Formation of Whiskers on the Electrode Surface by the Electrolysis of 3,3′,5,5′-Tetramethylbenzidine

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Crystalline whiskers were produced on the electrode surface by the electrolysis of 3,3′,5,5′-tetramethylbenzidine.

Electropolymerization techniques are used to produce electroconductive polymers on the electrode surface and great attention has been focused on them recently.[1—6] Most electropolymerized polymers are amorphous, and there are few reports on the formation of single crystals by these techniques. However, electrolysis techniques (electrocrystallisation) are applied to the growth of single crystals of charge transfer complexes,[7—10] some of which exhibit superconductivity.[11] We now report the formation of needle-like crystals (whiskers) by the electrolysis of 3,3′,5,5′-tetramethylbenzidine (TMB).

TMB was dissolved in 0.1 M aq. H_2SO_4 at 60 °C under an ultrasonic field to form an acidic 0.1 M solution. Figure 1 shows cyclic voltammograms for the electrolysis of TMB at 60 °C. Two anodic peaks appear at 0.6 and 1.3 V [*vs.* standard calomel electrode (S.C.E.)], but no corresponding cathodic peak appears. The solution gradually turned yellow as the reaction progressed, with the electronic absorption spectrum maximum at 460 nm. Such an absorption is characteristic of the radical cation of benzidines,[12] the intermediate product in the electrolysis of TMB. By increasing the number of sweeps, needle-like products appeared on the Pt electrode surface, which grew further into whiskers. Figure 2 shows a photograph of whiskers growing from the Pt wire electrode; the radialized growth of the whiskers is seen under the surface of the solvent. Long whiskers (>1 cm) are produced easily by slow galvanostatic electrolysis on a fine Pt wire electrode, and at a lower concentration of TMB, 0.01 M, similar whiskers are formed by electrolysis.

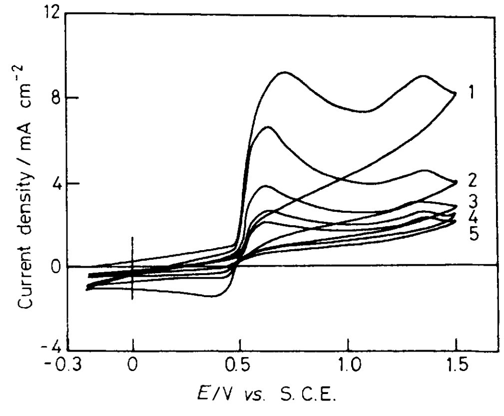

Figure 1. Cyclic voltammograms for the electrolysis of 3,3′,5,5′-tetramethylbenizidine (TMB), 0.1 M TMB/0.1 M aq. H_2SO_4, 60 °C. Sweep rate, 60 s/V.

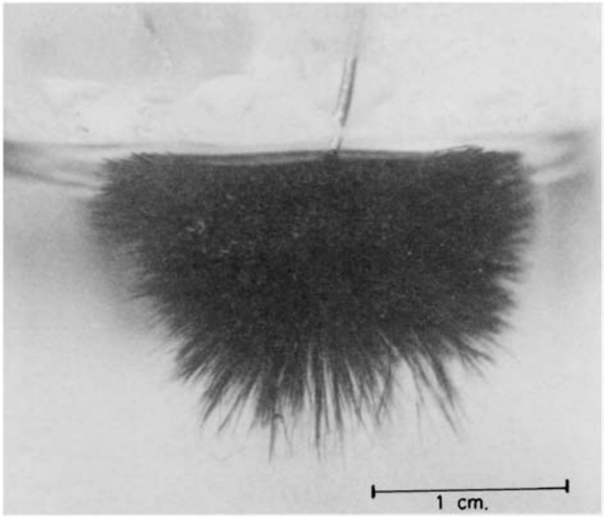

Figure 2. Formation of whiskers on the Pt wire electrode.

