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Assembly of europium organic framework–gold nanoparticle composite thin films on silicon substrate

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ABSTRACT

Metal organic frameworks are a sub-class of coordination polymers and rapidly generating huge research interests in several technological areas. One of the emerging areas of their potential applications is the photovoltaics. The present study proposes the assembly of europium organic framework–gold nanoparticle nanocomposite thin film on silicon substrate. Microscopic, X-ray diffraction, surface area measurement and thermal studies have indicated the formation of the desired thin film. Spectral studies have been used to highlight their solid state optical property. Current–voltage studies have established semiconducting property of the above thin films.

1. Introduction

Metal organic frameworks (MOFs) are a relatively new class of porous crystalline materials, which have attracted tremendous attention in the last few years [1–4]. MOFs are considered as a sub-branch of coordination polymers, and their structures can be tuned according to the desired properties. This can be done either by careful selection of metal centers and functional linkers or through doping of other nanostructures [5–8]. Apart from several other properties of MOFs, structural tunability, high porosity and high surface area are crucial functional features, and play a crucial role in extending the material application to technological areas of gas storage, separation, nanoreactors, thin films, molecular sensing, drug delivery, magnetism, fluorescence, catalysis, electrochemistry etc. [9–18]. Inorganic materials like platinum nanotubes (PNTs) [19], flower like ZnO (zinc oxide) [20,21] and TiO_2 (titanium dioxide) nanorod [22] nanostructures are also grown on fluorine-doped tin oxide substrates for energy applications.

MOFs have also been reported useful in the development of photovoltaic devices [23]. A polymer composite containing Mg-based metal–organic framework (MOF) is efficiently used as an electrolyte for quasi-solid dye-sensitized solar cells (DSSCs) [24]. ZIF-8 based solar cells are known to enhance the open circuit voltage (V_{oc}) of DSSCs [25]. Dye sensitized solar cell activity of ZnO microparticles was obtained from one-step thermolysis of porous homochiral MOFs [26]. A compound, $Zn_4O(2,6\text{-NDC})_3\text{-}(DMF)_{1.5}(H_2O)_{0.5}.4DMF.7.5H_2O$ (UTSA-38, 2,6- NDC = 2,6-naphthalenedicarboxylate) has been shown to exhibit photoresponse properties for photovoltaic devices [27]. MOF-5 deposited on ITO plate, zinc imidazole framework interfaced with ZnO thin films, and Al_2 (BDC)$_3$ [BDC = benzene di-carboxylate] have been demonstrated to offer better DSSC efficiency in terms of open circuit potential [28–30]. Incorporation of quantum dots in MOF systems is reported for the development of highly luminescent and improved photon harvesting systems [31,32].

Though some photoactive MOFs are reported for solar cell applications, their formation as substrate still remains a challenging area to explore. This manuscript reports the synthesis of a nanocomposite thin film comprising a europium based metal organic framework (EuOF) and gold nanoparticles (AuNPs) assembled on a silicon substrate. Use of AuNPs in DSSCs is known to provide higher short-circuit current density and better photovoltaic performance [33]. Assembly of the EuOF/AuNP thin film on the Si substrate has been verified using microscopic and diffractometry techniques. Some preliminary investigations on the current–voltage properties of the proposed thin film of EuOF/AuNP nanocomposite have indicated their semiconducting properties. The property of the substrate along with the solid state photoluminescence may be useful for the development of highly efficient photovoltaic platform.

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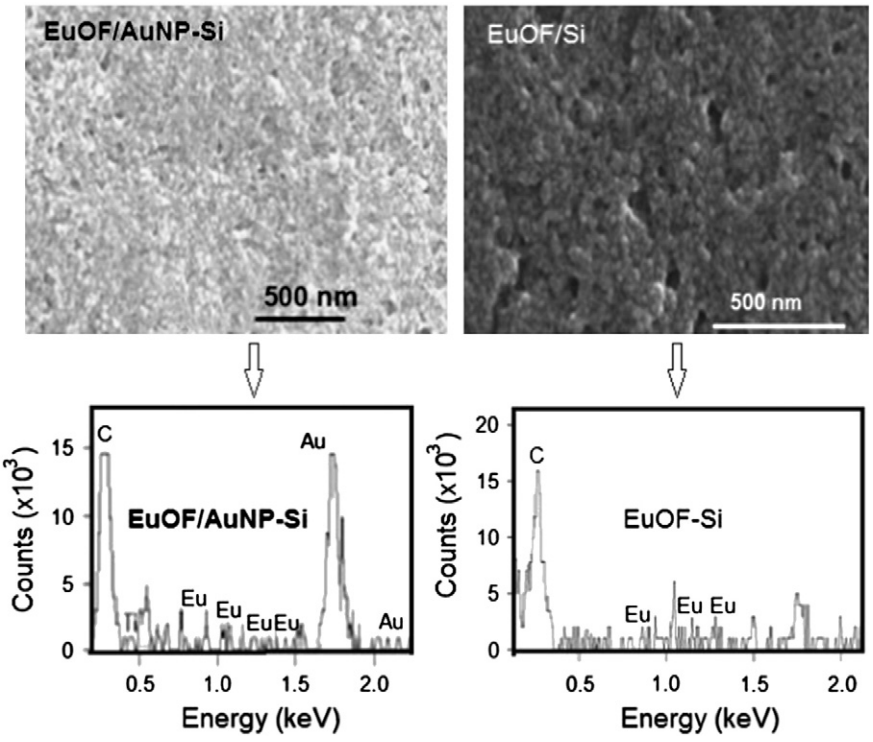

