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Graphene–cobalt phthalocyanine based on optoelectronic device for solar panel tracking systems

A. Tataroğlu [a], H. Tuncer [b], Ahmed A. Al-Ghamdi [c], A. Dere [d], B. Arif [c], S. Yol [b], N. Ozdemir [e], Farid El-Tantawy [f], F. Yakuphanoglu [c,d,*]

[a] Department of Physics, Faculty of Science, Gazi University, Ankara, Turkey
[b] Department of Chemistry, Faculty of Science, Firat University, Elazig, Turkey
[c] Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia
[d] Department of Physics, Faculty of Science, Firat University, Elazig, Turkey
[e] Department of Metallurgical and Materials Science, Faculty of Technology, Firat University, Elazig, Turkey
[f] Department of Physics, Faculty of Science, Suez Canal University, Ismailia, Egypt

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ABSTRACT

The photoconducting properties of graphene–cobalt phthalocyanine organic semiconductor photodiodes were investigated. GO doped cobalt phthalocyanine (CoPc) thin films were prepared with various graphene oxide (GO) contents. The electrical properties of the diodes were analyzed by using current–voltage and capacitance/conductance–voltage measurements. The reverse current of the diodes increases with the increasing illumination intensity. The transient photocurrent, photocapacitance, and photoconductance measurements of the diodes were also investigated. The photocurrent, capacitance and conductance increase after illuminating and returns to original value after turning off the illumination. Graphene–cobalt phthalocyanine based on optoelectronic device exhibited both a photodiode and photocapacitor behavior under solar light illuminaton.

1. Introduction

Organic semiconducting materials play an important role for optoelectronic applications and devices. One of them is organic compound based on metallophthalocyanine (MPc) such as CoPc, ZnPc, CuPc and MgPc which have high chemical resistance and thermal stability [1–7]. Metallophthalocyanines (MPcs) which possess very interesting optical and electrical properties can easily sublimate resulting in pure thin films without decomposition. In addition, the MPcs are two dimensional (2D) organic macrocyclic molecular catalysts (MN4) with metal atoms at the center, and these materials are a class of macrocyclic organic semiconductors. Moreover, the metallophthalocyanines are very useful as transporting and injection layers in optoelectronics devices, and can be utilized for optoelectronic applications and devices such as bulk heterojunction solar cells, light-emitting diodes, photovoltaic cells and organic field effect transistors.

Organic/inorganic heterojunctions have attracted great attention due to the availability of numerous organic semiconducting materials [8–10]. Organic/inorganic heterojucntions play important role in controlling the operation and performance of multilayered organic optoelectronic devices. Electrical properties of organic semiconductor based devices depend on ambient conditions such as light, humidity and temperature. Especially, crystalline molecular semiconductors exhibit rectification when deposited onto inorganic semiconductor substrates such as Si, GaAs and CdS [11–13].

The organic and inorganic semiconductor based on heterostructures are new class of metal/semiconductor junctions. There are more studies on these devices to the discover new devices. The combination of inorganic and organic semiconductors gives interesting electrical characteristics for diode applications. In present study, 9,16,23-tetrakis[7-oxo-3-chloro-4-methylcoumarin] phthalocyaninatocobalt was synthesized because it offers the low cost diode and optoelectronic device production. Thus, the aim of present study is to fabricate a novel optoelectronic device based on graphene: 9,16,23-tetrakis [7-oxo-3-chloro-4-methylcoumarin] phthalocyaninatocobalt nanocomposites based on heterojunction diodes. The electrical characterictics of the fabricated diodes were analyzed by using current–voltage (I–V) and capacitance–conductance–voltage (C–G–V) measurements.

* Corresponding author at: Department of Physics, Faculty of Science, Firat University, Elazig, Turkey. Tel.: +90 424 2370000/3496; fax: +90 424 2330062.
E-mail address: fyhan@hotmail.com (F. Yakuphanoglu).

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2. Experimental

2.1. Synthesis of 2,9,16,23-tetrakis[7-oxo-3-chloro-4-methylcoumarin] phthalocyaninato cobalt (II)

Compond I (3-chloro-7-(3,4-dicyanophenoxy)-4-methylcoumarin) was prepared by a base catalyzed nucleophilic aromatic nitro displacement of 1,2-dicyano-4-nitrobenzene with 3-chloro-7-hydroxy-4-methylcoumarin [14]. A mixture of 3-chloro-7-(3,4-dicyanophenoxy)-4-methylcoumarin **I** (0.30 g, 0.89 mmol) and metal salt [$Co(CH_3COO)_2{\cdot}4H_2O$ (0.054 gr, 0.22 mmol)] was heated at 160 °C with dry *N*,*N*-dimethylformamide (DMF) (4 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (4-5 drops) in a sealed tube, and stirred for 24 h under argon atmosphere. After cooling, the green reaction mixture was treated with ethanol (5 mL), and the precipitate that formed was filtered off and washed with water to remove unreacted $Co(CH_3COO)_2{\cdot}4H_2O$. The green product was purified by washing with methanol, tetrahydrofuran, chloroform, dichloromethane, acetonitrile, acetone, ethylacetate, ether and then dried. The compound is soluble in dimethylformamide and dimethylsulfoxide. Yield: 0.21 g (67.74%); m.p. > 300 °C; IR υ_{max} (cm^{-1}) (KBr): 3085-3065 (aryl CH), 2830-2940 (alkyl CH), 1723 (C=O, lactone), 1605 (C=C), 1585 and 1475 (Ar C=C), 1231 (Ar–O–Ar), 859 (C=C—Cl). ^1H NMR (DMSO-d_6) δ_H (ppm): 6.89-8.45 (m, 24H, Ar–H), 2.46 ppm (s, 12H, CH_3). UV–Vis (DMF) λmax (log ε) (nm): 675 (4.85), 610 (4.25), 315 (4.65). Anal. Calc. for $C_{72}H_{36}Cl_4N_8O_{12}Co$: C, 61.45; H, 2.56; N, 7.96. Found: C, 61.70; H, 2.85; N, 7.35%. MS (MALDI-TOF) *m*/*z*: 1405 $[M]^+$, 1407 $[M+2]^+$.

