Wang, X. D.; Song, J. H.; Liu, J.; Wang, Z. L. Science 102(2007)102.
- 15.Zhang, Z.; Yi, J. B.; Ding, J.; Wong, L. M.; Seng, H. L.; Wang, S. J.; Tao, J. G.; Li, G. P.; Xing, G. Z.; Sum, T. C.; Huan, C. H. A.; Wu. T. J. Phys. Chem. C, 112(2008)9579.
- 16.Z.H. Cai, C.R. Martin. J. Am. Chem. Soc. 111(1989)4138.
- 17.H.T. Ng, J. Han, T. Yamada, P. Nguyen, Y.P. Chen, M. Meyyappan, Nano Lett. 4(2004)1247.
- 18.C. Soci, A. Zhang, B. Xiang, S.A. Dayeh, D.P.R. Aplin, Y.H. Lo, D. Wang, Nano Lett. 7(2007)1003,
- 19.M.M. Rahman, A. Jamal, S.B. Khan, M. Faisal. J. Phys. Chem. C. 115(2011)9503.
- 20.X.D. Wang, J.H. Song, J. Liu, Z.L. Wang, Science 316(2007)102.
- 21.M.M. Rahman, M.J.A. Shiddiky, M.A. Rahman, Y.B. Shim. Anal. Biochem. 384(2009)159.
- 22.C.C. Wang, Y.C. Weng, T.C. Chou. Sens. Actuator. B 122(2007)591.
- M.M. Rahman, A. Jamal, S.B. Khan, M. Faisal. Biosens. Bioelectron. 28(2011)127.
- 24.M.M. Rahman, A. Umar, K. Sawada. Sensors and Actuators: B 137(2009)327.
- 25.D. Chakraborti, J. Narayan, J.T. Prater. Appl. Phys. Lett. 90(2007)062504.

- 26.K. Hara, T. Horiguchi, T. Kinoshita, H. Arakawa. Sol. Energy Mater. Sol. Cells 64(2000)115.
- 27.Z.L. Wang. J. Phys.: Conden. Matt. 16 (2004) R829.
- 28.Z. Zhang, J.B. Yi, J. Ding, L.M. Wong, G.Z. Xing, T. C. Sum, T. Wu. J. Phys. Chem. C, 112 (2008) 9579.
- 29.Z. Zhang, J.B. Yi, J. Ding, L.M. Wong, G.Z. Xing, T. C. Sum, T. Wu. J. Phys. Chem. C, 112(2008)9579.
- 30.M.M. Rahman. Current Proteomics 9(2012)272.
- 31.A. Tao, F. Kim, C. Hess, J. Goldberger, R. He, Y. Sun, Y. Xia, P. Yang. Nano Lett. 3(2003)1229.
- 32.J.J. Vijaya, L.J. Kennedy, G. Sekaran, B. Jeyaraj, K.S. Nagaraja. J. Hazard. Mater. 153(2008)767.
- 33.M.M. Rahman, S.B. Khan, M. Faisal, A.M. Asiri, K.A. Alamry. Sens. Actuator. B 171-172(2012)932.
- 34.P.P. Sahay, R.K. Nath. Sens. Actuator. B 134(2008)654.
- 35.Q.H. Li, Y.X. Liang, Q. Wan, T.H. Wang, Appl. Phys. Lett. 85(2004)6389.
- 36.M.M. Rahman, A. Umar, K. Sawada. Sensors and Actuators: B 137(2009)327.
- 37.C.J. Lee, T.J. Lee, S.C. Lyu, Y. Zhang, H. Ruh, J. Lee. J. Appl. Phys. Lett. 81(2002)3648.
- Wongchoosuk, A. Wisitsoraat, A. Tuantranont, T. Kerdcharoen. Sens. Actuator. B. 147(2010)392.
- 39.F. Wang, S. Hu. Microchim. Acta 165(2009)1.
- 40.M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. R. Russo, P. Yang. Science 292(2001)1897.
- 41.M.M. Rahman. J. Biomed. Nanotech. 7(2011)351.
- 42.W.O. Milligan, J. Holmes. X-Ray Diffraction Studies in the System CuO-Fe₂O₃. J. Am. Chem. Soc., 63 (1941)149-150.
- 43.E. Sasaoka, M. Hatori, H. Yoshimura, C. Su, M.A. Uddin. Role of H₂O in Oxidation of Spent High-Temperature Desulfurization Sorbent Fe₂O₃ and CuO in the Presence of O₂. Ind. Eng. Chem. Res. 40(2001) 2512–2517.
- 44.M.M. Rahman. Reusable and mediator-free cholesterol biosensor based on cholesterol Oxidase immobilized onto TGA-SAM modified smart bio-chips. PLOS ONE 9(2014)e100327.
- 45.M.M. Rahman. Development of mediator-free acetylcholine sensor co-immobilized with acetylcholine oxidase using micro-chips. Current Proteomics 9(2012)272-279.
- 46.H.M. Fan, G.J. You, Y. Li, Z. Zheng, H.R. Tan, Z.X. Shen, S.H. Tang, Y.P. Feng. Shape-Controlled Synthesis of Single-Crystalline Fe₂O₃Hollow Nanocrystals and Their Tunable Optical Properties. *J. Phys. Chem. C* 113(2009)9928–9935.
- 47.S. Ghosh, M. Roy, M.K. Naskar. A Facile Soft-Chemical Synthesis of Cube-Shaped Mesoporous CuO with Microcarpet-Like Interior. *Crystal Growth & Design*, 14(2014)2977–2984.
- 48.P.M. Rao, X. Zheng. Rapid Catalyst-Free Flame Synthesis of Dense, Aligned α-Fe₂O₃ Nanoflake and CuO Nanoneedle Arrays. Nano Lett., 9(2009)3001–3006.
- 49.Z. Tian, Y. Zhou, Z. Li, Q. Liu, Z. Zou. Generalized synthesis of a family of multishelled metal oxide hollow microspheres. J. Mater. Chem. A 1(2013)3575-3579.
- 50.H. Zhou, S.S. Wong. A Facile and Mild Synthesis of 1-D ZnO, CuO, and α -Fe₂O₃Nanostructures and Nanostructured Arrays. ACS Nano, 2(2008)944–958.
- 51.A.F. Carley, P.R. Davies, K.R. Harikumar, R.V. Jones, M.W. Roberts. Reactivity and Structural Aspects of Cesium and OxygenStates at Cu(110) Surfaces: An XPS and STM Investigation. J. Phys. Chem. B, 108(2004)14518–14526.
- 52.X. Deng, J. Lee, C. Wang, C. Matranga, F. Aksoy, Z. Liu. Reactivity Differences of Nanocrystals and Continuous

