

多金属氧酸盐四硫富瓦烯衍生物荷移盐超薄导电膜

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Conducting Thin Film of Charge-transfer Salt Based upon Polyoxometalate and Organic Donor ET

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The conducting thin film of charge-transfer salt based upon polyoxometalate $[\text{VW}_5\text{O}_{19}]^{3-}$ and bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF or ET) was fabricated on the gold substrate by electrochemical approach. The sub-micronic grains uniformly covering the gold plate was evidenced by scanning electron microscope (SEM). The film of charge-transfer salt exhibits semiconducting behavior with a room-temperature conductivity $4.8 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$.

Keywords: polyoxometalate charge-transfer salt ET conducting film

0 Introduction

The charge-transfer (CT) salts based planar π -electron donor ET as a class of molecule-based materials have been studied extensively in the past twenty years, because of their metallic conductivity and even superconductivity^[1-6]. In recent years, polyoxometalates

have attracted more and more attention in various fields such as electrochemistry, photochemistry, catalysis and material science, owing to their chemical, structure and electronic versatility^[7-9]. Polyoxometalates (POM) which in some cases can be reduced by one or more electrons giving rise to mixed valency clusters, have been found to be extremely versatile in-

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organic building blocks for the construction of functionally molecule-based materials. They can act as inorganic counterions with organic electron donor ET for new types of charge-transfer salts combining two or more functional properties^[9-14], such as coupling conductivity or semiconductivity with magnetic properties^[15-17]. The studies of this kind of CT salts have concentrated mostly on single crystals. However, these crystals are fragile, insoluble, and extremely difficult to process, resulting in their technological limitation and precluding their practical use^[4].

In order to prepare these CT salts for potential advantages in device application, such as Diodes, light emitting diodes, and field effect transistors, the most desirable form of the material is that of a thin film^[18]. Thus, from both the scientific and technical points of view, it is interesting to prepare the films of the charge-transfer salts with ET and POM. However, to the best of our knowledge, the organic-inorganic thin films of ET salts are based largely on the system from ET with highly volatile halogen constituents such as ET/I₂, while that based on other systems are relatively rare^[18-21]. The films of ET charge-transfer salts based on polyoxometalates as acceptor have never been described. In this communication, we report the first example of conductive thin film of charge-transfer salt based on inorganic polyoxometalates and organic donor ET by electrochemical approach, to overcome the known technological limitations of single crystals. The film was characterized by using Raman microscopy, X-ray photoelectron spectroscopy (XPS), electron spin resonance spectroscopy (ESR). The surface morphology of the film was observed by scanning electron microscopy (SEM). The conductivity of the film was also measured.

1 Experimental

Electrodeposition was carried out with gold plates (~10×5×0.2 mm³) as anodes and platinum wires (1 mm diameter) as cathodes. ET in 1,1-dichloroethane, mixed with (NBu₄)₃VW₅O₁₉ (prepared following previously described procedures^[22]) in acetonitrile, was

poured into the electrobath with no glass frit between cathode cell and anode cell to ensure reproducible experimental conditions and to avoid from any overpotential build-up. The cleaned platinum wire sealed into the bottom of cathodes cell, and the cleaned gold electrode sealed into the bottom of anode cell were connected to an external constant current power supply. At 22 μA·cm⁻², a densely black thin film was coated on the gold electrode after 2 h.

2 Results and Discussion

The Raman spectrum of the thin film in the 400~2 000 cm⁻¹ range is shown in Fig.1. Four peaks are seen in the figure, which can be assigned to the ν_2A_g , ν_3A_g , ν_9A_g and $\nu_{10}A_g$ modes of the ET donor molecules. The peaks in 1 450 cm⁻¹ and 1 475 cm⁻¹ are the totally symmetric (A_g) stretching vibrations of central and ring bands respectively. From the peaks value, and previous reported Raman spectra of charge-transfer salts with ET or its analogues, the thin film is clearly identified as the (ET)₅VW₅O₁₉^[23].

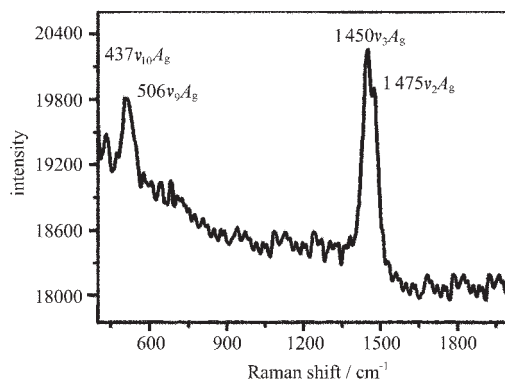


Fig.1 Raman spectrum of the conducting film of (ET)₅VW₅O₁₉ on a gold plate at room temperature

XPS analysis of the film gives an atomic W/C ratio of 0.095, quite close to the theoretical value (0.1). The XPS binding energy of the S(2p) band for the thin film is 164.1 eV, which differs from that of the individual ET 163.6 eV^[24]. This indicates that charge transfer from donor to acceptor takes part in the film. The result further confirms that thin film of (ET)₅VW₅O₁₉ is indeed formed by using electrochemical approach.

