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# Acetone sensing behaviour of optical fiber clad-modified with γ-CuBr nanocrystals

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ABSTRACT

Nanocrystalline copper bromide (γ-CuBr) has been synthesized by hydrothermal method. The as-synthesized sample was characterized for its structural and microstructural properties using powder X-ray diffraction, electron diffraction and high resolution transmission electron microscope. The surface characteristics and optical properties of the sample were further studied with spectroscopy techniques such as FT-IR transmittance, diffused reflectance and fluorescence. Further, γ-CuBr nanocrystals was used as a gas sensing material in clad-modified optical fiber gas sensing system to explore its sensing behaviour for acetone ($C_3H_6O$), ammonia ($NH_3$) and ethanol ($C_2H_5OH$). As compared with other gases, γ-CuBr nanocrystals showed superior sensitivity and specificity to acetone gas. The mechanism involved in the present, clad-modified optical fiber acetone sensor was discussed in detail.

## 1. Introduction

Gas sensing with a small portion of optical fiber clad-modified using nanocrystalline material based coatings [1–10] is one of the most promising areas of research in sensor technology. In this regard, nanocrystalline oxides such as ZnO [5], $Sm_2O_3$ [11] and $CeO_2$ [12] are showed superior sensitivity against even trace amount of ammonia, ethanol and methanol gases respectively. But several issues such as sensitivity, specificity or selectivity and response time needs to be addressed in this upcoming research area. In the typical clad-modified optical fiber gas sensing system, approximately few centimetres of the clad was removed by either mechanical or chemical procedures at the center of the optical fiber. Then, a lump-free paste obtained from nanocrystalline material was coated as a clad to serve as a gas sensing material. To perform the measurement, the clad-modified optical fiber was carefully introduced into the gas sensing chamber, and then one end of the fiber was connected to a light source and the other with a fiber optic spectrophotometer or a photodetector. If such a system was exposed to the gas environment, the gas molecules initiate interaction with the surface of nanocrystalline materials that tailors the refractive index of the material due to chemical reactions and creates an optical loss through evanescent waves. It influence on spectral intensity modulation can be captured at the output end with a fiber optic spectrophotometer or a photodetector automated with data acquisition system. Generally, nanocrystalline materials exhibit superior properties when compared with its respective bulk sample because of high surface area and more volume fraction of atoms in the grain boundaries. Hence, nanocrystals with different grain sizes or morphologies are commonly investigated to understand its influence on gas sensing behaviour for sensitivity and selectivity.

Copper bromide (CuBr) is a p-type semiconductor, which exists in three different polymorphisms namely, FCC (α-phase), wurtzite (β-phase) and zinc blende (γ-phase). All the three phases are a subject of research because of its fascinating electrical, optical and catalytic properties [13]. It exhibits superior resistive sensing behaviour for ammonia gas [14,15], ultraviolet dosimeter [16], blue light emitting electroluminescent nature [17] and high efficient reusable catalyst for 1,2,3-triazoles synthesis [18]. Prakash et al., reported the influence of the grain size on clad-modified optical fiber gas sensor using cubic phase nickel oxide (NiO) coatings [19] and showed an unambiguous evidence for surface area effect using nanocrystalline and microcrystalline samples. In the present work, we report the acetone sensing behaviour of optical fiber clad-modified with γ-CuBr nanocrystalline coatings.

## 2. Experimental details

High pure analytical grade copper sulphate ($CuSO_4{\cdot}5H_2O$) and

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potassium bromide (KBr) were used as the copper and bromine sources in as-received condition for the synthesis process. In a teflon lined stainless steel 100 ml autoclave, 0.01 mol of the above said precursors along with an appropriate amount of glucose ($C_5H_{11}O_5$ CHO) was added into 80 ml of double distilled water and stirred until a homogenous solution was obtained. Then, the autoclave was sealed and maintained at 100 °C for ten hours using a calibrated box furnace. Because of the long incubation period, both temperature and autogenerated pressure serves as a driving force for the oxidization of glucose to gluconic acid ($C_5H_{11}O_5$ COOH) which reduces $Cu^{2+}$ to $Cu^{+}$. The gluconic acid was removed along with the by-products ($K_2SO_4$ and $H_2SO_4$) using repeated washing with double distilled water. The as-prepared product was further dried at room temperature for several hours to remove moisture prior to subjecting it for characterization.

The phase purity of the powder sample was investigated using Seifert X-ray diffraction (XRD) instrument equipped with copper target (Cu-K$\alpha_1$, $\lambda$ = 1.5406 Å) in a wide range of Bragg angles 2θ (20–70°) and a scanning step rate of 0.02°/s. Bruker Alpha-T Fourier transformed infrared (FT-IR) spectrophotometer were applied to identify the presence of functional groups at surface of CuBr crystallites in the wavenumber region of 400–4000 $cm^{-1}$. To further examine the crystallites morphology, high resolution transmission electron microscope (HRTEM) was performed using Tecnai G2 Twin instrument. Prior to the HRTEM measurement, the sample was dispersed in ethanol using a bath ultrasonic agitator for ten minutes in order to break the aggregation between crystallites. Then, a drop of dispersant was placed on top of the carbon coated copper grid and dried at room temperature. Diffused reflectance spectroscopy was performed using PerkinElmer Lambda 650 machine to estimate the bandgap of CuBr. Fluorescence spectra of CuBr were measured at room temperature using a Horiba FluoroMax-4 with ozone free Xe lamp as an excitation source.

