Journal of Electrochemistry

Volume 18 | Issue 5

2012-10-28

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Recommended Citation
Li Huang, Yixian Wang, Michael V. Mirkin, Bin Ren, Dongping Zhan. Electrochemical Synthesis of Silver-Tetracyanoquinodimethane Nanorods at Agar Supported Water/1,2-Dichloroethane Interface[J]. *Journal of Electrochemistry*, 2012 , 18(5): Article 3.
DOI: 10.61558/2993-074X.2611
Available at: https://jelectrochem.xmu.edu.cn/journal/vol18/iss5/3

第 18 卷 第 5 期
2012 年 10 月

电化学
JOURNAL OF ELECTROCHEMISTRY

Vol. 18 No. 5
Oct. 2012

Artical ID:1006-3471(2012)05-0405-05

Electrochemical Synthesis of Silver-Tetracyanoquinodimethane Nanorods at Agar Supported Water/1,2-Dichloroethane Interface

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Abstract: Silver-tetracyanoquinodimethane (AgTCNQ) is an important charge transfer salt due to its high conductivity and other electronic properties. In this communication, we report the synthesis of AgTCNQ at the liquid/liquid interface. Agar was used as a gelling agent to support water/1,2-dichloroethane (DCE) interface. Silver ions were transferred from the hydrogel into DCE phase, where they combined with $TCNQ^-$ to form AgTCNQ nanorods. The developed method can provide a new route for synthesis of functional materials based on the electrochemistry at the liquid/liquid interface.

Key words: liquid/liquid interface; silver-tetracyanoquinodimethane; electrochemical synthesis; nanorods

CLC Number: O646 **Document Code:** A

1 Introduction

AgTCNQ has attracted significant interest during several decades due to its high conductivity, electrical switching properties and its applications in sensors and electronics[1-2]. Different approaches to the synthesis of AgTCNQ have been reported, including the "spontaneous electrolysis" in which metal silver reacts with dissolved TCNQ in organic solvents[3], vacuum vapor deposition of TCNQ onto Ag metal films[4], and reactions of TCNQ in organic solvent with metal precursors[5]. Electrochemical methodologies have been useful for studying the formation of nano-structured AgTCNQ crystals in acetonitrile, water and ionic liquids because they provide the means for precise control of the nucleation and growth processes[6-9]. Nevertheless, questions remain open about the mechanism of the AgTCNQ formation process. Both silver and silver salts can react with $TCNQ/TCNQ^-$ spontaneously, which makes it difficult to distinguish the direct chemical precipitation from electrocrystallization of AgTCNQ.

To exclude the direct chemical precipitation and focus on the electrochemically induced crystallization, one can take advantage of the hydrophilicity of Ag^+ and hydrophobicity of TCNQ. This can be achieved by conducting AgTCNQ synthesis at the interface between two immiscible electrolyte solutions (ITIES), e.g., the interface between a hydrogel and 1,2-dichloroethane (DCE). The immiscible water/organic interface can also hinder the diffusion of reactants, thus, reducing the overall reaction rate. This approach was previously used to synthesize nanoparticles and further modify their surface[6-7]. When electrolytes are introduced into each phase, the water/oil interface can be polarized to induce charge transfer reactions[8-9], including the ion transfer of Ag^+[10]. Electrosynthesis can involve either ion transfer or electron transfer across the ITIES. An ex-

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Received: 2012-07-01, Revised: 2012-10-08 *Corresponding author, E-mail: dpzhan@xmu.edu.cn

This work was supported by National Science Foundation of China (No. 20973142, No. 21061120456, and No. 21021002), National Basic Research Program of China (2011CB933700) and the National Science Foundation (CHE-1026582; MVM).

ample of the former approach is the oxidation of *cis*-cyclooctene in DCE by MnO_4^-, which involved phase transfer catalysis[11]. Oxidation of 4-methylanisole by Ce^{4+} at the water/DCE interface involved interfacial electron transfer[12].

