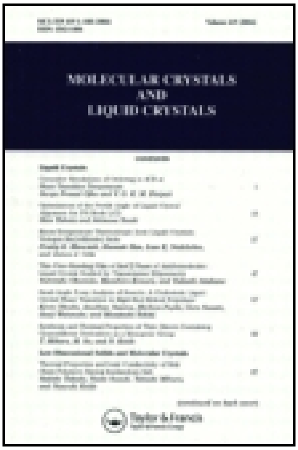

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Electrochemical Polymerization of Fullerene in Organic Solvents

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The new method of fullerene polymerization initiated by electrolysis of C_{60} toluene-DMFA solutions in the presence of supporting electrolytes at stationary or rotating Pt, graphite, stainless steel electrodes have proposed. Formation of insoluble in toluene polyfullerene suspension is observed during the electrolysis at the fixed potential which is similar to the third wave of fullerene reduction. The suspension may be deposited on the transparent ITO electrodes or silicon substrate for producing the fullerene-based nanostructures. According to scanning electron microscopy the polymeric form of C_{60} consist a piece of films and the linear particles, which have a length about 100 μm. Mechanism of polymerization includes the anion – radical initiating particles $(C_{60}{}^{n-})^{\bullet}$ formation followed by the consequential reduction of C_{60}.

Keywords: fullerene; electrochemical polymerization; electron scanning microscopy

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INTRODUCTION

Design of production method of polymeric forms of fullerene C_{60} is topically now due to develop nanotechnology and to need a production photosensitive materials for nanolitography. The composites of conducting polymers with fullerenes and polyfullerenes are promised materials with high photoconductivity. Significance delocalization of electrons in C_{60} under photoinduced transition brings to appear free charge carrier and stimulate conductivity [1-6].

The known methods of fullerene polymerization initiated by photo-excitation, electron irradiation , high pressure and chemical reactions require the hard reaction conditions and are very time consumption (photoexcitation time for fullerene water dispersion is over 52 h [3]). From the other hand fullerene molecules as an excellent electron acceptor have ability to electrochemical reduction at electrode surface in the organic solvents solution. Process of C_{60} electrochemical reduction in-cludes 3 or 4 consequent peaks of cathodic current, peaks position are depended on electrode materials and solvent nature. Based on these properties of fullerene molecules the possibility of electrochemical polymerization of fullerene could be supposed. Moravskyi A.P. [7] obtained polymerized fullerene film by electropolymerization of origi-nal fullerene film, which have been deposited onto an electrode before.

The present paper is devoted an electropolymerization of fullerene from solution without previously deposition of fullerene films onto an electrode.

EXPERIMENTS

Fullerene C_{60} has been produced by arc method and purified according wideused techniques. Purity of C_{60} was determined no less 98.5 wt.% by mass-spectrometry. The solvents have been purified by distillation before used.

Electrochemical investigation was carried out by cyclic voltammetry measurements and potentiostatic polarising curves in three-com-partments electrochemical cell at T = 298 K. Stationary or rotating pla-tinum, graphite, stainless steel electrode were used as work one, the counter electrode was platinum, and reference electrode was Ag/AgCl, in 0,1 M tetrabutylammonium chloride (TBACl) in DMF. The fulle-rene solution was prepared from toluene –DMF (4:1) solvents, as sup-porting electrolyte tetrabutylammonium perchlorate (TBAP) has been used.

For investigation fullerene precipitate up to and after electrolysis it had been washed by DMF solvent and deposited on conductive surface SnO_2 by solvent evaporation in vacuum.

Microphotography of deposition was made by Scanning Electron Microscopy ISI-DS-130. 150 and 250-fold magnification were used.

RESULTS AND DISCUSSION

The cyclic voltammogram of the electrochemical reduction of pure fullerene at scan rate v=0,2...2,0 V/c in toluene-DMF solution exhibits three reversible one-electron reduction steps (see Figure 1). These data agree well with literature [1,7-9]. The electrochemical oxidation-reduction proccess of fullerene under potentiodynamic conditions doesn't provide the formation of polymeric fullerene forms.

