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Photoinduced Oxidation of Water to Oxygen in the Ionic Liquid BMIMBF$_4$ as the Counter Reaction in the Fabrication of Exceptionally Long Semiconducting Silver-Tetracyanoquinodimethane Nanowires

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Abstract: The synthesis of exceptionally long semiconducting silver tetracyanoquinodimethane (AgTCNQ) nanowires has been achieved in the room temperature ionic liquid, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF$_4$) by photochemical reduction of TCNQ to TCNQ$^-$, coupled with use of benzyl alcohol as the sacrificial electron donor. The presence of Ag(I) in the ionic liquid allows formation of mm length AgTCNQ nanowires onto both conducting and insulating surfaces, via a nucleation and diffusion-controlled growth mechanism. Remarkably, photocrystallization also can be achieved using adventitious or deliberately added water present in the ionic liquid as the sacrificial electron donor. In this case, oxidation of water produces O$_2$ as the counter reaction in the photoreduction of TCNQ. In contrast, irradiation in "dried" ionic liquids fails to induce any detectable photochemistry. Molecular structural differences, relative to the situation encountered in more conventional solvent media, are believed to account for the more favorable kinetics available for oxidization of water in ionic liquids. Water assisted photocrystallization in viscous BMIMBF$_4$ where diffusion rate are slow leads to slow growth of AgTCNQ, thereby allowing easy manipulation of AgTCNQ morphology from small nanoparticles to extremely long single nanowires by tuning the irradiation and ripening time. Infrared and Raman spectroscopic data, elemental analysis, and scanning electron microscopic images all confirm the formation of highly pure AgTCNQ nanomaterials. This study highlights the significant role that water present as an adventitious impurity may play in photochemical studies in ionic liquids and also suggests that ionic liquids may provide a favorable environment for photochemically based water splitting.

Introduction

Semiconducting metal-7,7,8,8,-tetracyanoquinodimethane (TCNQ) materials have been of considerable interest since the 1970s, owing to their novel electrical and/or magnetic properties.[1−14] To date, applications have been reported in optical and electrical recording,[15−17] energy and data storage,[18−20] sensors[21−26] and electrochromic and magnetic devices.[27,28] In particular, the discovery of electrically and optically bistable

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behavior and memory effects available with both AgTCNQ and CuTCNQ has stimulated considerable renewed interest of these materials in nonvolatile-based memory devices.[29−44] Complementary metal oxide semiconductor (CMOS) devices fabricated from these TCNQ materials have been downscaled in size to an area of 0.25 μm^2.[41] One-dimensional (1D) nanostructures generally favor size reduction needed in this area of technology.[44−47] In this context, it has been found that AgTCNQ nanowires can be used in high density integration of nanodevices.[48,49] Importantly they have a much higher on−off ratio than thin films.[48]

Many AgTCNQ preparation procedures are based on reaction of TCNQ dissolved in acetonitrile with metallic Ag. In these so-called "spontaneous electrolysis" methods, metallic Ag is oxidized to the Ag^+ cation and TCNQ reduced to the $TCNQ^-$ radical anions to give AgTCNQ at the metal surface.[30,38,39,50] Morphology and thickness of the AgTCNQ films can be modulated by changing the experimental conditions to yield microwires, needle-shaped crystals and also dendrites.[38,39,50] In addition to these "wet" methods, AgTCNQ films also can be prepared by "dry" procedures, such as chemical vapor deposition of TCNQ onto Ag metal surfaces[8,49] and thermal codeposition of TCNQ and Ag.[49] Synthetic methods derived from TCNQ and Ag salt precursors also have been widely used.[2,14] Early studies based on electrocrystallization of AgTCNQ employed oxidation of Ag substrate electrodes in acetonitrile solutions containing a $TCNQ^-$ (LiTCNQ) salt.[6,51] Electrochemical methods based on solid−solid interconversion at an aqueous TCNQ electrode interface, or reduction of TCNQ in the presence of Ag salts also have been used.[52] Recently, O'Mullane et al. developed a photochemical method which takes advantage of photoinduced electron-transfer between TCNQ (electron acceptor) and a sacrificial electron donor (benzyl alcohol) to generate $TCNQ^-$, which then reacts with metal cations such as Ag^+ dissolved in the acetonitrile solution, to form metal-TCNQ materials.[42] The morphology of the photocrystallized products depends on the cation and ranges from microrods to nanowires.

In the past decade, use of ionic liquids (ILs), as "green" replacements for conventional organic solvents in chemical processes has received much attention.[53−55] Ionic liquids provide an attractive medium for synthesis because of properties such as (i) large electrochemical potential windows, which provide access to electrodeposition of metals and semiconductors not possible from conventional aqueous or organic electrolytes;[55−58] (ii) low interfacial tension, which makes them easy to adapt to other phases and results in high nucleation rates and generally smaller nanoparticles;[59] (iii) high thermal stability, which allows syntheses to be conducted at temperatures above 100 °C without using high-pressure vessels; (iv) functionalized ILs, which can modify material surfaces and control the size and improve the stability of nanoparticles;[60,61] (v) highly structured hydrogen bonding, which can provide templates for formation of well-defined and extended nanostructures.[59,62] Recognition of these properties has led to synthesis of metal nanoparticles,[63,64] TiO_2 nanospheres[65] and hollow microspheres,[66] Te nanorods and nanowires,[67] Sb_2S_3 and Bi_2S_3 nanorods,[68] CoPt nanowires,[69] ZnO flowers,[70] and porous silica sponge,[71] and electrodeposition of nanostructured metals,[56−58] semiconductors and conducting polymers.[56,58,72] A few recent reports also have described the use of ionic liquids as a medium for photochemical reactions[73] and for synthesis of Au nanoparticles.[74,75]

In this report, we describe, for the first time, the application of ionic liquid as a medium for synthesis of charge transfer

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metal-TCNQ complexes by photocrystallization. Parameters that affect the photocrystallization and growth processes, such as sacrificial electron donor, irradiation time, ripening time and water content present in the ionic liquid have been investigated in detail. Significantly, the study leads to the surprising discovery that water in the ionic liquid $BMIMBF_4$, present either as an adventitious impurity or deliberately added, can be photooxidized to oxygen and hence serve as a sacrificial electron donor in this kind of environment. Thus $BMIMBF_4$ provides a favorable medium for photooxidation of water as well as for synthesizing technologically important metal-TCNQ materials with nanowire morphologies.