In this communication, we present a new electrosynthetic method based on ion transfer at the agar hydrogel/DCE interface. When the interface is polarized, Ag^+ gets transferred from the aqueous gel to DCE phase, where it reacts with $TCNQ^-$ (the product of the TCNQ reduction by $TPBCl^-$) to form AgTCNQ nanorods.

2 Experimental

DCE, Ag_2SO_4, Na_2SO_4, and agar powder were provided by National Chemicals Ltd., China. Bis(triphenylphosphoranylidene)-ammonium chloride (BTPPACl) and potassium tetrakis(4-chlorophenyl) borate (KTPBCl) were purchased from Sigma, while 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) was from Alfa. Purified DCE was used for preparing organic solutions. All the chemicals were reagent grade and were used as received. All aqueous solutions were prepared with deionized water (Milli-Q, Millipore Corp.).

Bis(triphenylphosphoranylidene) ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl) was prepared through the precipitation between BTPPACl and KTPBCl and recrystallized from acetone. Agar was dissolved in 100 mmol·L^{-1} Na_2SO_4 aqueous solution with a mass ratio of 1:10 at 80 ℃ and then transferred into a 4-inch-diameter Petri dish. After cooling in a vacuum chamber, the thickness of Agar gel was about 1 mm. A glass tube with an inner diameter of 0.7 mm was inserted into the Agar gel, which plugged its orifice.

As depicted in Fig. 1A, an aqueous solution was injected into the prepared glass tubing and then an Ag wire was inserted into the aqueous solution. An AgTPBCl coated silver wire was immersed in the DCE phase. The pair of Ag wires was used to control the potential drop across the water/DCE interface. A Pt wire in the DCE phase acted as counter electrode. All the electrochemical experiments were performed using a CHI 660a workstation (CHI Instrument Co.).

The synthesized AgTCNQ nanorods on the agar surface were collected and washed successively with water and DCE several times to remove the residual electrolytes. A drop of dispersed AgTCNQ nanorods was placed on a Si wafer and dried in the vacuum chamber for an hour. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) of AgTCNQ nanorods were performed using HITACHI S-4800 SEM (Hitachi

