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Formation and Characterization of Europium Bisphthalocyanine Organic Nanowires by Electrochemical Deposition

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Abstract: Europium bisphthalocyanine ($EuPc_2$) nanowires were prepared by electrochemical deposition method. Scanning electron microscopy (SEM) images show the evolution of the morphologies of nanowires obtained under different deposition time (T_d). The optical properties of europium bisphthalocyanine films were studied by UV-Vis absorption spectra. The morphology of $EuPc_2$ nanowires could be controlled by changing deposition conditions, which provides a useful method to make organic nanowires.

Keywords: Europium bisphthalocyanine, electrochemical deposition, organic nanowires.

Bisphthalocyanines, a kind of organic semiconductors withπ-conjugated macrocycles, have remarkable properties such as nonlinear optics and electrochromism, *etc.*, and show wide applications in the fields of gas sensors, solar cells and other optoelectronic devices[1].

As we know, the properties of many nanostructure materials are substantially different from those of bulk materials. Therefore, organic nanostructures, including nanowires, nanotubes, nanopaticles and nanorods, have drawn a significant amount of attention[2]. A lot of approaches have been developed to prepare organic nanostructures, such as self-assembly, chemical reaction, solution precipitation, and milling. However, to our knowledge, few efforts have been made to prepare organic nanowires by chemical deposition method[3]. In this paper, we report the preparation and characterization of europium bisphthalocyanine ($EuPc_2$) nanowires by using electrochemical deposition approach, and their optical properties as nanowires.

Europium bisphthalocyanine ($EuPc_2$) with sandwich structure was synthesized and purified according to the literature[4]. The electrochemical deposition solution was prepared by adding trifluoroacetic acid (TFA) into the solution of $EuPc_2$ in polar solvent, which became transparent due to the coordination of protons to periferic aza nitrogen atoms of the phthalocyanines rings[3b].

$EuPc_2$ thin film was grown by using an indium/tin oxide (ITO)-coated glass and a

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graphite plate as the cathode and anode electrodes, respectively. Direct current voltage was applied between the two electrodes. $EuPc_2$ films were deposited on ITO glass substrates for different electrolysis time: 0.5, 3, 8, 12 mins. The morphology was studied by using a JSM-5510 scanning electron microscope. UV-Vis absorption was recorded on a CARY Bio100 spectrophotometer to investigate the optical properties.

Figure 1 shows the SEM images of $EuPc_2$ films formed by electrochemical deposition for different electrolysis time. It is very clear that the morphology depends heavily on the electrolysis time Td. In the initial deposition stage with Td shorter than 1 min., the film consists of microcrystallites distributed randomly in the plane of the substrate. The microcrystallites increase in size with increasing Td, and nanowires are formed for Td>3 mins. The ITO substrates are completely covered by $EuPc_2$ nanowires between which there are depleted zones, suggesting an Ostwald ripening. The diameters of the nanowires for Td = 3, 8, 12 mins are 30, 46, and 66 nm, respectively, indicating that the nanowires are enlarged with increasing Td. The nanowires become curved clearly for Td > 8 mins when compared with the original straight ones. It means that a compact film containing $EuPc_2$ nanowires can be obtained for Td > 8 mins.

The UV-Vis absorption spectra of $EuPc_2$ in $CHCl_3$ and the protonated $EuPc_2$ in $CHCl_3$/TFA mixed solution before and after electrolysis for 20 mins are recorded in **Figure 2**. $EuPc_2$ in $CHCl_3$ shows Soret band and Q band absorptions, which coincide with the literature[5]. Upon adding TFA to the $EuPc_2$ solution, Q band of $EuPc_2$ undergoes red shifts from 671 to 721 nm and 605 to 694 nm. These shifts can be interpreted in terms of protonation of each phthalocyanine ring [6]. The absorption spectrum of $EuPc_2$ solution in $CHCl_3$/TFA mixed solution after deposition for 20 mins is almost identical to that of the original protonated solution with the exception of a slight blue shift from 694 to 688 nm due to the partly deprotonation in the solution.

The absorption spectra of $EuPc_2$ nanowires formed by electrochemical deposition for different electrolysis time are presented in **Figure 3**. All the $EuPc_2$ nanowires show absorptions at Soret and Q bands. The absorption at Q band exhibits only one broad peak, which is however split into several peaks for $EuPc_2$ in solution. With increasing Td from 3 to 12 mins, Q band is blue shifted by 16 nm from 671 to 655 nm, indicating the existence of H-aggregate bisphthalocyanines, which is formed when bisphthalocyanines arrange themselves in a near vertical stack[7, 8] and the stack axis is parallel to the substrate.

In conclusion, $EuPc_2$ nanowires on ITO-coated glasses have been successfully obtained by using electrochemical deposition method. The evolution of morphology for $EuPc_2$ films with increasing electrolysis time can be analyzed by scanning electron microscopy (SEM). H-aggregate is convinced in $EuPc_2$ nanowires by combining UV-Vis absorption and SEM measurements. Further work is being done to study the optical and optoelectronic properties of $EuPc_2$ nanowires. Electrochemcial deposition provides a useful method to grow organic nanowires.