Experimental Section

Materials and Chemicals. Ionic liquid, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) from Merck (high purity grade, ≥99.0%, batch code 4.91049.0100), 98% tetrakis(acetonitrile) silver(I) tetrafluoroborate ($Ag(MeCN)_4BF_4$) and silver(I) tetrafluoroborate ($AgBF_4$) from Sigma, 98% 7,7,8,8,-tetracyanoquinodimethane (TCNQ), absolute ethanol and benzyl alcohol from Aldrich and acetonitrile from Omnisolv were used as provided by the manufacturer.

Photochemical Procedures. Initially, an irradiation procedure described for photocrystallization in acetonitrile was modified for ionic liquid applications[42] under benchtop laboratory conditions. Subsequently, procedures were repeated on samples of known water content in a nitrogen filled glovebox (see details below). Typically, 4.5 mM $Ag(MeCN)_4BF_4$ or $AgBF_4$ and 4.5 mM TCNQ were dissolved in $BMIMBF_4$ using 3 min sonication, if required. The sacrificial electron donor benzyl alcohol was added at a 10% v/v concentration. The ionic liquid solution was then drop cast onto an indium tin oxide (ITO) or glass substrate (2.5×2.5 cm^2) to give a liquid drop, or a thin liquid film. A thin glass rod was used to spread the drop. Owing to the very low vapor pressure of $BMIMBF_4$, liquid drops or thin films do not evaporate, even over the long duration of some experiments (up to 1 week). The ionic liquid drop or thin film are then irradiated from above at a distance of 0.5 cm using an optical fiber attached to a light source (Newport Scientific, Model 6292 200 W Hg(Xe) lamp), typically for 30 min.

The irradiation generated a ca. 3.2 mm diameter blue spot associated with the formation of AgTCNQ. Due to the high viscosity of $BMIMBF_4$, the blue AgTCNQ crystals formed in the liquid drop do not precipitate onto the substrate surface. Ten microliters of ionic liquid was then removed from the middle of the blue spot containing AgTCNQ and redrop cast onto a 2.5 cm diameter membrane filter having a pore size of 0.1 μm (Super 100, Gelman Science, MI). This substrate facilitates ionic liquid removal and hence rapid precipitation of AgTCNQ onto the membrane surface. This substrate is particularly suitable for isolating materials having relatively large structures (at least in one dimension), as small structures may be rinsed through the membrane pores. Alternatively, microscopic glass slides (2.5×2.5 cm^2) were used as the substrate for drop recasting. In this case, the substrate with the blue ionic liquid drop was stored in the dark overnight to allow precipitation of AgTCNQ to occur onto the glass surface. The ionic liquid was then removed with a tissue (Kimwipe). Next, the substrate was gently immersed into water bath for 10 min to allow complete removal (by dissolution) of $BMIMBF_4$ and then gently rinsed by adding drops of acetonitrile and ethanol, which were then removed with a tissue. Finally, the substrate was dried under a gentle N_2 stream.

To obtain larger quantities of AgTCNQ, the above procedure was adapted to a specimen tube (12 mm diameter, SAMCO) filled with ionic liquid solution which was irradiated at $\lambda = 425$ nm (from below at a distance of approximately 4 cm) with a Polilight PL6 xenon lamp (300 W, Rofin Australia) fitted with a light guide cable. Water was then added to the specimen tube to reduce the viscosity and AgTCNQ material was collected by centrifugation after washing 3 times sequentially with acetonitrile and ethanol, and finally drying under vacuum.

Detection of Benzaldehyde. The course of benzaldehyde generation from benzyl alcohol was monitored by employing a Varian 3700 gas chromatograph and HP3396 integrator with a 6′ × 1/4” Carbowax 20 M column. Its identity was confirmed by comparison of the retention time of the peak with that found using an authentic sample of benzaldehyde, and the concentration quantified by standard addition. Further details are available in reference.[76]

Electrochemical Detection of O_2. The photochemical experiments with voltammetric detection of oxygen (and $TCNQ^-$) were undertaken in a homemade nitrogen-filled glovebox[55] using a BAS 100B/W Electrochemical Analyzer (Bioanalytical System, West Lafayette, IN). The oxygen concentration inside the dry box was constantly monitored by a Series 800 Oxygen Analyzer (Illinois Instruments, Johnsburg, IL) and was always below 1 ppm. A glassy carbon (GC) macrodisk electrode from Cypress (Cypress Systems, Lawrence, KS), having an effective electrode area of 0.0299 cm^2, or a 1 μm diameter Pt microelectrode were used as the working electrodes. Prior to each experiment, the working electrode was polished with 0.3 μm Alumina (Buehler, Lake Bluff, IL) on a clean polishing cloth (Buehler), sequentially rinsed with distilled water and acetone and finally dried with lint free tissue paper. A Pt wire was used as a counter electrode and a Ag wire sealed in a frit containing $BMIMBF_4$ was used as a quasi-reference electrode (QRE).

Measurement of Changes in Hydrogen Ion Concentration. The change of acidity of the ionic liquid solution (4 mM TCNQ + 7% (v/v) water) upon irradiation at 425 nm for 20 min was monitored by measurement of the apparent “pH” obtained with a glass electrode (Metrohm Model 744 pH electrode, Herisau, Switzerland). The apparent “pH” value of the same ionic liquid solution (4 mM TCNQ + 7% (v/v) water), but without irradiation, was also recorded as a control. The apparent “pH” values were recorded when the value becomes stable.