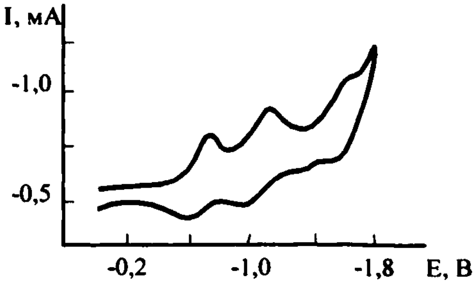

FIGURE 1. CVA of 0.001 M fullerene on Pt electrode in 0.1 M TBAP toluene-DMF (4:1) solution. V=200 mV/s

By the method of the potentiostatic polarized curves (see Figure 2) we revealed that under cathodic polarization of platinum, steel, or graphite electrodes in the range current density i = 5-8,5 мA/cm^2 or potentials E = - (1,7-1,9) V electrochemical reduction of fullerene take a place. Particles with ability to initiate polymerization process appear at these ranges of potential and current under stationary conditions (without scanning potential or current). The reduction process follows by depression of the background current. After 20-40 min of electrolysis duration under galvanostatic or potentiostatic conditions the appearance of insoluble suspension of polymerized fullerene C_{60} was observed. The color of suspension is brown that agree with [6,10] .

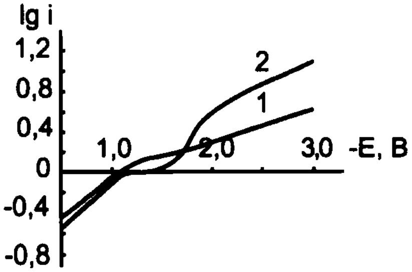

FIGURE 2. Polarization curves, obtained on Pt electrode in 0.1 M TBAP toluene-DMF (4:1) solution: (1) - without fullerene, (2) – in presence 7 10^{-4} M fullerene C_{60}

Based on these data it could be assumed that mechanism of fullerene polymerization includes the anion - radical initiating particles (C_{60} $^{n-}$)$^{\bullet}$ formation followed by the consequential electrochemical reduction of C_{60}. The depression of current on the first stage of process may be caused by the absorption of fullerene onto electrode surface (see Figure2) . Such explanation is in good agreement with [7], where the polymerization of fullerene film deposited onto electrode was carried out at potential negative to second cathodic wave.

According to scanning electron microscopy the polymeric form of C_{60} includes pieces of films as well as linear particles, which have an outer diameter 100-200 nm and a length about 100 μm. Also numbers of nuclei are observed on SEM image.

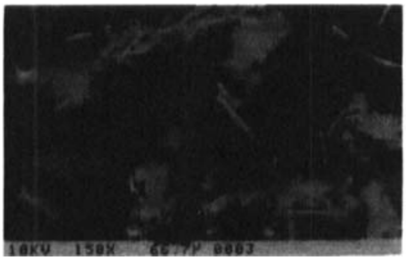

FIGURE 3. SEM microphotography of polyfullerene particles on current track after electrolysis of 10^{-3} M fullerene C_{60} solution on platinum electrode into mixed toluene-DMF (4:1) solvent with 0.1 M TBAP.. Electrolysis duration 40 min, current density i = 5 MA/cm^2 , 150-fold magnification.

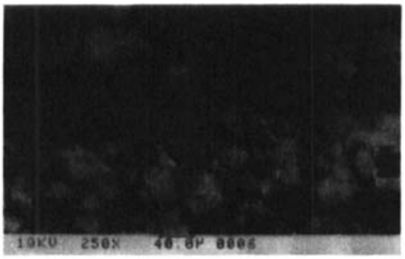

FIGURE 4. SEM microphotography of fullerene C_{60} dispersion before electrolysis, obtained on SnO_2 surface after evaporation of solvent. 250-fold augmentation.

To compare the morphology of polymerized and original forms of fullerene the microphotography of original fullerene films, which had been produce by evaporation of solvents, was made (see Figure 4). The morphology of those two fullerene forms is quite different. The films of original fullerene have more rough structure and consist of sphere grains with diameters about 40 µm. The surface of polymeric fullerene form is smoother. Such polymeric suspension can be deposited on transparent ITO, SnO_2, or single crystal Si-electrodes to produce

nanostructure pattern based on polyfullerenes according the method proposed in [10].

CONCLUSIONS

It was established that electropolymerization of fullerene from toluene-DMF solution at stationary potential, which closed to third cathodic wave of fullerene reduction is took a place. The polymeric fullerene suspension could be deposited onto conductive substrates to future used in nanotechnology applications.

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