Nanocomposite films of CNPs/CuO structures by electrophoresis method

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Abstract. The article discusses the results of ordering a composite of carbon nanoparticles (CNPs) coated copper oxide (CuO) on the silicon substrate by the electrophoresis method and, particles size and chemical composition have analyzed by Raman spectroscopy, an Atomic Force Microscope, and Scanning Electron Microscope. Carbon nanoparticles from Single-walled Carbon Nanotubes (SWCNTs) using the centrifugation method are applied by a pipette (by the drop method) on the silicon substrate with copper electrodes under the direct electric field to obtain CNPs-CuO nanocomposite films. It has been shown that carbon nanoparticles in solutions upon dispersion in an ultrasonic bath and subsequent centrifugation have a limiting particle size of 38 nm and CNPs solution can be controlled to obtain the nanocomposite films by the electrophoretic forces.

1. Introduction
Carbon nanoparticles (CNPs) from carbon nanomaterials have a unique place in nanoscience and nanotechnology as their extraordinary properties. It could be a good method to improve the sensors’ applications and properties by coating carbon nanoparticles with metals or semiconductors. The carbon nanomaterials based on carbon nanoparticles coated metal oxides (titanium, zinc, copper, vanadium, nickel, etc.) have been used as a support material for the dispersion and stabilization of metal and semiconductor due to their large chemically active surface and stability. It can be used as an effective sensor for infrared radiation due to its ability to absorb the infrared spectrum [1]. Among these metal oxides, copper oxide (CuO) is a typical material, which has been extensively investigated for use in many other areas such as semiconductors, catalysts, sensors. It has prospected that CNTs-CuO nanocomposite has great outstanding properties that are expected carbon nanoparticles coated copper oxide based on sensors due to a good charge transporting and good conductivity properties, and excellent absorption of light spectrum properties to photovoltaic of CuO [2, 3].

Methods for ordering a system of carbon nanoparticles (CNPs) by electrophoretic synthesis have become very popular for improving the field of nanotechnology [4]. In this case, the formation of ordered nanostructures from carbon nanoparticles (CNPs) with copper electrodes by electrophoretic forces makes it possible to obtain a thin film for the creation of high-strength reinforcing components. The ordering of CNPs-CuO nanocomposites occurs in unpolarized solutions under the action of electrophoretic forces [5]. CNPs-CuO nanoparticles are oriented opposite to the direction of the external electric field strength vector, forming conducting structures from the negative electrode to the
positive one. This work aimed to determine the particle size and chemical composition of CNPs coated CuO nanocomposite films on the silicon substrate using the electrophoretic method.

2. Materials and Methods

The CNPs-CuO nanocomposite films were fabricated by the electrophoretic method under the direct electric field. Firstly, the original SWCNT (carbon nanotube TUBALL TM: 0.2%, lignosulfonate vanisperse A: 1%, water: 98%, batch number 19HO05.N1.003) and distilled water (0.09% v/v) was mixed 30 minutes by an ultrasonic bath (Quick 218). The single-walled carbon nanotubes (f-SWCNT) solution was centrifuged three times at 13400 rpm using the centrifugation method (miniSpin Eppendorf AG 5452, 22331 Hamburg) and each time of the solution took 50% at the top of the volume to obtain the carbon nanoparticles (CNPs) solution. As the centrifugation method, the SWCNT solution is different the two types that the button of the volume is nanotubes and the top of the volume has become nanoparticle in the centrifugation tubes. The types of nanotubes can be used to improve the field of nanowires and published on the electric conductivity of structured carbon nanotubes in [6]. Carbon nanoparticles coated metal oxides have a heightened sensitivity to investigate the effective sensor for the IR spectrum [1].

Figure 1 shows the process of CNPs-CuO nanofilm in which carbon nanoparticles solution applied the droplet method into the copper electrodes gap (1000 µm) of a printed circuit board made by photolithography on a silicon substrate with a magnetron film made of copper. A constant voltage (varied from 15 to 30 V) was applied to the copper electrodes from a power source. The micrograph (figure 2) shows the cathode and anode with a distance between them of 1000 microns, marked “+” and “–”, respectively. In the experiment, CNPs solutions were applied using a pipette (by the droplet method) onto the surface of a silicon substrate with copper electrodes under the direct electric field. The CNPs solution coated copper particles from the copper electrodes due to the controlled direct electric current during the electric field. After the droplet is drying due to the electric force, the CNPs-CuO nanocomposite films were formed on the silicon substrate. In this case, the concentration of the solution and controlling the electrophoretic force are important to obtain the nanocomposite film. The CNPs-CuO composite structures were characterized by confocal microscopy, Raman scattering of light (Omega Scope™ Confocal Raman microscope, 532 nm, 0.8 cm⁻¹), the Atomic Force Microscope (AIST-NT SmartSPM), and Scanning Electron Microscopy (JEOL JSM-6610).

