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A new morphology of copper 7,7,8,8-tetracyano-*p*-quinodimethane

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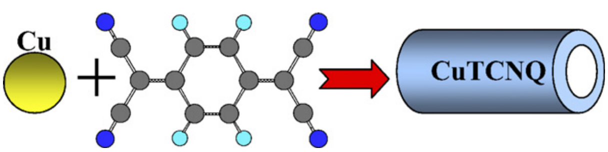
Abstract

Morphology control is a long-standing problem that needs to be solved for making the switching mechanism of copper 7,7,8,8-tetracyano-*p*-quinodimethane (CuTCNQ) understood all the time, but up till now how many morphologies CuTCNQ possesses and which morphology should be responsible for the on/off switching phenomenon are still unclear. A new morphology of CuTCNQ, namely the tubular structure, has been obtained and characterized in our experiment, whose formation mechanism has also been investigated. Through characterizing, we can conclude that the tubular structure belongs to the phase I, which can be further confirmed by the electrical measurements. From the *I–V* plots, the carrier mobility of the tubular structure is estimated to be $\sim$0.1 $cm^2\ V^{-1}\ s^{-1}$, which suggests the potential application of CuTCNQ in devices.



Keywords: CuTCNQ; Tubular structure; Nanojunction

1. Introduction

Copper 7,7,8,8-tetracyano-*p*-quinodimethane (CuTCNQ) has attracted attention since 1970s due to its potential application in electronics/photonics (Azcondo et al., 1997; Benson et al., 1983; Borissov, 1987; Fan et al., 2003; Gong and Osada, 1992; Gu et al., 1993; Gu et al., 1995, 1998; Hoshino et al., 1986; Jortner and Ratner, 1997; Kaur et al., 1998; Kamitsos et al., 1982; Kamitsos and Risen, 1983; Liu et al., 2005a; Mahler et al., 1996; Matsumoto et al., 1991; Oyamada et al., 2003; Potember et al., 1979, 1980, 1982a,b; Sato et al., 1990; Tour, 2003; Wachtel et al., 1995; Yamaguchi and Potember, 1996; Yamaguchi et al., 1991), such as in switch and memory devices. It is known that CuTCNQ forms multi-morphologies, such as wires, rods, plates, amorphous structure, etc. (Cao et al., 2005; Duan et al., 1989; Heintz et al., 1999; Hoagland et al., 1993; Liu et al., 1996a,b,c; Liu et al., 2005a; Neufeld et al., 2003; Sun et al., 1997, 1998) and that different morphology exhibits different property (Duan et al., 1989; Heintz et al., 1999). However, how many morphologies CuTCNQ possesses and which morphology should be responsible for the on/off switching phenomenon are still unclear up till now. In our experiment, a new morphology of CuTCNQ, namely the tubular structure, has been obtained and characterized. The phase and formation mechanism of CuTCNQ with the tubular structure have been investigated, and its electrical properties have also been measured through nanojunctions. The demonstration of the tubular structure and the identification of its electrical properties benefit to clarify the polymorphs of the charge-transfer complex, and can also establish good foundation for its further application in molecular electronics.

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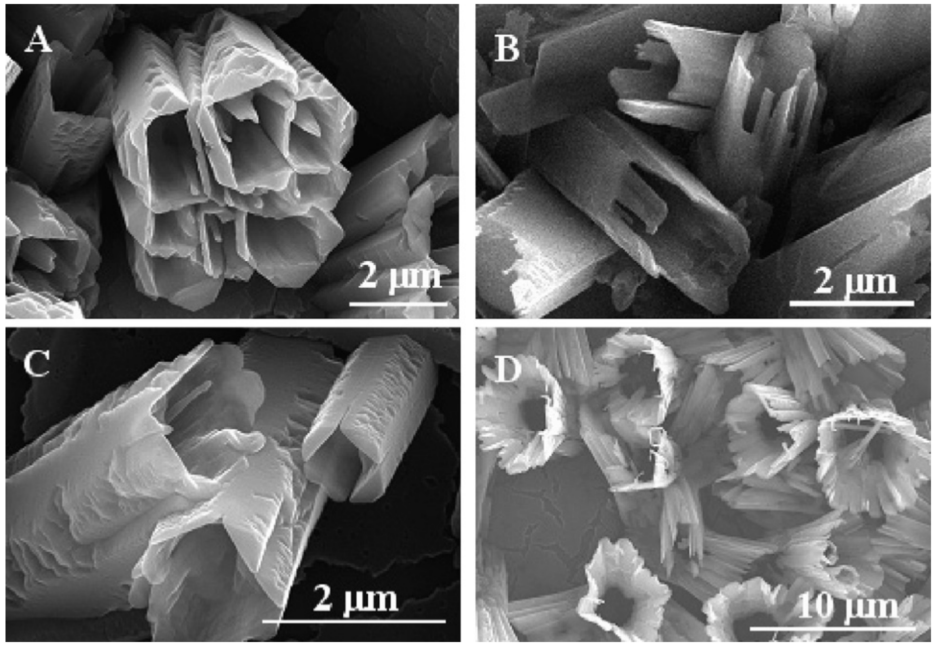

