One-step chemical bath deposition of Cu$_2$O flowers grown on ITO seed layer coated glass substrate

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Abstract. Here, the growth of Cu$_2$O flowers on a glass substrate were successfully fabricated using one-step chemical bath deposition method at low growth temperature. These flowers were grown on ITO seed layers that were prepared on glass substrate by magnetron-frequency RF sputtering. The structure and surface morphology of the products of Cu$_2$O flowers were characterized in detail using X-ray diffraction and microscopy of field emission scanning electron. Optical properties were examined through the ultraviolet/visible spectroscopy. The results showed that the Cu$_2$O flowers were uniformly formed on ITO seeds-coated glass substrate, grow in the cubic structure with film preferential (111) plane orientation, high transmittance, and good crystallinity. The value of band gap is approximately 2.53 eV. This study helps to be the basis for more research on the growth of Cu$_2$O at low-temperature and low cost-effective substrate.

1. Introduction
Cuprous oxide (Cu$_2$O) is an attractive semi-conductor material, a cubic crystal structure, and p-type bandgap energy of 2.0-2.6 eV [1]. In addition, its superior physical, chemical, and photo-electronic properties, non-toxic material, natural abundance, and simple setup procedures. Cu$_2$O nanostructures has produced importance in different uses, such as photovoltaics [2], photo-chemical hydrolysis into H$_2$ and O$_2$ [3], catalysis [4], change of solar energy to energy of chemical or electrical [5], batteries [6], photo degradation of dye molecules [7], hetero-junction in solar cells [8], biosensing [9], and electrode materials in batteries of ion-lithium [10]. Requires success in different applications the control and definition of the size, dimension, and geometry of the nanostructured materials [11]. So, tailoring the growth Cu$_2$O nanostructure is important for specific production orientations, sizes, and surface densities. Preparation of Cu$_2$O has been carried out by various chemical and physical methods such as electro deposition, sintering, vacuum deposition, spray pyrolysis and deposition of chemical bath (CBD). Among these methods, CBD is inexpensive, simple, cost-effectiveness, and suitable chemical method (wet method) which has been used for preparation of a multiplicity of nanostructured materials [12].

The layer of ITO seeds is very important in promoting the growth of Cu$_2$O nanostructures. Consequently, the kind and relationship of seed layer with nanostructure is very important because the properties of nanostructures depend mainly on seeds properties, like grain size, morphology, crystalline density, and roughness. So, making a high-quality seed layer is one of the important roles toward developing the nanostructures performance, which can help expand the improvement of novel devices and possible applications [13]. The aim of this research is to use a low-cost substrate in a deposition of the Cu$_2$O nanostructures on a glass substrate by using chemical bath deposition method at low growth temperature.
2. Experiment details

Prior to the growth process of Cu₂O flowers, ITO seeds were prepared on glass substrates by magnetron-frequency RF sputtering with power of 100W and chamber pressure at 10⁻⁵ mbar. The thickness of ITO seed layer was always saved at 75 ± 5 nm. The Cu₂O flowers were grown using CBD employing a double distilled water (100 ml) was mixed with copper (II) chloride dehydrate (CuCl₂. 2H₂O) (1.705 g) to obtain copper chloride solution (0.1 M). The solution was moved for 1 h at room temperature to get a magnetic stirrer for a well-dissolved and transparent solution. With 15 min boiling, the solution was prepared to boil at temperatures of 70 °C. In order to taken out loosely and larger bonded particles, the ITO/glass substrate was taken away from the bath and rinsed in double distilled water using ultrasonic bath for about 10 min.

The thickness of the Cu₂O film was obtained using an Filmetrics F20 (optical reflectometer). The optical properties, surface morphology, and crystal structure of the flowers nanostructures were investigated using UV–Vis spectrophotometry, X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM).

3. Results and discussion

The morphologies of Cu₂O flowers on ITO seeds/glass substrate by CBD at low growth temperature of 70 °C were measured by FESEM with low and high magnification as shown in Figure 1 (a, b). Clearly, the substrate surface were densely covered with the spherical clusters of the Cu₂O that contain the high-density with size of smaller particle which provide a closer view of typical flower morphology. The dimension of flower particle sizes ranges 85 nm width and length.