Fig. 1. FE-SEM (morphological) and EDX (elemental) analysis of EuOF/AuNP-Si and EuOF/Si thin films.

2. Experimental details

2.1. Chemicals and equipment

Europium (III) nitrate pentahydrate, 1,3,5-tris(4-carboxyphenyl) benzene (H_3BTB), carboxylated gold nanoparticles (15 nm diameter), 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride, N-hydroxysulfosuccinimide, triethylamine, aminopropyltriethoxysilane (APTES) and other required solvents were high purity grade chemicals from Sigma Aldrich/Merck/Fisher Scientific. Boron doped p-type (111) silicon wafers (resistivity 10^{-3}–40 Ω cm) were products of Sigma Aldrich. X-ray diffraction (XRD, Shimadzu 6000) with tungsten (W) as X-ray source (2 kW type, broad focus 2.7 kW) using wavelength of 1.54060 Å of CuKα radiation was used. Morphological and elemental studies were carried out with field emission scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (FE-SEM–EDX, Hitachi 4300/SN). For EDX studies, the system was operated at 15 kV (X-ray take-off angle = 30°, emission current = 36,000 nA) keeping the working distance of 15 mm. Atomic force microscopy (AFM, Park Systems XE-NSOM) in non-contact mode was used to study the topology and film roughness. Scan rate for these studies was kept to 0.5 Hz and set point was maintained to 10.12 nm. Nitrogen isotherms were recorded using Micromeritics ASAP- 2020 sorptometer at liquid nitrogen temperature. The samples were degassed at 120 °C for 20 h before taking the adsorption measurements. Thermogravimetric (TGA) analysis was carried out on SDT Q600 system (TA Instruments) within temperature range of 25 °C to 900 °C (step 10 °C/min). The optical properties were measured by Varian's Cary 5000 UV–Vis spectrophotometer and photoluminescence spectra using Varian's Cary Eclipse fluorescence spectrophotometer.

2.2. Growth of EuOF/AuNPs

17.12 mg of $Eu(NO_3)_3$ and 17.54 mg of 1,3,5-tris(4-carboxyphenyl) benzene (H_3BTB) were mixed in 30 mL methanol and continuously stirred for 10 minutes. 100 μL of the –COOH functionalized AuNPs was pre-added in the above reaction mixture. To initiate the growth of the desired product, triethylamine was slowly added and the contents

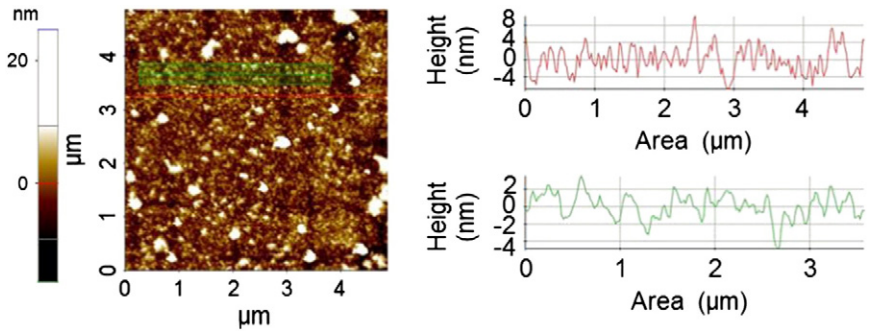

Fig. 2. AFM topography image and film roughness (area and line analysis) determination of EuOF/AuNP-Si thin film.