Physical Characterization Procedures. The $BMIMBF_4$ water content was determined by Karl Fischer titration (831 KF Coulometer, Metrohm). $BMIMBF_4$ NMR investigations were undertaken at 20 °C (magnetic field strength of 7.04 T) with a Varian Unity-Plus 300 NMR Spectrometer. The chemical shifts for ^{11}B and ^{19}F were referenced to tetraborate and $CFCl_3$ respectively. Spectral shimming was achieved via free induction. Viscosity measurements on $BMIMBF_4$ were undertaken with an Anton Paar AMVn automated micro viscometer. Scanning Electron Microscopy (SEM) measurements were made with a JEOL 6300F Field Emission Gun (FEG) scanning electron microscope with a WinEDS energy dispersive X-ray (EDAX) analysis system. AgTCNQ samples photocrystallized onto glass, ITO or a membrane filter, were sputter coated with 10 nm Pt (Dynavac SC150 Sputter Coater) before imaging, to increase the production of secondary electrons. Infrared spectra were obtained with a Bruker IFS Equinox Fourier transform IR system equipped with a Golden GateTM single bounce diamond Micro-ATR (Attenuated Total Reflectance) cell. Raman spectra were collected with a Renishaw RM 2000 Raman spectrograph and microscope using a laser strength of 18 mW at a wavelength of 780 nm. Electronic spectra were obtained with a Varian Cary 5 UV−visible spectrophotometer (Varian OS2 software) using a 1 cm path length cell under benchtop laboratory conditions.

Results and Discussion

Preliminary Studies. The room temperature ionic liquid $BMIMBF_4$ was chosen for use in this study because of the much

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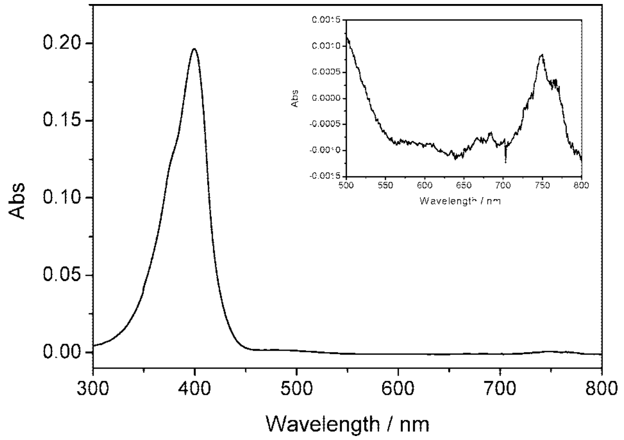

Figure 1. UV−visible spectrum of 3 μM TCNQ in $BMIMBF_4$. (Inset) Highlight of the visible region.

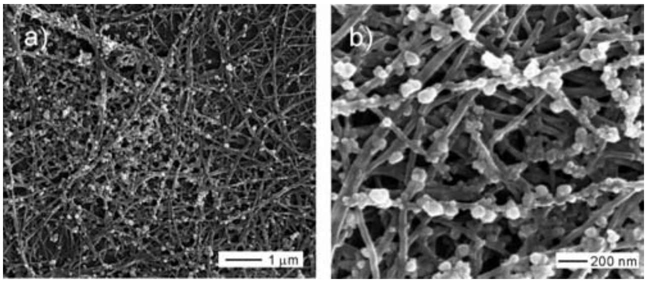

Figure 2. SEM images of AgTCNQ formed on a membrane substrate after 5 min irradiation (λ= 380 nm) of a liquid film of $BMIMBF_4$ containing 10% v/v benzyl alcohol and equimolar (4.8 mM) TCNQ and Ag^+.

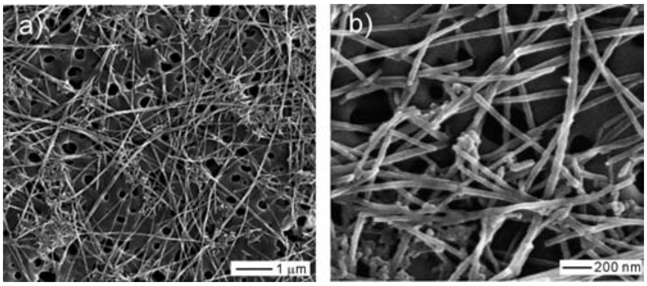

Figure 3. SEM images of AgTCNQ formed on a membrane substrate after 30 min irradiation (λ= 380 nm) of a liquid film of $BMIMBF_4$ containing 10% v/v benzyl alcohol and equimolar (4.8 mM) TCNQ and Ag^+.

higher solubility of TCNQ than that found in other ionic liquids. Initially, photochemical properties of TCNQ in $BMIMBF_4$ were probed by UV−visible absorption spectroscopy. The UV−visible spectrum for 3 μM TCNQ in $BMIMBF_4$ (Figure 1) exhibits a strong adsorption band with λ_{max} = 399 nm with a molar adsorption coefficient of 6.5×10^4 M^{-1} cm^{-1}.This band resembles that reported in an organic solvent[42,77−79] and hence may be assigned to the well-understood $^1A_g \rightarrow {}^1B_{3u}$ transition for TCNQ. The weak absorbance, over the wavelength range of 700−800 nm (Figure 1, inset), is attributed to the absorbance from trace amounts of $TCNQ^-$ present and is assigned to the $TCNQ^-$ $^2B_{2\,g} \rightarrow {}^2B_{1u}$ transition.[77−79]

UV−visible absorption spectra obtained in $BMIMBF_4$ containing equimolar (3 μM) TCNQ and a Ag salt and 10% v/v benzyl alcohol mixture do not exhibit new bands at wavelengths over the range 200−800 nm attributable to a Ag-TCNQ charge transfer complex being formed in the ground state. In a control experiment, irradiation at λ= 380 nm of an ionic liquid drop containing the Ag salt showed no formation of Ag metal, which could subsequently react spontaneously with neutral TCNQ to form AgTCNQ. Storage of an equimolar (4.8 mM) mixture of TCNQ and Ag salt in the dark and normal laboratory light conditions for 24 h leads to no visual detection of blue AgTCNQ solid, but a slight color change from yellow to yellow-green was observed. These results are essentially in accordance with those reported in acetonitrile.[42]