In order to further characterize the (ET)₅VW₅O₁₉

of thin film, electron spin resonance(ESR) experiment was carried out at 293 K. The ESR spectrum of the thin film on a gold substrate shown in Fig.2. exhibits one line of a 25G (peak-to-peak in width) species with g factor 2.001, typical of the free radical of ET, in accordance with that of charge-transfer salts based on ET in powder form. This characteristic line confirms the partial oxidation of the ET, because these donor molecules in their neutral state are inactive to ESR.

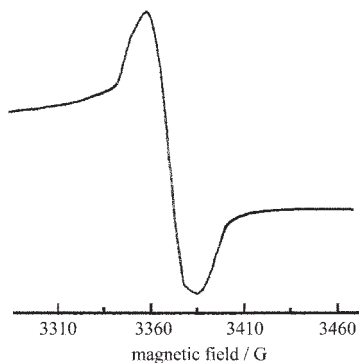


Fig.2 ESR spectrum of the thin film of $(\text{ET})_5\text{VW}_5\text{O}_{19}$ at 293 K

The conductivity of the thin film vertical to the substrate is $4.8 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$, exhibiting semiconducting behavior. It is calculated according to the following equation from the resistance value measured by electrometer.

$$\text{conductivity} = 1/\rho = l / (R \times A)$$

where ρ is the resistivity of the conductor; l is the thickness of the thin film (29 μm) estimated by image of SEM for the thin film; A is the interfacial contact area between the film and the contacting silver paste; and R is the resistance measured by electrometer. This conductivity value is about four order of magnitude lower than that of the corresponding $(\text{ET})_5\text{VW}_5\text{O}_{19}$ crystal ($1.4 \times 10 \text{ S} \cdot \text{cm}^{-1}$). This result may be due to two possible events, one is that some ion salt of ET existed among grains of $(\text{ET})_5\text{VW}_5\text{O}_{19}$; another is that the conducting layers were constructed by highly oriented nanocrystals with the crystallographic c^* axis vertical to the film surface. Sequently, the conductivity of the thin film vertical to the substrate decreased largely^[25].

Surface morphology of the conducting film was obtained by SEM. Fig.3 shows the SEM image of the conducting film. As can be seen, the microcrystallines

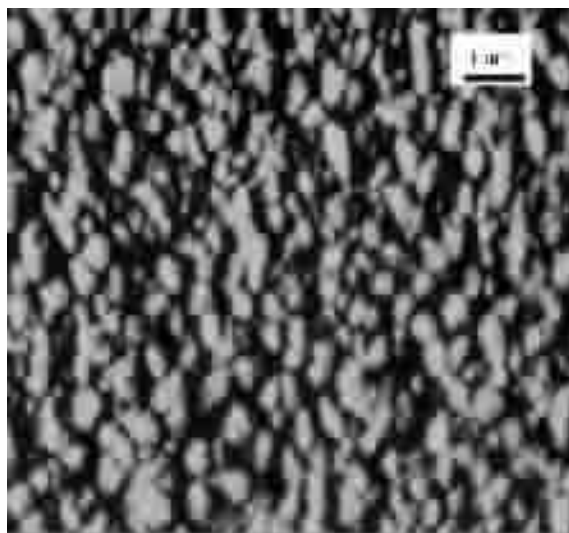


Fig.3 SEM image of the thin film of $(\text{ET})_5\text{VW}_5\text{O}_{19}$ on a gold electrode

with mean microscopic dimensions of 200~400 nm are dispersed randomly and are oriented a relatively smooth surface on the substrate. The microcrystalline network fully covers the entire substrate surface, providing good contacts between microcrystallines. As we know, the contacts between the microcrystallines have a great influence on the film transport property. Good contacts allow well conductivity along the surface^[25]. Therefore, the conducting film is expected to exhibit good conductive behavior along the surface, though we have not been able to measure the conductivity along the surface of thin film in this work. The results provide an implication that semiconducting thin film could be fabricated by the organic donor ET and inorganic acceptor polyoxometalate.

The film is environmentally stable in the period of this work (several months) as the properties of the film mentioned above has hardly changed during this period. The thermal stability of the film contains a topic for future study.

3 Conclusion

In conclusion, it is the first report of the conducting thin films of charge-transfer salt based on polyoxometalate as acceptor and BEDT-TTF as donor successfully prepared on the gold substrate by using electrochemical approach. The thin film displays a

semiconductor behavior. This opens a way to fabricate processible functional film materials to overcome the known technological limitations of single crystals of charge-transfer salts containing polyoxometalate.

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