3. Results and Discussion

CNPs-CuO nanocomposite structures were appeared on a silicon substrate after about 5 minutes evaporation process by the electrophoretic force and it was characterized by Confocal microscopy. It can be seen that formation of ordering nanoparticle structures on the silicon substrate in the direction of static electric field strength in figure 2.
Figure 2. Confocal image of CNPs-CuO nanocomposite film on the silicon substrate in the direction of the static electric field strength.

Figure 3. Raman resolution in the region of tangential modes (D, G) from CNPs-CuO film after evaporation. In the inset, the nanocomposite film analysis area of low-energy frequency.

In figure 3, the chemical composition of CNPs-CuO film shows that the properties of CNPs peaks and the interaction of carbon nanoparticles and copper nanoparticles at the low energy frequency in the inset. In Raman scattering of light (Omega Scope™ Confocal Raman microscope, 532 nm, 0.8 cm⁻¹), lines on the CNPs-CuO nanocomposite film found that D-1340 cm⁻¹ for the disorder (defective mode), G-1587.9 cm⁻¹ from the stretching of the C-C bonds (the in-plane vibrations of sp²-bonded crystalline carbon), 2D-2672 cm⁻¹ secondary D peak (graphene layer). The ratio of the intensity of D and G peaks (I_D/I_G) is a measure of the defects present in carbon nanomaterials structure. There are defects in carbon material as the ratio of I_D/I_G (0.5) higher than pristine material (0.4) [7-9].

The inset of figure 3 shows the region of complex structures in which consist of carbon material, copper (II) oxide, and copper oxide on the silicon substrate. The radial breathing mode of carbon nanoparticles (ω_RBM) peaks (the low-energy frequency regions) had appeared in 148 cm⁻¹ and 165.22 cm⁻¹ regions by Raman spectroscopy. The calculations of the diameter of radial breathing mode (d) frequency were carried out according to the equation from the radial breathing mode (ω_RBM) peaks on SiO₂/SiO substrates for SWCNT [10, 11]:

$$\omega_{\text{RBM}} = A \cdot d^{-1} + B$$

where, the constant value of A is 248 cm⁻¹ and B is 0. So, the diameter of radial breathing mode (d) from ω_RBM frequencies of 148 cm⁻¹ and 165.22 cm⁻¹ can be described as 1.7 nm and 1.5 nm respectively. Radial breathing mode frequencies can be determined semiconducting region at laser excitation energy 2.3 eV [12]. The vibrational spectra of CuO nanostructures were appeared at 282 cm⁻¹ (A_g mode) [13], 327 cm⁻¹[14] and 333 cm⁻¹ (B_g mode) [15]. After the electrophoretic synthesis, the Raman spectra of substrate were appeared at 369 cm⁻¹ (SiO₂₄), 444 cm⁻¹ (SiO) and 470 cm⁻¹ (SiO₂) [16]. There are described the low energy frequency region of CNPs-CuO nanocomposite film.

CNPs-CuO nanoparticles were uniformly arranged on the silicon substrate after evaporation. It can be seen the formation of nanoparticles structures by the Atomic Force Microscope (AIST-NT SmartSPM) and was analyzed the size of nanoparticles 14–38 nm shown in figure 4.
Figure 4. AFM image of CNPs-CuO nanoparticles film and the size of nanoparticles.

The formation of CNPs-CuO nanoparticles structure can be seen by Scanning Electron Microscopy (JEOL JSM-6610) of CNPs-CuO with the size of nanoparticles in figure 5.

Figure 5. SEM image of CNPs-CuO nanocomposite film.

Table 1. Elemental composition of CNPs-CuO film.

| Element | Line type | Conditional Concentration | weight (%) |
|---------|-----------|---------------------------|------------|
| C       | K series  | 0.73                      | 23.34      |
| O       | K series  | 2.73                      | 10.97      |
| Si      | K series  | 36.99                     | 55.46      |
| Cu      | K series  | 5.69                      | 10.22      |

The obtained results are also confirmed by elemental analysis using an energy dispersive attachment on a scanning electron microscope (JEOL JSM-6610). The result is CuO coated the surface of carbon nanoparticles from copper electrodes, so carbon nanoparticles can help in stabilizing the metal particles in solution [17]. The EDS results show in the
table 1, that the CNPs-CuO nanocomposites contain carbon, oxygen, silicon, and transition metal element of copper.

4. Conclusions
The method of electrophoretic synthesis makes it possible to obtain nanofilms based on carbon nanoparticles with a high degree of continuity. In addition, Raman scattering data in the low-energy frequency regions have corresponded to mixed types of metallic and semiconductors show that the observed nanostructures of CNPs coated CuO in the work can be used for the development of various systems for nanoelectronics and nanoelectromechanical devices.

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