Photocrystallization of AgTCNQ in $BMIMBF_4$ in the Presence of the Sacrificial Electron Donor Benzyl Alcohol. A wavelength of 380 nm, which is slightly less than λ_{max}, was chosen for the excitation of TCNQ in initial photocrystallization experiments. To achieve photoreduction of TCNQ to $TCNQ^-$ and subsequent AgTCNQ formation requires the occurrence of a counter oxidization reaction. Benzyl alcohol was introduced into the system as a sacrificial electron donor since this has been previously shown to be oxidized to benzaldehyde in an organic solvent when irradiated by solar light in the presence of electron acceptors, such as polyoxometalates[76] or TCNQ.[42] Irradiation at λ= 380 nm for 5 min of a liquid film of $BMIMBF_4$ containing 10% v/v benzyl alcohol as well as equimolar (4.8 mM) TCNQ and Ag^+ rapidly leads to visual detection of a blue spot in the yellow liquid film, which turns to dark blue with extended irradiation times. This is consistent with the photoreduction of TCNQ to $TCNQ^-$ and subsequent formation of blue AgTCNQ. The quantitative loss of benzyl alcohol and generation of benzaldehyde was confirmed by gas chromatography. A drop of blue suspension from the middle of the blue spot was then transferred to a solid substrate (membrane filter) surface and prepared for SEM imaging, according to the procedure described in the experimental section. SEM images after 5 min irradiation (Figure 2a) reveal the formation of a mixture of an extensive nanocrystal network consisting of very long nanowires and nanoparticles. Images taken at higher magnification (Figure 2b) imply that these wires are derived from clusters of nanoparticles and that they have rather rough surfaces. These images represent an early growth stage of the AgTCNQ nanowire formation. Elemental EDAX analysis shows both the nanowires and the nanoparticles contain Ag, C, and N, as expected if both wires and nanoparticles are AgTCNQ. After an increase for the irradiation time to 30 min, an extensive network of extremely long nanowires is formed (Figure 3a), with some nanowires exceeding a millimeter length and hence the SEM detection limit. These nanowires typically have a fairly uniform width of 30 to 50 nm, but a few thicker ones exhibit widths of up to 100 nm. The variation in width is attributed to the fusion or dissolution of nanowires at late growth stages. Inspection at higher magnification (Figure 3b) shows that most nanowires are smooth, even in width, and have a quadrangular cross section. Some nanoparticles and/or nanorods are also observed among the nanowire network, possibly derived from breakage of long nanowires.

Raman spectra of photocrystallized AgTCNQ nanowires (Figure 4a) exhibit the four expected characteristic principle vibration modes at 1204 cm^{-1} (C=CH bending), 1385 cm^{-1} (C−CN wing stretching), 1605 cm^{-1} (C=C stretching), and 2211 cm^{-1} (C−N stretching). Comparison with the Raman

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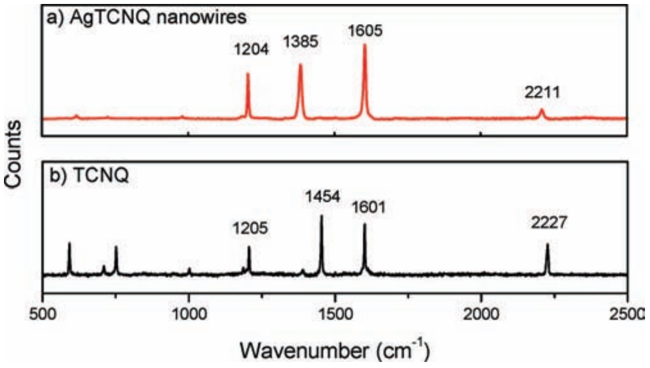

Figure 4. Raman spectra of (a) photocrystallized AgTCNQ nanowires and (b) TCNQ crystals.

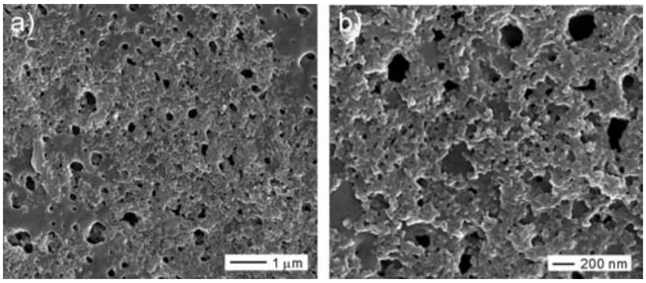

Figure 5. SEM images of AgTCNQ formed on a membrane substrate after 1 h irradiation (λ= 380 nm) of a liquid film of $BMIMBF_4$ containing equimolar (4.8 mM) TCNQ and Ag^+.

spectrum of neutral TCNQ (Figure 4b) reveals that the two principle vibration modes of TCNQ at 1455 cm^{-1}(C−CN wing stretching) and 2227 (C−N stretching) are red-shifted by 70 cm^{-1} and 16 cm^{-1} respectively in AgTCNQ. The decrease in the vibrational energy is consistent with that obtained from other metal-TCNQ compounds and can be attributed to the charge transfer between atomic Ag and free TCNQ, when TCNQ is reduced to $TCNQ^-$ to form AgTCNQ.[80] IR spectra further confirm the formation of AgTCNQ by exhibiting the expected characteristic bands at 2197, 2183, 2160, 1504 and 822 cm^{-1}.[14]

Photocrystallization of AgTCNQ in $BMIMBF_4$ in the Absence of a Deliberately Added Sacrificial Electron Donor. Intriguingly, photocrystallization of AgTCNQ in $BMIMBF_4$ under open bench laboratory conditions also could be achieved even in the absence of a deliberately added electron donor such as benzyl alcohol. Thus, irradiation at $\lambda = 380$ nm for 1 h of a liquid film of $BMIMBF_4$ containing equal molar (4.8 mM) TCNQ and Ag^+, surprisingly, also leads to visual detection of a blue/green spot in the yellow liquid film. Again, with increasing irradiation time, the spot becomes dark blue. Transferal of a drop of the blue suspension to the membrane filter substrate, followed by SEM imaging, reveals that the blue solid formed in this way consists of numerous nanoparticles (Figure 5a, b) having diameters of ca. 30−50 nm. Elemental analysis using EDAX confirms the presence of Ag, C, and N, which is consistent with AgTCNQ. Raman spectra confirmed the formation of AgTCNQ by the presence of band at 1204, 1385, 1604, and 2209 cm^{-1}.[80] A small quantity of residual unwashed $BMIMBF_4$ also remains between some nanoparticles (Figure 5).