Figure 1 SEM images of $EuPc_2$ nanowires and microcrystallites formed by electrochemical deposition under applied voltage of 30V/cm for different electrolysis time: (a) 0.5 mins, (b) 3 mins, (c) 8 mins, and (d) 12 mins

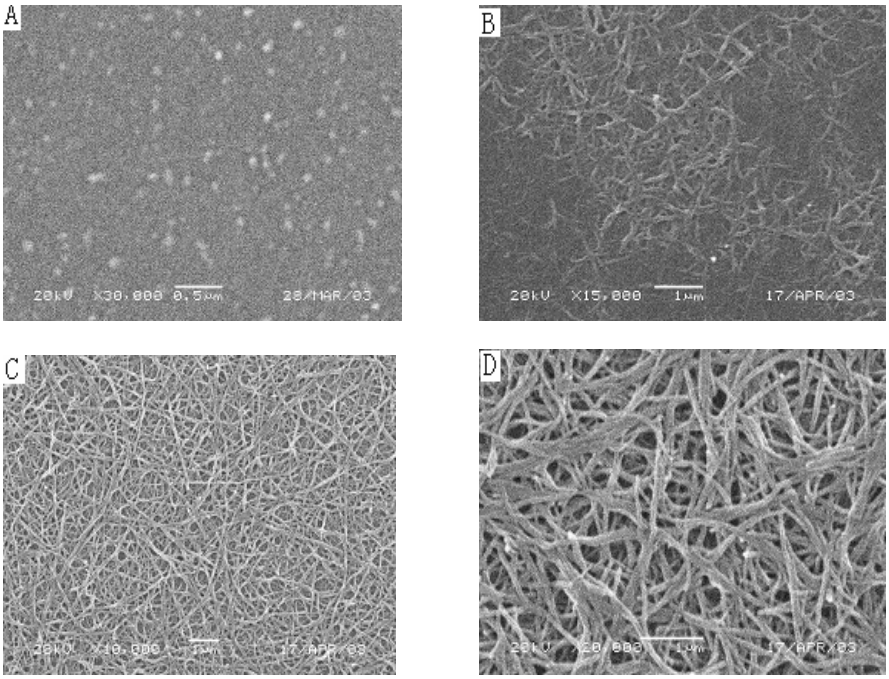


Figure 2 UV-Vis absorption spectra of $EuPc_2$ in $CHCl_3$ (a) and the protonated $EuPc_2$ in $CHCl_3$/TFA mixed solution before (b) and after electrolysis for 20 mins (c)

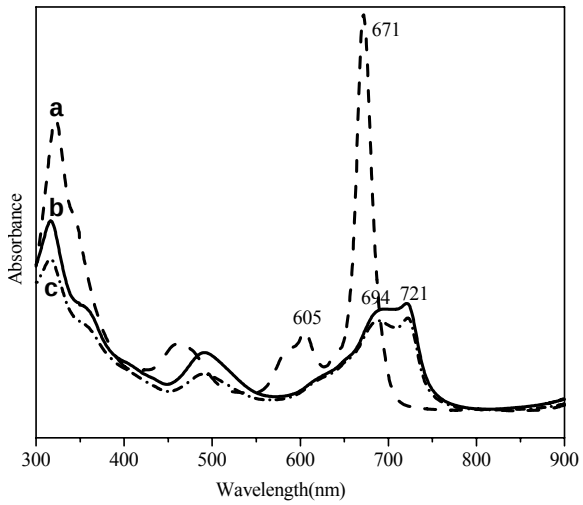
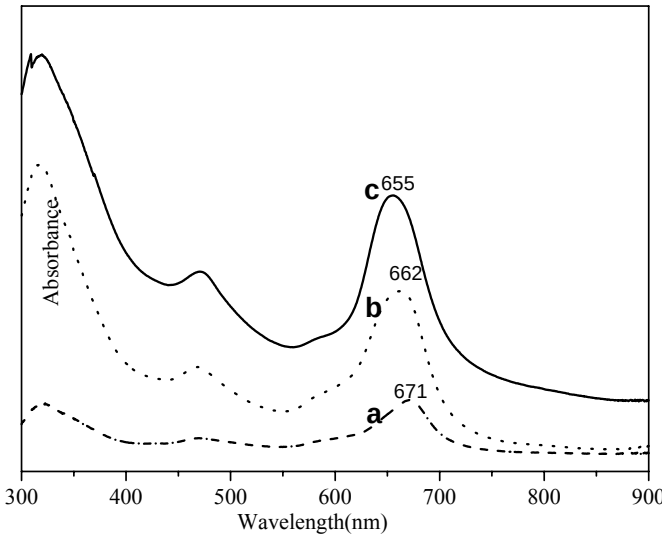


Figure 3 UV-Vis absorption spectra of $EuPc_2$ films formed by electrochemical deposition under applied voltage of 30V/cm for different electrolysis time: (a) 3 mins, (b) 8 mins, and (c) 12 mins.



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