Fig. 1. Tubes of CuTCNQ on different substrates: (A) Cu, (B) Au, (C) Si and (D) quartz.

2. Experimental

TCNQ (98%) was purchased from Aldrich and re-crystallized twice from acetonitrile prior to use. Copper plates, gold, quartz and silicon wafers were used as substrates in our experiment. With the exception of copper plates, all the other substrates were cleaned successively with concentrated sulfuric acid, pure water, hot acetone, hot ammonia–hydrogen peroxide solution (ammonia:hydrogen oxide:water, l:l:5), pure water, pure ethanol and finally by argon plasma for 15 s. After that, copper layers were deposited onto the substrates by vacuum deposition or electroplating. Copper plates were cleaned only with concentrated sulfuric acid and then by argon plasma for 15 s. The tubular structure of CuTCNQ used in this study was synthesized by ‘‘spontaneous electrolysis’’ (Potember et al., 1979, 1980, 1982a,b; Sato et al., 1990; Gu et al., 1993; Wachtel et al., 1995; Yamaguchi and Potember, 1996; Fan et al., 2003; Liu et al., 2005a), and the products were characterized by UV–vis (U3010) spectroscopy, Fourier transform Raman (FT-Raman) spectroscopy (PE2000), X-ray photoelectron (XPS) spectroscopy (ESCALab220I-XL), X-ray diffraction pattern (XRD) (D/max2500) and scanning electron microscopy (SEM) (Hitachi S-4300). Au nanogap electrodes were prepared by electron beam lithography on Ti-primed (∼50 Å) SiO_2 substrates (300 nm), and the gap width of the nanogap electrodes was around 100 nm. The current–voltage (*I*–*V*) characteristics were recorded with a Keithley 4200 SCS and a Micromanipulator 6150 probe station in a clean and shielded box at room temperature.

3. Results and discussion

The tubular structure of CuTCNQ as shown in Fig. 1 was synthesized by dipping the substrate covered with a copper layer into the TCNQ/acetonitrile solution. This morphology of CuTCNQ has never been observed previously. Seen from Fig. 1, we can find that the tubes grown on different substrates only have some differences in the shape and the diameter, which means that the formation of the tubular structure is weakly dependent on the substrates and that it is the intrinsic property of CuTCNQ itself. Through controlling the reaction conditions carefully, the tubular structure can be formed in large area on substrates (Fig. 2).

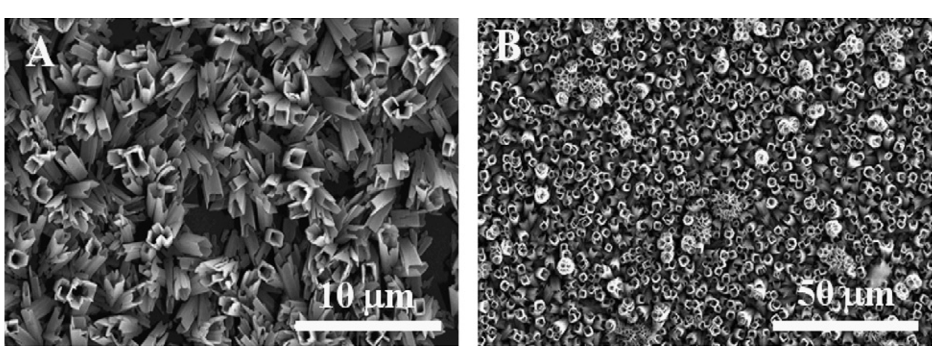

Fig. 2. The tubular structure formed on substrates in large area.