Clad-modified optical fiber gas sensing system was designed with a commercial multimode step index poly (methyl methacrylate) optical fiber having 750 μm diameter (735 μm core, 15 μm thick clad, NA = 0.51) and 42 cm length. The refractive index of the poly (methyl methacrylate) optical fiber core is 1.492 and the clad is 1.402. At the middle of an optical fiber around three centimetres of the clad was completely removed to serve as a gas sensing region. Nanocrystalline CuBr powder was mixed with an appropriate amount of isopropyl alcohol to form a lump free paste and ~ 30 μm thick coating was deposited on top of the clad removed area by slurry deposition process. The nanocrystalline CuBr coated optical fiber was dried at room temperature in air atmosphere without any further processing and then inserted into a gas sensing test system. A commercial scientific white light (Model SL1, Stellar Net Inc., USA) was attached to one end of the clad-modified optical fiber source and other with a miniature optic fiber spectrophotometer (EPP-2000, Stellar Net Inc., USA) interfaced with a dedicated computer for data collection and analysis. Test volatile organic compound gases (ammonia, ethanol and acetone) were prepared using respective solutions in different concentrations up to 500 ppm and supplied into the gas sensing test system through flow regulator. Before performing the sensitivity measurement, the test gas was continuously supplied for ten minutes time interval to create much interaction between gas molecules with the surface of each crystallites of the sensing material since the measurement was carried out at room temperature.

## 3. Results and discussions

### 3.1. Structural and microstructural analysis

The powder X-ray diffraction pattern obtained for as-synthesized copper bromide was shown in Fig. 1(a). Totally, five peaks were observed at two theta positions 27.12, 31.40, 45.02, 53.34 and 65.54 between the scanned region and all these peaks were indexed with joint committee for powder diffraction standard (JCPDS) file 06–0292 and respectively assigned to (111), (200), (220), (311) and (400) planes of γ-CuBr. There was no additional peak observed other than the cubic γ-CuBr. In order to reconfirm the phase purity, selected area electron diffraction (SAED) pattern of copper bromide acquired using transmission electron microscope and the pattern obtained was shown in Fig. 1(b). Indexing and assigning of (*hkl*) planes for SAED pattern reveals the existence of sample CuBr in γ-phase alone without any other secondary phases or impurities. Crystallite morphology of the as-synthesized γ-CuBr sample was shown in Fig. 1(c) which reveals that, crystallites are not in uniform dimension, but with an average dimension of 200 nm. Energy dispersive X-ray analysis (EDAX) confirmed the elements present in nanocrystalline γ-CuBr sample and the obtained EDAX pattern was presented in Fig. 1(d). The analysis reveals that, $K_\alpha$ line for oxygen, copper and bromine respectively occurs at 0.525 keV, 8.040 keV and 1.53 keV, whereas the $L_\alpha$ line of copper occurs at 0.930 keV. This clearly shows the presence of copper, bromine and oxygen elements in the sample. It is supposed to show only the peaks corresponds to copper and bromine alone, but it also shows a relatively less amount of oxygen presence. It may be due to surface oxidization of the crystallites during the measurement or post synthesis processing. Similar behaviour was recently reported in copper micro-flakes synthesized by hydrothermal route [20].

### 3.2. Spectroscopic analysis

Spectroscopic analysis of nanocrystalline γ-CuBr powder sample using FTIR, diffused reflectance and fluorescence were performed. The spectra obtained were respectively shown in Fig. 2(a), (b) and (d). Prior to the FTIR measurement, both pure KBr commercial powder and nanocrystalline γ-CuBr mixed with KBr were compacted to get cylindrical pellets using a hydraulic pressing machine. The pure KBr cylindrical pellet was used for the baseline correction, and then the measurement was performed with the sample mixed with KBr. The broad absorption peak at 1606 $cm^{-1}$ is attributed to the bending mode of O-H and peaks at about 3414, 3517 $cm^{-1}$ are assigned to the O-H stretching vibrations. Analysis of the obtained DRS spectra reveals the percentage of reflectance in the visible part of the electromagnetic spectrum is around 35% and the reflectance onset is 419.6 nm [21]. Further, to estimate the energy band gap of the sample from the diffused reflectance data shown in Fig. 2(c), Kubelka-Munk (K-M) function calculation was performed. The obtained data was plotted between $[F(R).(h\nu)]^{1/2}$ and energy was shown in Fig. 2(c). The extrapolation onset in Fig. 2(c) intercepts the x-axis and gives the direct transition energy band gap and it was found to be 2.82 eV. This estimated energy band gap value matched with the values in previously published literatures [22]. Room temperature fluorescence emission behaviour of nanocrystalline γ-CuBr was shown in Fig. 2(d). The obtained single emission peak at 425.5 nm is the characteristics fluorescence peak of γ-CuBr obtained with excitation wavelength 350 nm. The emission peak energy is 2.91 eV and a stoke shift from the reflectance spectra is about 0.09 eV. Such a single high intense peak reveals the crystallites with low defects and emission peak has been observed in the literature earlier [23].

### 3.3. Gas sensing behaviour

A schematic representation of clad-modified optical fiber gas sensing set-up is shown in Fig. 3 and the gas sensing behaviour of optical fiber clad-modified with nanocrystalline copper bromide coating for the gases ethanol, ammonia and acetone were respectively shown in Fig. 4(a)–(c). The spectral intensity variation was recorded using spectrophotometer for each concentration of all the test gases. Further analysis reveals that, nanocrystalline γ-CuBr coating was showed superior sensitivity and specificity to acetone gas when compared with ethanol and ammonia. During the gas sensing measurement, the optical fiber leaks the evanescent wave through the nanocrystalline γ-CuBr coating. If the test gas was exposed in an appropriate concentration, it