The chemical structure of 2,9,16,23-tetrakis[7-oxo-3-chloro-4-methylcoumarin] phthalocyaninatocobalt is shown in Scheme 1. Graphene oxide was prepared by Hummers method. The graphene oxide doped CoPc composites were prepared for various molar ratios of GO:CoPc = 2/10, 4/10, 6/10 and 8/10.

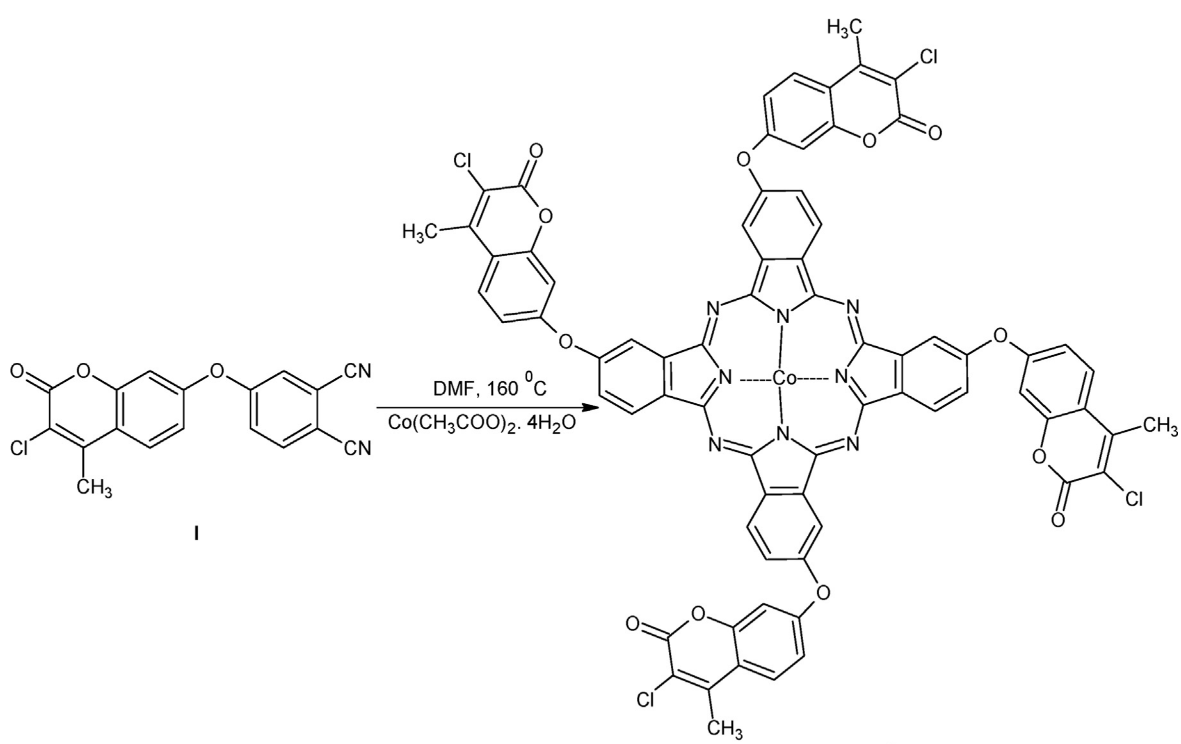
2.2. Preparation of the diodes

GO doped CoPc films were deposited on the p-Si using the drop coating method. Firstly, p-type silicon wafer was cleaned to remove the native oxide layer by etching with HF and then rinsed in deionised water using an ultrasonic bath for 10–15 min. After this process, the silicon wafer was chemically cleaned using the baths of methanol and acetone. Top contact of the diodes was prepared by Au metal. For this, Au metal was evaporated by thermal evaporation system in the form of circles with area of 3.14×10^{-2} cm^2. The current –voltage (*I*–*V*) characteristirics of Au/CoPc:GO/p-Si/Al diodes were measured using a Keithley 4200 semiconductor characterization system under dark and illumination conditions using a solar simulator. The intensity of the light was measured by solar power meter (Model TM-206). The capacitance–voltage and conductance–voltage measurements were performed with Keithley 4200 semiconductor characterization system.

3. Results and discussion

3.1. Current–voltage characteristics of the diodes

The semi-logarithmic *I*–*V* characteristics of the heterojunction diodes with GO doped CoPc thin films under dark and llumination conditions are shown in Fig. 1a and c. As seen in Fig. 1a and c, the diodes exhibited a rectifiying behavior as the forward bias current is significantly higher than that of the reverse bias current. The dark current–voltage characteristics of the diodes can be analyzed by thermionic emission (TE) mechanim, in which current assumes that only electrons with energies greater than the energy of the potential barrier add to the current flow. According to this theory, the current is described by the following relation [15–17]



I

II

Scheme 1. Chemical structure of 9,16,23-tetrakis[7-oxo-3-chloro-4-methylcoumarin]phthalocyaninatocobalt (II).