Films of α-Fe₂O₃ on Au(111) Studied with In Situ X-ray Photoelectron Spectroscopy. J. Phys. Chem C 114(2010)22619-22623.

- 53.J. Morales, J.P. Espinos, A. Caballero, A.R. Gonzalez-Elipe, J.A. Mejias. XPS Study of Interface and Ligand Effects in Supported Cu₂O and CuO Nanometric Particles. J. Phys. Chem. B, 109(2005)7758-7765.
- 54.S. Pokrel, C.E. Simon, V. Quemener, N. Bârsan, U. Weimer (2008) Investigation of conduction mechanism in Cr₂O₃ gas sensing thick films by ac impedance spectroscopy and work function changes measurements, Sens Actuator B: Chem 133(2008)78-83.
- 55.C. Wang, X.Q. Fu, X.Y. Xue, Y.G. Wang, T.H. Wang. Surface accumulation conduction controlled sensing characteristics of p-type CuO nanorods induced by oxygen adsorption, Nanotech. 18(2007)145506.
- 56.J. Hagen. Heterogeneous Catalysis: Fundamentals, Wiley-VCH, Weinheim, (1999)83-206.
- 57.M.M. Rahman, A. Jamal, S.B. Khan, M. Faisal, A.M. Asiri. Fabrication of Highly Sensitive Acetone Sensor Based on Sonochemically Prepared As-grown Ag₂O Nanostructures. Chem. Engineer. J. 192(2012)122-128.
- 58.K. Sahner, R. Moos, M. Matam, J.J. Tunney. Hydrocarbon sensing with thick and thin film p-type conducting perovskite materials, Sens. Actuator. B 108(2005)102-112.
- 59.K.I. Choi, H.R. Kim, K.M. Kim, D. Liu, G. Cao, J.H. Lee. C₂H₅OH sensing characteristics of various Co₃O₄ nanostructures prepared by solvothermal reaction. Sens Actuator B: Chem 146(2010)183-189.
- 60.Y.C. Weng, J.F. Rick, T.C. Chou. A sputtered thin film of nanostructured Ni/Pt/Ti on Al2O3 substrate for ethanol sensing, Biosens. Bioelectron. 20(2004)41-51.
- 61.M.M. Rahman, A. Jamal, S.B. Khan, M. Faisal. Highly sensitive ethanol chemical sensor based on Ni-doped SnO₂ nanostructure Materials. Biosens. Bioelectron. 28(2011)127-134
- 62.B. Tao, J. Zhang, S. Hui, L. Wan. An amperometric ethanol sensor based on a Pd-Ni/SiNWs electrode. Sens. Actuator. B Chem. 142(2009)298-303.
- 63.M. Faisal, S.B. Khan, M.M. Rahman, A. Jamal, A.M. Asiri, M.M. Abdullah. Smart chemical sensor and active photocatalyst for environmental pollutants. Chem. Engineer. J 173(2011)178-184.
- 64.Y.C. Weng, T.C. Chou. Ethanol sensors by using RuO2modified Ni electrode. Sens. Actuator. B Chem. 85(2002)246-255.
- 65.S.B. Khan, M. Faisal, M.M. Rahman, A. Jamal. Exploration of CeO₂ nanoparticles as a chemi-sensor and photocatalyst for environmental applications. Sci. Total. Environ. 409(2011)2987-2992.
- 66.Yang Z, Huang Y, Chen G, Guo Z, Cheng S, et al (2009) Ethanol gas sensor based on Al-doped ZnO nanomaterial with many gas diffusing channels. Sens. Actuator B Chem 140: 549-556.
- 67.M Faisal, Khan SB, Rahman MM, Jamal A, Umar A (2011) Ethanol chemi-sensor: Evaluation of structural, optical and sensing properties of CuO nanosheets. Mater. Lett. 65: 1400-1403
- 68.Rahman MM, Jamal A, Khan SB, Faisal M (2011) Fabrication of Highly Sensitive Ethanol Chemical Sensor Based on Sm-Doped Co₃O₄ Nanokernels by a Hydrothermal Method. J. Phys. Chem. C 115: 9503-9510.
- 69.M.M. Rahman, S.B. Khan, A.M. Asiri. Fabrication of Smart Chemical Sensors Based on Transition-Doped-

Semiconductor Nanostructure Materials with u-Chips. PloS One 9(2014)e85036.

DOI: 10.1039/C5RA08224B

Journal Name