![Figure 1](image)

**Figure 1.** Low and high-magnification FESEM image of Cu₂O flowers on ITO seeds coated glass substrate.

The ratio of O to Cu is appear in Figure 2. EDX revealed that Cu₂O flowers has 65.8 and 34.2 At% of Cu and O, respectively; and these values represents the best stoichiometry for the Cu₂O.
Figure 2. EDX spectra of the Cu$_2$O flowers on ITO seed layer coated glass substrate.

The quality of crystal and orientation of the Cu$_2$O flowers grown on ITO/glass substrate via CBD were examined by XRD. Figure 3 shows the located of diffraction peaks were at $2\theta = 29.4^\circ$, $36.3^\circ$, $42.2^\circ$, $61.3^\circ$ and $73.4^\circ$, that corresponded to the (110), (111), (200), (220) and (311) diffraction of the Cu$_2$O. The plots of XRD were matched with the Cu$_2$O reference (JCPDS-05/0667), having a cubic crystal structure.

![XRD pattern of Cu$_2$O flowers on ITO seeds coated glass substrate.](image)

Figure 3. The XRD pattern of Cu$_2$O flowers on ITO seeds coated glass substrate.

Fig. 4 shows the UV–vis transmission of the Cu$_2$O flowers on ITO seed layer coated glass substrate in a wavelength range of 220–800 nm and the absorption. The Cu2O flowers are transparent in the visible region (Fig. 4). Up to nearly 500 nm, the flowers nanostructures are absorbent. The transmittance of the Cu$_2$O film increases strongly between 500 and 1800 nm. At long wavelengths, the transmittance values is estimated to be 67%. The transmittance spectrum displays an interference pattern with a sharp fall of transmittance at the band edge. In the visible light range, the high optical transmittance of Cu2O flowers indicates the low-surface roughness and high-homogeneity [14]. The inset displays the typical variation of $(\alpha h\nu)^2$ as a function of photon energy $(h\nu)$ for the Cu$_2$O flowers.

In order to calculate the energy gap $(E_g)$ of the Cu2O flowers, the absorption coefficient is estimated using the relationship [15]:

$$\alpha = \frac{1}{D} \ln \left( \frac{1}{T} \right)$$  \hspace{1cm} (1)

where $D$ is thickness, $T$ is transmittance, and $\alpha$ is absorption coefficient of the Cu2O flowers.

$E_g$ is given for direct transition using [16]:

| Element | Atomic % |
|---------|-----------|
| O       | 34.2      |
| Cu      | 65.8      |
| Total:  | 100       |
\[ \alpha \ h \nu = A \ (h \nu - E_g)^{1/2} \] 

(2)

where \( h \nu \) is the energy of incident photon, and \( A \) being a constant.

A Cu2O flowers absorbs the light below a threshold wavelength (\( \lambda_c \)) i.e \( h \nu \geq E_g \) or:

\[ h \nu = \frac{1240}{\lambda} \] 

(3)

The \( E_g \) of the film is resultant using planning the Tauc formula and taking the extrapolation of the linear portion from the plot of \( (\alpha h \nu)^2 \) versus the photon energy \( (h \nu) \). The \( E_g \) of the Cu2O flowers is 2.53 eV, as shown inset of Figure 4. The reduction \( E_g \) value comparison with bulk value is caused by different contributions of the excitonic emissions and their phonon replicas

![Graph of UV–vis transmission of Cu2O flowers](image)

**Figure 4.** UV–vis transmission of the Cu2O flowers. The typical variation of \( (\alpha h \nu)^2 \) as a photon energy function \( (h \nu) \) of Cu2O flowers is shown in the inset.

4. Conclusion

The growth of Cu2O flowers was successfully conducted on ITO seeds coated glass substrate using one-step chemical bath deposition method at low growth temperature of 70 °C with 15 min boiling. ITO seeds was prepared on glass substrates by magnetron-frequency RF sputtering with thickness of approximately 75 ± 5 nm. This approach will helps to be the basis for more research on the growth of Cu2O at low-temperature and low cost-effective substrate which can be advantageous in numerous solid-state and opto-electronic device.

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6. References

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