A distinctly different morphology is achieved if the suspension from the middle of blue spot is transferred to a glass or an ITO substrate (instead of to a membrane filter substrate that rapidly soaks up the ionic liquid) then stored in dark for 24 h. Figure 6 shows SEM images obtained after 30 min irradiation followed by 24 h incubation in the dark. Exceptionally long nanowires are now detected over the entire substrate surface. The higher magnification images reveal that most of the nanowires have diameters lying in the range of 40−50 nm. Images at smaller magnification (not shown) reveal that these nanowires are extremely long (mm or greater and exceed the upper detection limit of the SEM instrument). A small number of isolated nanoparticles were also observed among the network of nanowires. Physical characterization of material formed in this manner by EDAX elemental analysis, IR spectroscopy and Raman spectroscopy confirm the formation of AgTCNQ.

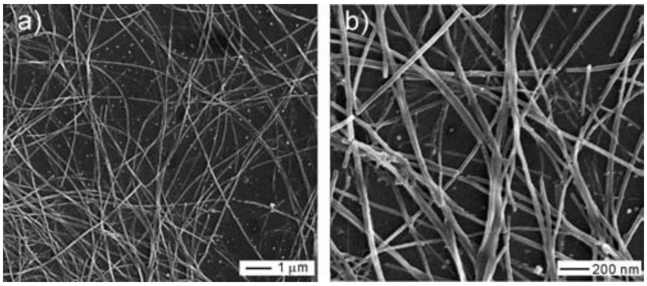

Figure 6. SEM images of AgTCNQ formed on a ITO glass substrate after 1 h irradiation (λ = 380 nm) of a liquid film of $BMIMBF_4$ containing equimolar (4.8 mM) TCNQ and Ag^+ followed by 24 h of incubation in the dark.

Mechanism of AgTCNQ Formation and Modified Properties in Ionic Liquids That Facilitate Oxidation of Water. Formation of extremely long AgTCNQ nanowires, which might be coiled, is both fundamentally interesting and potentially of technological importance. The exceptional length may be attributed to the anisotropic growth of the AgTCNQ itself and the nanostructured anisotropic environment in ionic liquids, which favors the production of one-dimensional structures.[59,62,74] Scheme 1 provides a cartoon form of presentation of the processes hypothesized to lead to the AgTCNQ nanowire formation. Irradiation gives rise to photoexcitation of TCNQ. The oxidation of the sacrificial electron donor such as benzyl alcohol to benzaldehyde then leads to formation of reduced $TCNQ^-$ anion (Scheme 1a). TCNQ has only a very short photoexcited-state lifetime. This is attributed to dicyanomethylene units in TCNQ, which dissipate excited-state energy through a free-rotor effect.[81] Consequently, interaction with benzyl alcohol in the photoexcited state may be assumed to be highly favorable. AgTCNQ is then formed via reaction between $TCNQ^-$ and Ag^+, and precipitated slowly in the form of small clusters (or nuclei) through homogeneous nucleation under conditions of supersaturation (Scheme 1b). A continuous supply of AgTCNQ enables these nuclei to serve as seeds for extended highly anisotropic growth along the columnar stack of TCNQ to form a nanorod (Scheme 1c). Continuation of irradiation provides more AgTCNQ, which allows each end of the rod to grow at a rate which is controlled by very slow diffusion in the highly viscous $BMIMBF_4$. The process is assumed to be directed by the anisotropic nanostructure of the ionic liquid, to produce very long nanowires (Scheme 1d). In principle, the growth of the nanowires is endless, provided that AgTCNQ is constantly

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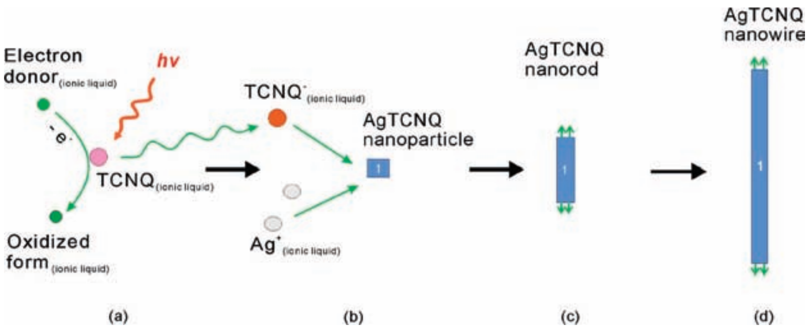
Scheme 1. Schematic Representation of the Photocrystallization and Growth of AgTCNQ Nanowire[a]



[a] (a) Photoreduction of TCNQ to $TCNQ^-$, and counter photooxidation of a sacrificial electron donor such as benzyl alcohol or water, (b) formation of AgTCNQ nuclei via homogeneous nucleation, (c) formation and growth of nanorod at both ends at a diffusion controlled rate, (d) formation of a nanowire of AgTCNQ.

supplied from the bulk ionic liquid solution and other conditions remain uninterrupted. In summary, AgTCNQ formation in the presence of a deliberately added electron donor benzyl alcohol in $BMIMBF_4$ can be summarized by eqs 1 and 2.

$$2TCNQ_{(BMIMBF_4)} + C_6H_5CH_2OH_{(BMIMBF_4)} \xrightarrow{hv} 2TCNQ^-_{(BMIMBF_4)} + C_6H_5CHO_{(BMIMBF_4)} + 2H^+_{(BMIMBF_4)} \quad (1)$$

$$2TCNQ^-_{(BMIMBF_4)} + 2Ag^+_{(BMIMBF_4)} \rightarrow AgTCNQ_{(solid)} \quad (2)$$

