

Tuning Reaction Processes for the Synthesis of Micron and Nanometer Sized, Single Crystalline Lamellae of Copper 7,7,8,8-tetracyano-*p*-quinodimethane (Phase II) with Large Area

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ABSTRACT

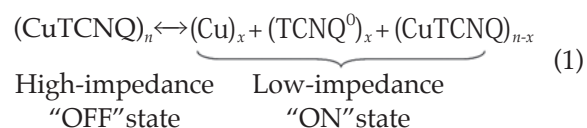
Two simple methods have been demonstrated to obtain large area, single crystalline lamellae of copper-7,7,8,8-tetracyanoquinodimethane (CuTCNQ). The formation of the lamellae was a result of fine tuning of the processes during the synthesis processes of CuTCNQ phase II. This facile synthesis of large area single crystalline lamellae suggests bright prospects for the study and understanding of the electrical switching of CuTCNQ by using single crystals of its phase II, and future applications of the material in memory and switching devices.

KEYWORDS

CuTCNQ, lamellae, single crystals, phase II

Molecular materials with bistable electrical switching behavior are particularly attractive due to their potential applications in ultrahigh density memory devices and switches [1–6]. The bistable states phenomenon of copper 7,7,8,8-tetracyano-*p*-quinodimethane (CuTCNQ) was discovered in the 1970s [7], and a worldwide study has been pursued since then [8–57]. However, despite the extensive effort devoted to understanding it, the detailed switching mechanism of this material remains unclear. It has been variously suggested that (i) the electrical switching behavior is caused by the mixed valence characteristics of this compound, and

the reaction is reversible under an electric field as depicted in Eq. (1) [7]:



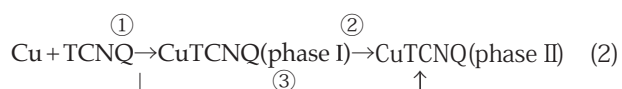
(ii) the switching is related not to the changes in the bulk sample but to the formation of channels created from the contact of the aluminum electrode with the irregular surface of the CuTCNQ films or the native aluminum oxide layer formed between CuTCNQ and the aluminum electrode [34–39]; (iii) the switching results from the change of crystal

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phases between the high conductivity phase I and low conductivity phase II [40]. A natural question is what causes this divergence of opinion? This is a very complicated question to answer at the moment since pure samples of phase II of CuTCNQ are still unavailable. Maybe this phase plays a significant role in the switching behavior of the devices [40]. Dunbar et al. have demonstrated that CuTCNQ has two distinct polymorphs, a “needle or rod-like” kinetic product known as phase I and a “lamella-like” thermodynamically stable material known as phase II [40]. Both phases can be synthesized via “spontaneous electrolysis” [7] to give dark purple, crystalline materials. Their chemical composition and electronic characteristics are identical, but their structures and properties are quite different (e.g., the conductivity of phase I was found to be high but that of phase II was rather low) [40]. The most intractable problem is that both phases readily form simultaneously in thin films of CuTCNQ during the growth process, and subtle differences in reaction conditions can lead to variable quantities of the two phases. This is an important reason for the inconsistencies in reported studies of CuTCNQ [40].

In our previous studies, CuTCNQ single crystals of phase I with different morphologies were examined and their semiconductor properties were studied. It is generally believed that CuTCNQ phase I itself is not responsible for the switching of the material [41–44]. It is highly possible that phase II plays a significant role in the switching behavior of CuTCNQ as suggested by Dunbar et al. [40]. Therefore, the controlled synthesis of phase II of CuTCNQ, especially as single crystals, has become a key scientific challenge in the study of the switching mechanism of CuTCNQ.

A generally accepted fact is that for short reaction times in acetonitrile solution the kinetic product (phase I) of CuTCNQ is first generated, and then this kinetic product slowly converts to a more thermodynamically stable material (phase II) [40, 43, 44]. The processes can be described by the following equation:



According to this equation, there are two possibilities for the generation of phase II of CuTCNQ. The first way is to transform phase I into phase II, following the processes ① and ② as depicted in Eq. (2). The process ① is a chemical reaction process wherein Cu and TCNQ react to generate CuTCNQ. The process ② is a phase transformation process. The crux of the controlled synthesis of phase II is how to tune both the processes ① and ② to exclude the existence of phase I in the final products. The second way is to synthesize phase II directly from Cu and TCNQ through process ③.