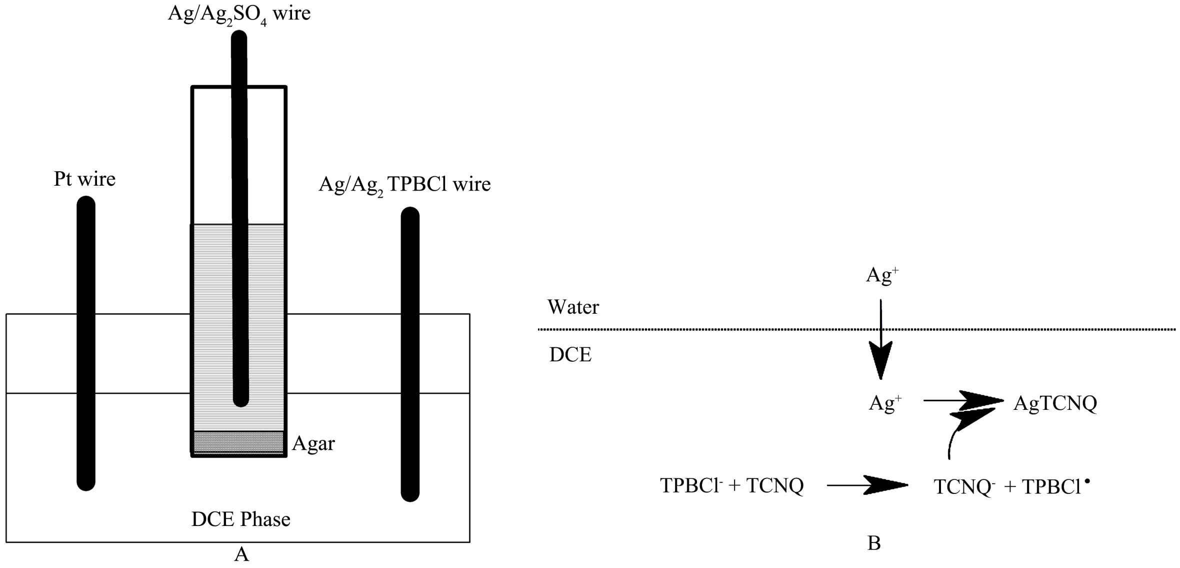


Fig. 1 Electrosynthesis of AgTCNQ at the liquid/liquid interface. A. Schematic diagram of the electrochemical cell. B. Scheme of the mechanism of the electrochemically induced crystallization of AgTCNQ at the water/DCE interface.

High-Technologies Co). Raman spectra were collected with a Renishaw RM 2000 Raman spectrograph (Renishaw Co).

3 Results and Discussion

Fig. 2 shows three ion transfer voltammograms obtained at the hydrogel/DCE interface. The background voltammogram (curve 1) obtained in Cell 1

Ag|100 mmol·L^{-1} Na_2SO_4||5 mmol·L^{-1} BTPPATPBCl|AgTPBCl|Ag　　(Cell 1)

shows that no ion-transfer occurred within the polarization window with no Ag^+ ions added to the aqueous phase. The addition of TCNQ to DCE did not result in appearance of any additional voltammetric wave (not shown). This could be expected because TCNQ is a neutral molecule and there was no electron donor in water phase. In contrast, reversible voltammograms of Ag^+ transfer (curve 2) were obtained in Cell 2.

Ag|1 mmol·L^{-1} Ag_2SO_4 + 100 mmol·L^{-1} Na_2SO_4|| 5 mmol·L^{-1} BTPPATPBCl| AgTPBCl|Ag　　(Cell 2)

The presence of a hydrophobic anion, $TPBCl^-$, facilitates the transfer of Ag^+ to organic phase. A similar wave of Ag^+ transfer to organic phase (curve 3) was recorded in Cell 3 after TCNQ was added to DCE solution.

Ag|1 mmol·L^{-1} Ag_2SO_4 + 100 mmol·L^{-1} Na_2SO_4|| 5 mmol·L^{-1} BTPPATPBCl + 10 mmol·L^{-1} TCNQ| AgTPBCl|Ag　　(Cell 3)

However, the reverse wave corresponding to the silver transfer back to the aqueous phase has completely disappeared, and solid substance precipitated at the hydrogel/DCE interface. The disappearance of the reverse transfer wave and the observed precipitation can be attributed to the interfacial crystallization of AgTCNQ that follows the ion transfer reaction:

$$Ag^+ (W) \rightarrow Ag^+ (DCE) \qquad (1)$$

$$Ag^+ (DCE) + TCNQ^- (DCE) \rightarrow AgTCNQ (s) \qquad (2)$$

This “EC”-type mechanism with a rapid subsequent crystallization reaction (2) can explain the observed irreversible ion transfer wave (curve 3 in Fig. 2). The only species in Cell 3 that can reduce TCNQ to $TCNQ^-$ is $TPBCl^-$, which is relatively easy to oxidize[13].

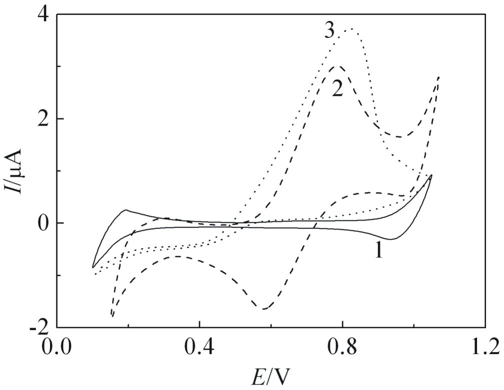
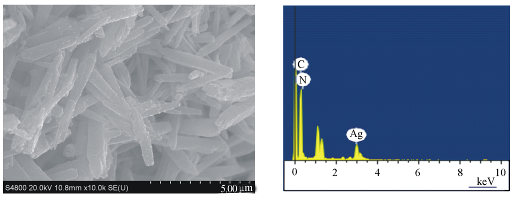


Fig. 2 Cyclic voltammograms of ion transfer reactions obtained in Cell 1 (curve 1), Cell 2 (curve 2) and Cell 3 (curve 3). The potential sweep rate is 100 mV·s^{-1}.