The photocrystallization of AgTCNQ in $BMIMBF_4$ in the absence of a deliberately added sacrificial electron donor was unexpected. The progressive formation of a large quantity of AgTCNQ materials upon irradiation indicates that the supply of this electron donor is abundant and steady. Given the composition of the system, possible counter reactions associated with photoreduction of TCNQ in $BMIMBF_4$ considered were oxidation of Ag^+ to Ag^{2+}, oxidation of the constituent ions in the ionic liquid itself, oxidation of trace acetonitrile present in the Ag salt, or oxidation of impurities such as adventitious water known to be present in the ionic liquid under open bench laboratory conditions. The oxidation of BF_4^- was ruled out because of its well-known excellent chemical stability, which is demonstrated, for example, by the wide voltammetric potential window (4.1 V at a Pt electrode).[53,54,56−58] Acetontrile also is a very stable and difficult to oxidize solvent, which has a potential window in excess of 6 V, provided that suitable supporting electrolytes are added.[82] Thus acetonitrile oxidation also is highly unlikely. Oxidation of Ag^+ to Ag^{2+} or oxidation of the $BMIM^+$ cation also is very difficult to achieve.

In view of the difficulty of oxidizing the species mentioned above and known to be present, we explored the possible role of impurities with respect to the counter oxidation process. $BMIMBF_4$ can contain a range of impurities that are derived from the synthetic processes or decomposition of the constituent cation or anion. Halides are a common impurity arising from the synthesis. The manufacturer's certificate of purity advises that the $BMIMBF_4$ sample used in this study contains <100 ppm halide,[83] a level which is unlikely to sustain the photoreduction of TCNQ. Impurities might arise from the hydrolysis of BF_4^-. Ionic liquids based on PF_6^- are well-known to react, in the presence of water[58] to give hydrolyzed species such as POF_4^-, $PO_2F_2^-$ and HF. However, analogous forms of hydrolysis are much slower in BF_4^- -based ionic liquids.[58] ^{19}F and ^{11}B NMR based investigations of the $BMIMBF_4$ sample used in this study showed that on the time scale of our experiments, no hydrolysis reaction product was detectable (see Figures S1 and S2, Supporting Information). Furthermore, likely BF_4^- hydrolysis products such as BOF_2^- and HF are also electrochemically stable toward oxidation.

The most common impurity in ionic liquids is water, which is easily oxidized, at least in a thermodynamic sense. Karl Fischer measurements showed that the $BMIMBF_4$ left exposed to open bench laboratory conditions employed for the photochemical studies described above contained up to 7.5% (wt.) water. $BMIMBF_4$ is fully miscible with water at temperature above 5 °C. Systematic studies have shown that "dried" $BMIMBF_4$ can absorb water from the gas phase to achieve a content of up to 25.2% (wt.).[84,85] Thus, the level of water available in open laboratory conditions provides an abundant supply, if water can serve as the electron donor. Thermodynamically, the oxidation of water is easy to achieve, but kinetically, the process usually is very slow.

To establish whether water is involved, a series of experiments were conducted with $BMIMBF_4$ dried under vacuum at 20 °C at 0.03 mBar for 48 h. Karl Fischer measurements demonstrated that the "dried" ionic liquid now contains less than 0.04% (wt.) water. Solutions containing equimolar (4.8 mM) TCNQ and $AgBF_4$, instead of $Ag(MeCN)_4BF_4$, and hence devoid of acetontrile, were then prepared using this "dried" $BMIMBF_4$ and sealed into a test tube in a nitrogen filled glovebox. The tube was then irradiated ($\lambda = 380$ nm) for 30 min at a distance of 0.5 cm from below the bottom of the test tube. These conditions failed to lead to visual detection of AgTCNQ (Figure 7a, no blue spot formed at the bottom of the tube). This result confirms that the counter reaction is not due to the oxidation of the ionic liquid itself or TCNQ and implies that water is the source of the counter reaction. As expected, addition of 10% benzyl alcohol to "dried" $BMIMBF_4$ still leads to AgTCNQ formation (Figure 7b, blue spot formed at the bottom of the tube).

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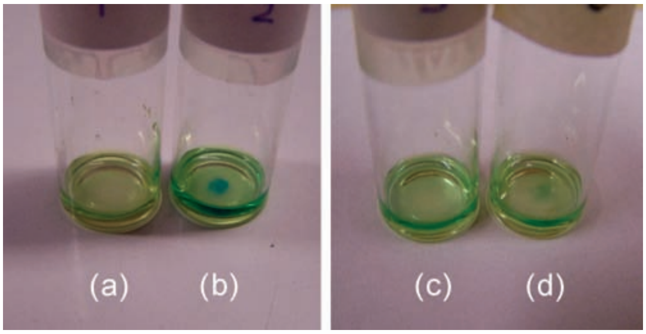

Figure 7. Photographs obtained after 30 min irradiation ($\lambda = 380$ nm) of a $BMIMBF_4$ ionic liquid solution under different conditions. (a) Mixture of equimolar (4.8 mM) TCNQ and $AgBF_4$ in "dried" $BMIMBF_4$; (b) mixture of equimolar (4.8 mM) TCNQ and $AgBF_4$ plus 10% (v/v) benzyl alcohol in "dried" $BMIMBF_4$; (c) mixture of equimolar (4.8 mM) TCNQ and $Ag(MeCN)_4BF_4$ in "dried" $BMIMBF_4$; (d) mixture of equimolar (4.8 mM) TCNQ and $AgBF_4$ in "dried" $BMIMBF_4$ with 10% (v/v) deliberately added water.