It is well known that the “spontaneous electrolysis” method is based on the fact that a solution of TCNQ reacts with a pre-cleaned copper plate to form dark blue CuTCNQ on the surface of the plate. The copper plate is a Cu “sea”, and the newly generated CuTCNQ phase I (process ①) and the concomitant conversion to CuTCNQ phase II (process ②) result in a mixture of the two phases on the Cu plate. When we review the formation of the lamellar structure of phase II, several facts can be noticed: (i) the formation of phase II needs long reaction times (several tens of hours); (ii) the generation of the lamellar phase II structure always takes place in solution, and is seldom observed in the solid state; (iii) the conversion of the kinetic products (phase I) to the lamellar structure (phase II) is a recrystallization process, i.e., the kinetic products are first dissolved into solution and then recrystallized as the lamellar structure on the substrate [44]. It is reasonable to deduce that a “slow solution–recrystallization process” is necessary for the synthesis of CuTCNQ phase II.

One way to achieve this is to use a TCNQ/ acetonitrile solution saturated with CuTCNQ as the “mother solution” for the “spontaneous electrolysis” and meanwhile to control the quantity of Cu source in order to limit the generation of new CuTCNQ so that the relative rates of the reaction (process ①) and phase conversion (process ②) can be fine tuned and controlled. In our method, the phase I products [41–44] were dissolved in TCNQ solution (with acetonitrile as solvent) to give a saturated CuTCNQ solution and then Si/SiO₂/Cu substrates were dipped into the saturated solution to afford crystallized lamellae of CuTCNQ. The quantity of



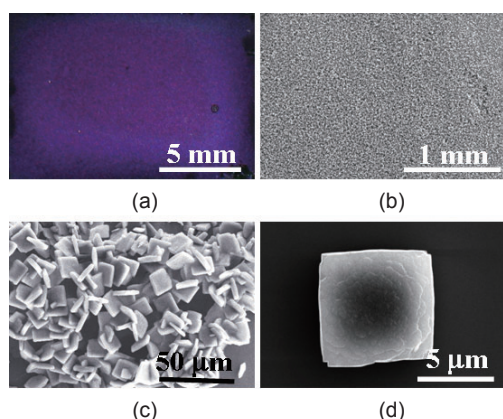


Figure 1 Controlled synthesis of lamellae of CuTCNQ by dipping substrates of Si/SiO₂/Cu (200 nm) into TCNQ/acetonitrile solution saturated with CuTCNQ for 48 h: (a) photo image, (b)–(d) SEM images at different magnification

Cu is controlled by using Si/SiO₂/Cu (200 nm) as a substrate instead of Cu plates (a copper “sea”). The results are shown in the photo and SEM images in Fig. 1. Large area, uniform CuTCNQ lamellae were obtained on the whole surface of the substrates (Figs. 1(a) and 1(b), 1 × 1.5 cm²) after 48 h reaction. All lamellae appeared as “squares” with side length around 4–10 μm and thickness from ~100 nm to several μm (Figs. 1(c) and 1(d)).

The UV–Vis absorption spectrum of the lamellae is shown in Fig. 2(a): the peak at ~393 nm can be assigned to neutral CuTCNQ⁰ and the peaks at ~420, 743, and 842 nm are attributed to the TCNQ radical anion of CuTCNQ [41–55]. The FT-IR spectrum (Fig. 2(b)) of the lamellae exhibited a band at 2209 cm⁻¹ due to the C≡N stretching absorption [40], and weak absorptions at 1570 and 1504 cm⁻¹ due to C=C ring stretching. The peak at 1504 cm⁻¹ is consistent with the conversion of TCNQ to TCNQ radical anions. The band at around 1358 cm⁻¹ is characteristic of the C=C wing stretching region. The XPS peaks of Cu2p_{3/2} and Cu2p_{1/2} of the lamellae (Fig. 2(c)) exhibited no evidence of shoulders or satellites due to Cu(II), suggesting that the products were essentially Cu(I). Meanwhile, the N1s orbitals appeared as a single feature at 398.2 eV (sometimes with a satellite at 400.0 eV), which was indicative of the presence of only one type of TCNQ [40, 56, 57]. The powder XRD pattern of the lamellae (Fig. 2(d)) showed a few intense features in the low-angle region which could be assigned to lamellae of phase II with a monoclinic