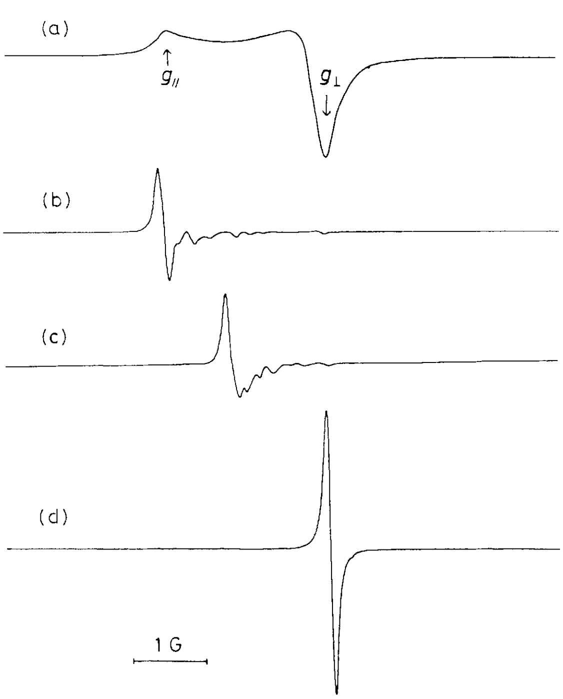

Figure 3. E.s.r. spectra of the whiskers: (a) whiskers crushed into a polycrystalline sample; (b) the long axis of a whisker is perpendicular to the magnetic field; (c) the angle between the long axis of a whisker and the magnetic field is 45°; (d) the long axis of a whisker is parallel to the magnetic field.

The *X*-ray diffraction measurements of these whiskers show sharp peaks attributable to a crystalline structure. Scanning electron microscopy shows that each whisker (*ca.* 50 μm) is the aggregate of many fine fibrils (*ca.* 0.5 μm) rather than a single crystal. These fibrils all grow in the same direction. The whiskers were black or black–purple, and almost insoluble in usual organic and inorganic solvents. The small proportion of soluble component in the whiskers was analysed by g.p.c. The g.p.c. elution pattern shows that the molecular weight of these components is of a dimer. The elemental analysis indicates that the whiskers have *ca.* one SO_4^{2-} anion for each benzidine unit.

The crystallinity should be reflected in the electric and magnetic properties of the electropolymerized product. We have taken e.s.r. spectra of the whiskers and, in general, e.s.r. signals of electroconductive polymers such as polyacetylene and polyaniline are singlet and isotropic because of their amorphous structure,[13—15] but the whiskers have a crystalline structure and so an anisotropic e.s.r. spectrum was expected.

Figure 3 shows the e.s.r. spectra of the whiskers; spectrum (a) is of a polycrystalline sample produced by crushing some of the whiskers. The signals appear around a similar magnetic field strength to those for DPPH [1,1-diphenyl-1-(2-picryl)-hydrazyl], so it is reasonable to assume that the radical free electrons are centred on nitrogen. The line shape of spectrum (a) is strongly indicative of *g*-factor anisotropy, typical of that for axial symmetry. From spectrum (a), anisotropic *g*-factors were determined as follows: $g_{\perp}$ (where the *z*-axis is perpendicular to the magnetic field) = 2.0024, and $g_{\parallel}$ (where the *z*-axis is parallel to the magnetic field) = 2.0037.[16—18]

The e.s.r. spectra for single whiskers are shown in spectra (b)—(d) in Figure 3. The peak-to-peak width, ΔH_{pp}, of the signals in Figure 3 is quite narrow and in spectrum (d), ΔH_{pp} is estimated to be 0.1 G ($1G = 1 \times 10^{-4}$ T); such a value is extremely small even in comparison with DPPH ($\Delta H_{pp} = 1.3$ G). Spectrum (b) shows the e.s.r. signal with the magnetic field perpendicular to the long axis of the whisker (whisker's growing direction); $g = 2.0038$. In spectrum (d), the long axis of the whisker is parallel to the magnetic field; $g = 2.0024$. When the angle between the magnetic field and the long axis is 45°, spectrum (c), the signal appears in the middle; $g = 2.0032$.

We are grateful to Professor M. Iwaizumi and Dr. Y. Ooba for their useful suggestions about the interpretation of the e.s.r. spectra.

Received, 10th August 1987; Com. 1168

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