In another control experiment, an equimolar (4.8 mM) TCNQ and $Ag(MeCN)_4BF_4$ solution prepared in "dried" $BMIMBF_4$ was irradiated at $\lambda = 380$ nm for 30 min. Again, no AgTCNQ formation was detected (Figure 7c, no blue spot formed at the bottom of the tube). However, importantly, addition of 10% (v/v) distilled water, followed irradiation at $\lambda = 380$ nm for 30 min does lead to visual detection of AgTCNQ (Figure 7d, blue spot formed at the bottom of the tube). The result again supports the hypothesis that that the counter reaction is associated with the presence of water rather than from other impurities present in $BMIMBF_4$. In summary, on the basis of the above control experiments it is postulated that adventitious water present in this ionic liquid serves as the electron donor in the photochemical generation of AgTCNQ. Nevertheless, on the basis of comparison of images in Figure 7 b and d, it is clear that benzyl alcohol is a superior electron donor to water.

If water is the counter reaction, then its oxidation to generate O_2 and H^+ should accompany the photochemical reduction of TCNQ to $TCNQ^-$. Direct evidence for concomitant and stoichiometric generation of $TCNQ^-$ and O_2 upon irradiation of TCNQ in $BMIMBF_4$ solutions containing water was accomplished by voltammetric measurements. The solubility of oxygen in ionic liquids is generally high.[86] In $BMIMBF_4$ its solubility of 3.4 mM, at 20 °C[87] is more than 1 order of magnitude higher than in water (0.29 mM, 20 °C).[88] Voltammetry is known to provide a sensitive and in situ method for the study of the reduction of O_2 in aqueous and organic solvents.[89] Recent studies also have reported the reductive voltammetry of O_2 in room temperature ionic liquids.[86,90−94]

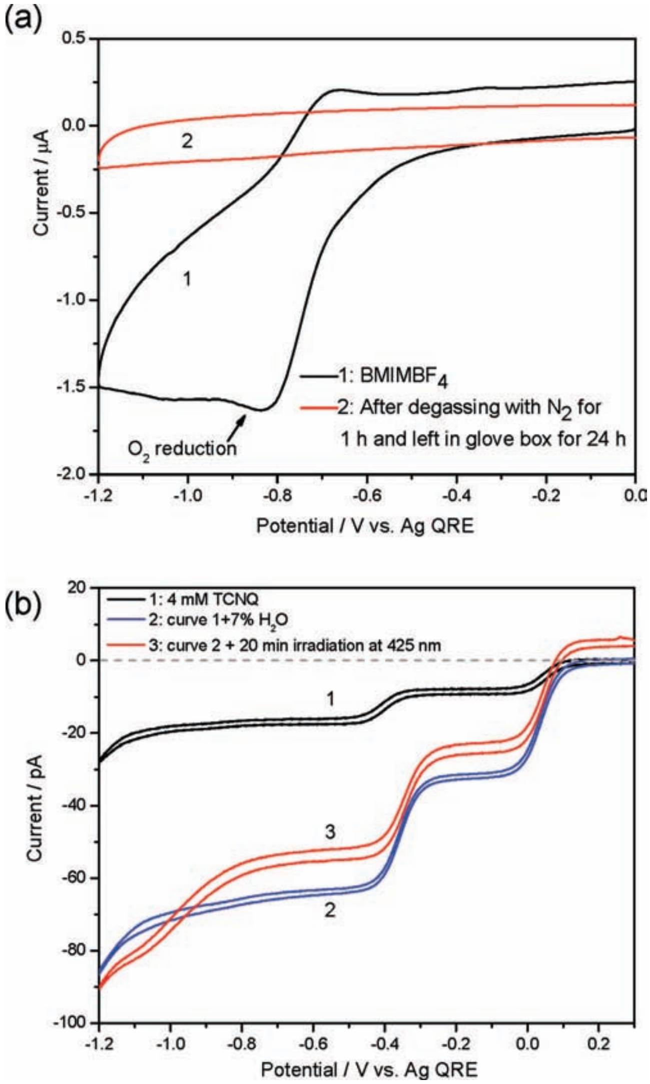

Figure 8. Voltammetric detection of O_2 and $TCNQ^-$ in $BMIMBF_4$ (a) cyclic voltammograms obtained at a scan rate of 100 mV s^{-1} showing both O_2 reduction at a glassy carbon macrodisc electrode (a1) and that absence of O_2 is maintained in the nitrogen-filled dry box over a 24 h period (a2); (b) steady-state voltammograms obtained at a 1 μm diameter Pt microelectrode at a scan rate of 50 mV s^{-1} under designated conditions before (b1, b2) and after (b3) irradiation that show the concomitant formation of O_2 and $TCNQ^-$ when TCNQ is photoreduced in the presence of water.

In Figure 8a, the voltammetric process at a glassy carbon electrode for O_2 reduction is first identified in $BMIMBF_4$. The irreversible reduction process detected at around −0.85 V (vs Ag QRE) is analogous to that reported in other ionic liquids. After degassing the $BMIMBF_4$ solution with N_2 for 60 min, the oxygen process fully disappears, as required for a process assigned to O_2 reduction. The degassed $BMIMBF_4$ solution was then left in the nitrogen-filled glovebox for 24 h without reappearance of the reduction process (Figure 8). This result confirms that no O_2 is leaking into the glovebox, in agreement with data provided from the oxygen analyzer (see Experimental Section). Clearly it is possible to irradiate oxygen free solutions of $BMIMBF_4$ containing TCNQ and water and then seek to simultaneously detect the generation of voltametrically active oxygen and $TCNQ^-$ as products. This is best done by steady-state measurements at a microelectrode.

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Figure 8, b (curve 1) shows the steady-state voltammogram obtained at a scan rate of 50 mV s^{-1} at a 1 μm diameter Pt microdisc electrode in "dried" and oxygen free $BMIMBF_4$ solution containing 4 mM TCNQ. Two well-resolved reversible one-electron, $TCNQ^{0/-}$ and $TCNQ^{-/2-}$ reduction processes[95] are observed with reversible potentials, $E^{0'}$, of 0.08 V and −0.37 V (vs Ag QRE). Addition of 7% (v/v) water leads to the significant current increase for both the $TCNQ^{0/-}$ and $TCNQ^{-/2-}$ processes (Figure 8b, curve 2). This is as a result of decrease of viscosity and concomitant increase in the diffusion coefficient of TCNQ.