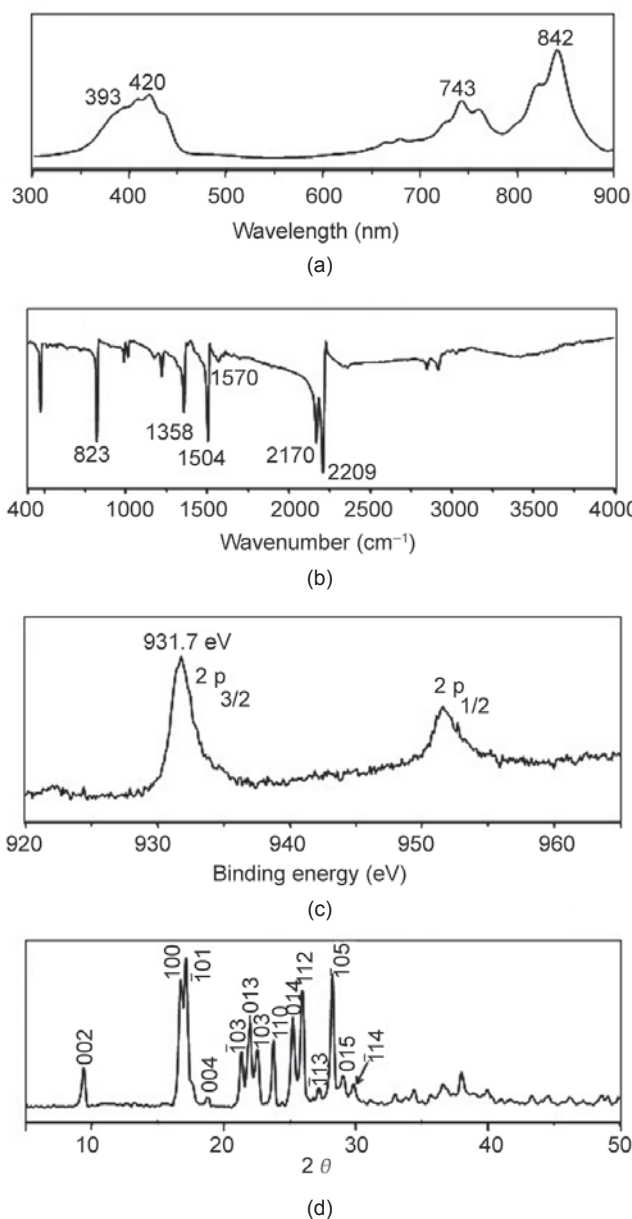


Figure 2 (a) UV–Vis spectrum, (b) FT-IR spectrum, (c) XPS spectrum, and (d) XRD pattern of the lamellae. The UV–vis spectrum was recorded at room temperature by dissolving CuTCNQ lamellae in acetonitrile, FT-IR was performed by using pressed pellets of a mixture of the lamellae and KBr, and XPS, and XRD were performed using a film of CuTCNQ lamellae on a Si substrate

unit cell [40]. Taken together, all the results indicate that the lamellae obtained in our study were pure phase II CuTCNQ. Figure 3 shows a typical TEM image of a lamella and its corresponding selected area electron diffraction (SAED) pattern. The SAED pattern was consistent at different part of the same lamella, indicating that the whole lamella was a single crystal. Furthermore, the SAED pattern could

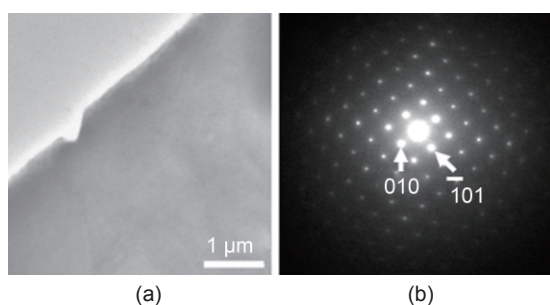


Figure 3 (a) TEM micrograph and (b) SAED pattern of an individual lamella of CuTCNQ

be indexed with the lattice parameters reported by Dunbar et al. [40].