The morphology of electrochemically induced crystalline AgTCNQ nanorods was characterized by scanning electron microscopy (SEM). The SEM images (Fig. 3) reveal high-aspect ratio of AgTCNQ nanorods. The surface is essentially smooth, and the rod diameter is in the 200 ~ 500 nm range, while its length is up to ~ 5 μm. EDS results further confirmed the elemental composition of the product. It can be observed obviously that there exist carbon, nitrogen and silver with a weight ratio of 36:44:20. Since EDS reflects the local surface components of the objects, the EDS results are not in accordance with the stoichiometric ratio. To confirm the composition of the nanorods, Raman spectra of Agar, TCNQ powder and the synthesized nanorods were collected and shown in Fig. 4. Comparing to TCNQ, AgTCNQ has a red-shift peak at 1386 cm^{-1} and a weak peak at 1603 cm^{-1}, which are in accordance with the previously reported results[9]. All the above results show that the AgTCNQ nanorods were obtained through the electrochemical method at liquid/liquid interface.

The investigation of the experimental factors that determine the size and shape of the AgTCNQ nanorods and the characterization of their electronic and photonic properties are in currently progress.



A B

Fig. 3 SEM image(A) and EDS analysis(B) of the synthesized AgTCNQ anaorods.

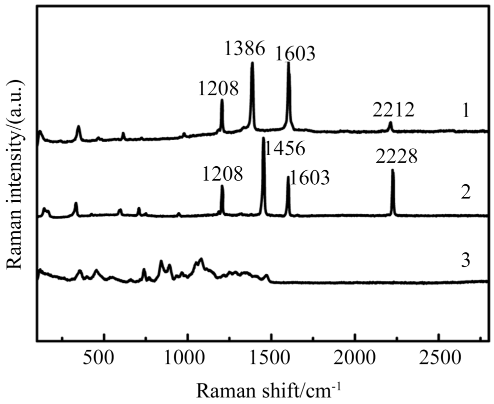


Fig. 4 Raman spectra of AgTCNQ synthesized at the ITIES (1), TCNQ powder (2), and agar (3).

4 Conclusions

We developed a novel method for synthesizing TCNQ-based conductive salt by electrochemistry at the ITIES. Metal ions were transferred from the aqueous hydrogel to organic phase containing a hydrophobic anion and combined with TCNQ$^-$ therein to form AgTCNQ nanorods. This approach can be used to produce charge-transfer complexes, which have potential applications in electronic and photonic microdevices.

Acknowledgement

This work was supported by National Science Foundation of China (No. 20973142, No. 21061120456, and No. 21021002), National Basic Research Program of China (No. 2011CB933700) and the National Science Foundation (CHE-1026582; MVM).

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基于琼脂支撑的液/液界面上 AgTCNQ 的电化学合成

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摘要：具有高导电性和独特电学性质的金属有机络合物 AgTCNQ 是一种重要的电荷转移盐. 本文采用琼脂作为胶凝剂构成水 |1,2- 二氯乙烷液液界面,施加电压时银离子由水相穿过水凝胶进入有机相,与 $TCNQ^-$ 反应生成 AgTCNQ 纳米棒. 结果表明液/液界面电化学方法为合成有机金属功能材料的有效途径.

关键词：液/液界面；银-四氰基对苯二醌二甲烷；电化学合成；纳米棒