Upon irradiation under glovebox conditions at $\lambda = 425$ nm for 20 min of the $BMIMBF_4$ solution containing 4 mM TCNQ + 7% (v/v) water, the initially yellow TCNQ solution turns green, indicating the occurrence of photochemical reduction of TCNQ to $TCNQ^-$. The microelectrode voltammogram now exhibits a significant O_2 reduction current (Figure 8b, curve 3), as required if the O_2 was produced during the photochemical reaction. Transient cyclic voltammograms obtained at a macrodisc GC electrode confirm production of O_2 during the irradiation procedure (Figure S3, Supporting Information). Additionally, the position of zero current (Figure 8b, curve 3), now lies part way through the $TCNQ^{0/-}$ process and has an oxidation as well as reduction component as required for a mixture of TCNQ and $TCNQ^-$ which confirms that $TCNQ^-$ is generated during the irradiation process. Furthermore, making reasonable assumptions about diffusion coefficients of TCNQ, $TCNQ^-$ and O_2 and reaction mechanisms in $BMIMBF_4$ leads to the conclusion that the reaction is stoichiometric and certainly not catalytic. Finally, the change in apparent "pH" value before and after irradiation from 4.70 to 1.39 is consistent with the generation of H^+ (no "pH" change detected in control experiments without irradiation). Given that the activity of the hydrogen ion in $BMIMBF_4$ is unknown, as are junction potentials, no quantitative significance may be attached to this "pH" change in terms of hydrogen ion concentation, but qualitatively the results are consistent with H^+ generation.

All evidence suggests that oxidation of the water present in $BMIMBF_4$ provides the counter reaction required for photoreduction of TCNQ. The formation of AgTCNQ may, therefore, be described by the following equations.

$$2TCNQ_{(BMIMBF_4)} + H_2O_{(BMIMBF_4)} \xrightarrow{hv} 2TCNQ^-_{(BMIMBF_4)} + 1/2O_{2(BMIMBF_4)} + 2H^+_{(BMIMBF_4)} \quad (3)$$

$$2TCNQ^-_{(BMIMBF_4)} + 2Ag^+_{(BMIMBF_4)} \rightarrow 2AgTCNQ_{(solid)} \quad (4)$$

The finding that H_2O may be used as the sacrificial electron donor in the photoreduction of TCNQ in $BMIMBF_4$ is unexpected, since the oxidation of water is not available for practical use when water is present in an organic solvent such as acetonitrile. Oxidation of water as the counter processes in ionic liquids is attributed to its significantly different molecular state, relative to that when dissolved in conventional solvents. Spectroscopic studies provide clear evidence that water molecules absorbed from the air into room temperature ionic liquids are predominantly embedded in the "free" state (no self-aggregation via strong hydrogen bonding with other water molecules).[96−100] Thus the water molecules are isolated from each other and tend to interact with the anions of the ionic liquids forming either a 1:1 type complex, H−O−H•••anion, or a symmetric 1:2 type complex, anion•••H−O−H•••anion.[96−99] This form of hydrogen-bonded environment and also the water-ion electrostatic interactions, which are generally strong in ionic liquids, inevitably affect the chemical properties of both the ionic liquid and the bound water,[96,97,99] and also modify the hydrogen bond lengths and angles. Thus, water molecules exhibit ionic liquid dependent polarities, a property which has been used as a measure of the polarity of the ionic liquids.[96,97] The removal of water−water H-bonds minimizes the "protection" of a water molecule from its neighboring water molecules, and is therefore postulated to lower the activation barrier required for oxidation of water in ionic liquids. In a molten salt hydrate, it has been also discovered that the water component is chemically quite different from that of the bulk water present in an aqueous solution with respect to properties such as enthalpy of evaporation, conductivity, and partial molar dilution enthalpy.[101−103] H-bonding of water molecules also has been shown to increases the basicity of the oxygen atom in water molecules.[104] All the modified features present when water is dissolved in an ionic liquid, can lower the energy barrier and hence in principle enhance the rate of the oxidation.

Conclusions

Very long nanowires of charge transfer AgTCNQ material have been synthesized by photochemical reduction of TCNQ in the presence of a silver salt in the ionic liquid $BMIMBF_4$ containing a sacrificial electron donor. The method should be generally applicable for photocrystallization of other metal-TCNQ complexes in ionic liquids. Photocrystallization of AgTCNQ in $BMIMBF_4$ in the presence of an efficient sacrificial electron donor such as benzyl alcohol allows relatively rapid formation of long AgTCNQ nanowires on conducting or insulting substrates. Importantly, AgTCNQ nanoparticles and nanowires could also be photocrystallized from this ionic liquid using oxidation of water as a counter reaction. However, photoreduction of TCNQ to $TCNQ^-$ occurs at a slower rate when water is use as the sacrificial electron donor. Finer nanoparticles or longer nanowires of AgTCNQ could be obtained by controlling the irradiation and ripening times. In the latter case, the growth of nanowires requires the sacrifice of dissolved AgTCNQ and of the smaller AgTCNQ nanoparticles produced during the irradiation stage.

The fact that water can be relatively easily photooxidized in the ionic liquid, but not in an organic solvent, implies the molecular structure and chemical activity of water are signifi-

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cantly different in these two kinds of media. Lowering of water–water hydrogen bonding in the ionic liquid and polarization shifts may be the major source of the lowered activation barrier. We believe that this finding may have at least two important implications. First, water absorbed from the air could provide a major source of the electron donor component in photochemical studies in ionic liquids. Adventitious water is present in almost every ionic liquid. Additionally, the implication that an ionic liquid environment may facilitate the photooxidation of water could lead to advances in the area of water splitting, needed for production of cheap hydrogen as an energy source, with avoidance of CO_2 emission.

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Supporting Information Available: Figures S1 and S2 containing ^{19}F and ^{11}B NMR spectra respectively of the neat ionic liquid $BMIMBF_4$ and Figure S3 containing a transient cyclic voltammogram which confirms the production of O_2 during the irradiation procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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