This fine control over the synthesis of crystalline lamellae can be attributed to the adoption of the CuTCNQ saturated solution as the “mother solution” which guaranteed that as soon as new CuTCNQ was formed, the solution became supersaturated and the same amount of CuTCNQ would crystallize out on substrate simultaneously until all the Cu on substrate was used up, and large area lamellae were formed on the substrate. It is clear that such tuning of the reaction processes is an efficient way to generate CuTCNQ phase II lamellae with large area. Moreover, if the saturated “mother solution” was substituted with TCNQ or an unsaturated CuTCNQ and TCNQ solution, phase I or a mixture of phase I and phase II was obtained after 48 h reaction.

Another method of controlling the synthesis of phase II is shown in Fig. 4. A zinc plate was totally covered with a 100 nm Au film and placed at the bottom of a bottle with saturated TCNQ solution, where the Au layer was used as a diffusion barrier to control the velocity of processes. A saturated solution of CuCl_2 and TCNQ in acetonitrile was dropped into the bottle. The results are shown in Fig. 5. As indicated in Fig. 5(a), the lamellae began to grow on the surface of the Au film. It is possible that Cu^{2+} or Cu diffused through the Au layer [58], especially at the grain boundaries and cracks in the polycrystalline Au film [59] to reach the Zn/Au interface, and was then reduced by Zn (see Fig. S-1 in the Electronic Supplementary Material (ESM)), so that the amount of the Cu source could be accurately controlled by the “displacement reaction” of $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$ at an atomic level. The resulting Cu reacted with TCNQ

through the “spontaneous electrolysis” process to form CuTCNQ (the TCNQ molecules also needed to diffuse through the Au layer to reach the Au/Zn interface and to react with Cu). The limited Cu source and TCNQ molecules in this case can be expected to guarantee that CuTCNQ molecules are not synthesized in large amount at any one time. Finally, the synthesized CuTCNQ at the Au/Zn interface dissolved into solution, diffused through the Au barrier layer and recrystallized out on the Au surface (Fig. 5(a)). With the synthesis processes continuing, the amount of lamellae grew quickly (Figs. 5(b) and 5(c)) and finally covered the whole surface of the substrate as shown in Fig. 5(d). The products were

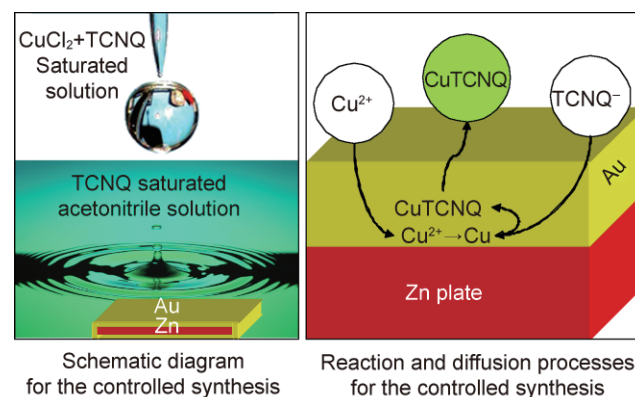


Figure 4 Schematic diagram and the possible “displacement reaction” and “diffusion-control” processes for the controlled synthesis of phase II of CuTCNQ

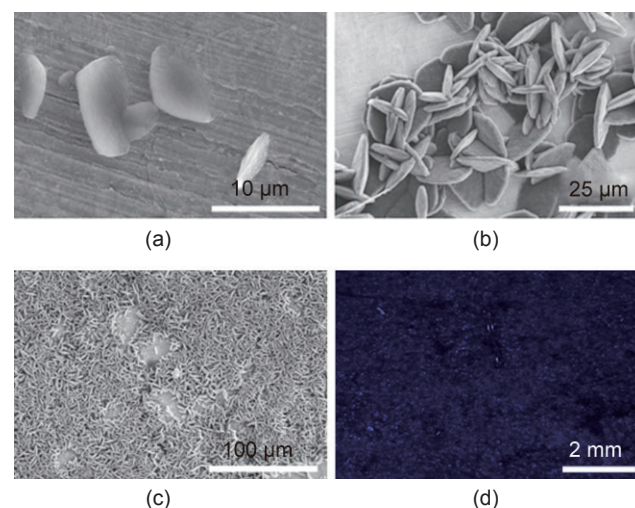


Figure 5 CuTCNQ lamellae grown on the surface of Au: (a) SEM image of several lamellae beginning to grow on the Au surface; (b), (c) SEM images of the lamellae grown on Au surface; (d) large area photo image of lamellae covering the surface of Au with the growth process continuing

also characterized by UV–Vis, FT-IR, XPS, powder XRD, TEM and SAED, and identical characteristics to those shown in Figs. 2 and 3 were observed for the lamellae shown in Fig. 5, indicating that the lamellae obtained by this method were pure phase II and each lamella was a single crystal.

The formation of the large area, pure phase II shown in Fig. 5 depends on the fine tuning of the reaction processes by: (i) the Au barrier layer for the control of diffusion processes, and (ii) the “displacement reaction” for the accurate control of the amount of the Cu source. If we used Au-covered Cu substrates instead of Zn substrates for the reaction to eliminate the “displacement reaction”, thus losing the control over the Cu source, a mixture of phase I and phase II was obtained (see Fig. S-2 in the ESM). Similarly, if the thickness of the Au barrier was reduced from 100 nm down to 20–30 nm to weaken the control over the diffusion processes, a mixture of phase I and phase II was also obtained (see Fig. S-2 in the ESM). However, it should be noted that too thick an Au layer would result in long times for the synthesis of phase II or even lead to Cu^{2+} being unable to diffuse through the barrier layer and undergo reduction.

There are still two possible explanations for the generation of the lamellae shown in Fig. 5: (i) the direct reaction of Cu and TCNQ through process ③ (as depicted in Eq. (2)) for the synthesis of phase II, or (ii) the transformation from phase I into phase II following the processes of ① and ② of Eq. (2). It is difficult to distinguish between these two and there seems no way to identify by which route the synthesis process proceeded (especially on the Zn/Au interface), because phase I and phase II have identical chemical composition and electronic characteristics [40]. Here, we can only confirm that the crystallized products on the Au surface are phase II, and cannot exclude the possibility that the molecules of phase I have passed through processes ① and ② involving a phase conversion before recrystallizing on the substrate. Most importantly, regardless of the exact synthesis process, it is clear that lamellae of CuTCNQ phase II with large area could be synthesized easily by this method by appropriate tuning of the reaction processes.

In conclusion, both methods mentioned above are very facile and easily carried out to afford lamellae of phase II of CuTCNQ with large area. The formation of the lamellae of phase II depends on the fine tuning of the processes as indicated in equation (2). The synthesis of large area single crystalline lamellae suggests bright prospects for the study and understanding of the electrical switching of CuTCNQ by using single crystals of its phase II, and future applications. Indeed, our preliminary results showed that individual lamellae exhibited a switching phenomenon (see Fig. S-3 in the ESM), which will allow the switching mechanism of the lamellar structures to be studied [40], and future practical applications of CuTCNQ in memory and switching devices. A detailed investigation is underway in our laboratory.

Experimental

TCNQ was purchased from Aldrich and recrystallized twice in acetonitrile prior to use. Silicon wafers, Si/SiO₂ wafers, and zinc plates were used as substrates after they were cleaned carefully. With the exception of the zinc plates, all the other substrates were cleaned successively with a hot solution of concentrated sulfuric acid and hydrogen peroxide (sulfuric acid:hydrogen peroxide=2:1), pure water, pure ethanol, pure acetone, and finally by argon plasma for several minutes. After that, copper and zinc layers were deposited onto the substrates by vacuum deposition under a vacuum of 10³–10⁴ Pa (ULVAC, VPC-260F).

The products were synthesized at room temperature and characterized by UV–Vis spectroscopy (Hitachi U3010), Fourier-transform infrared spectroscopy (FT-IR, PE2000), X-ray photoelectron spectroscopy (XPS, VG ESCALAB 220I-XL), X-ray diffraction (XRD, Rigaku D/max2500), scanning electron microscopy (SEM, Hitachi S-4300 SE), and transmission electron microscopy (TEM, JEOL 2010).

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Electronic Supplementary Material: XPS of Au films soaked in Cu^{2+} solution, SEM micrographs showing the co-existence of lamellae of CuTCNQ with different kinetic phase I products and SEM image and current–voltage characteristics of a device based on an individual lamella are available in the online version of this article at <http://dx.doi.org/10.1007/s12274-009-9065-0> and are accessible free of charge.

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