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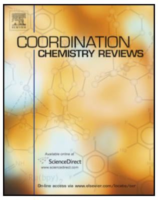

Review

Electrochemical and photochemical routes to semiconducting transition metal-tetracyanoquinodimethane coordination polymers

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ABSTRACT

$TCNQ^{\bullet-}$ radical anions (TCNQ = 7,7,8,8,-tetracyanoquinodimethane) form a wide range of semiconducting coordination polymers when coordinated to transition metals. Some materials such as CuTCNQ and AgTCNQ exhibit molecular switching and memory storage properties; others have intriguing magnetic properties and for example may behave as molecular magnets at low temperature. In this review, the electro- and photo-chemical synthesis and characterization of this important class of material is reviewed. In particular, the electrochemistry and the redox properties of TCNQ derivatives of coordination polymers based on Cu, Ag, Mn, Fe, Co, Ni, Zn and Cd transition metals are surveyed, with an emphasis on the mechanistic aspects of their electrochemical formation via nucleation-growth processes. Given that TCNQ is an extremely good electron acceptor, readily forming $TCNQ^{\bullet-}$ and $TCNQ^{2-}$, electrochemical reduction of TCNQ in the presence of a transition metal ion provides an ideal method for synthesis of metal-TCNQ materials by electrocrystallization from organic solvents and ionic liquids or solid–solid transformation using TCNQ modified electrodes from aqueous media containing transition metal electrolytes. The significance of the reversible formal potential ($E^0{}_f$) in these studies is discussed. The coupling of electrocrystallization on electrode surfaces and microscopic characterization of the electrodeposited materials reveals a wide range of morphologies and phases which strongly influence their properties and applications. Since TCNQ can also be photo-reduced in the presence of suitable electron donors, analogous photochemical approaches to the synthesis of TCNQ-transition metal derivatives are available. The advantages of electrochemical and photochemical methods of synthesis relative to chemical synthesis are outlined.

1. Introduction

TCNQ (7,7,8,8-tetracyanoquinodimethane, Fig. 1a) is one of the strongest known organic electron acceptors (electron affinity is 2.88 eV) and has long been regarded as a key candidate for formation of semiconducting organic/inorganic charge-transfer compounds [1–8]. Importantly, its reduced forms ($TCNQ^{\bullet-}$ and $TCNQ^{2-}$) (Fig. 1a) represent excellent ligands for synthesis of a diverse range of coordination polymers (CPs) and metal-organic frameworks (MOFs) upon reaction with transition metal (TM) or organic cations. These materials are usually only sparingly soluble in organic solvents, so the possibility of growing sufficiently large high quality single crystals, suitable for X-ray structural characterization, has presented a challenging task. As a result, the structures of many of TM-TCNQ based materials are as yet unknown. However, Fig. 1b provides an example of structurally characterized $[Mn(TCNQ)_2(H_2O)_2]$ coordination polymer network that contains the mono-reduced form of TCNQ. Fortunately, TCNQ-based materials are spectroscopically rich so that other methods of characterization of structures are available. Additionally, recent advances in X-ray structure analysis provided by synchrotron facilities are highly beneficial and structural data is now becoming more readily accessible in the TM-TCNQ field.

In the electrochemical sense, the electron transfer reactions given in Eqs. (1) and (2) are facile, although the generated radical anion is significantly more stable than the dianion under ambient conditions [9].

$$TCNQ + e^- \rightleftharpoons [TCNQ]^{\bullet-} \quad (1)$$

$$[TCNQ]^{\bullet-} + e^- \rightleftharpoons [TCNQ]^{2-} \quad (2)$$

The variability of the solubility of TCNQ in different solvents provides flexibility in electrochemical approaches that can be used to form transition metal coordination polymers (TM-CPs). In water, TCNQ is highly insoluble [12]. This property allows chemically modified TCNQ electrodes to be placed in an aqueous electrolyte media with minimal dissolution. Since TM-CPs are also insoluble in water, reduction of solid TCNQ can occur to form coordination polymers via solid–solid interconversion processes that involve uptake of the TM cation from the aqueous electrolyte. Thus, CuTCNQ, which has attracted substantial attention due to its high structural flexibility, reversible electrical/optical bistable switching and field emission properties [13–24], can be prepared by reduction of a TCNQ modified electrode in contact with an aqueous solution containing 0.1 M $CuSO_{4(aq)}$ as the supporting electrolyte [25]. In contrast, TCNQ is soluble in acetonitrile, therefore the electrocrystallization of sparingly soluble CuTCNQ also can be accomplished by electrochemical reduction of TCNQ dissolved in acetonitrile (0.1 M NBu_4PF_6) containing a $[Cu(MeCN)_4][PF_6]$ precursor [26]. Clearly, the mechanism of formation of CuTCNQ in the solid–solid interconversion and solution based approaches must be entirely different. The mechanistic details as well as the electrochemical methods employed to make the congeners (Ag, Mn, Fe, Co, Ni, Zn and Cd) TCNQ-based coordination polymers will be highlighted in this review. Another method of electrochemical synthesis involves bulk electrolysis of TCNQ to $TCNQ^{\bullet-}$ in acetonitrile (0.1 M NBu_4PF_6) followed by addition of a TM salt, which gives rise to precipitation of the coordination polymer. Analogous electrochemical procedures are available for the synthesis of $TCNQ^{2-}$ containing compounds.

Apart from synthesis of CPs, interest in the application of CuTCNQ and AgTCNQ based materials in molecular switching and memory storage devices, has led to the development of a diverse range of novel approaches to achieve precise control of the morphology, phase, structure, and purity. These include spontaneous electrolysis (reaction between dissolved TCNQ in acetonitrile and metallic substrate), vacuum vapor deposition of TCNQ onto metal surfaces at low temperature, and direct reaction of TCNQ and metal salt precursors in aqueous or organic solvents. Electrochemical techniques offer facile and versatile approaches to precisely control the nucleation and growth processes, as well as the purity, structure, and morphologies of the crystals, and often can be operated under ambient and benign conditions.

Since TCNQ-based coordination polymers are both spectroscopically and electrochemically rich, a wide range of spectroelectrochemical methods are available to probe structures and properties. Widely used techniques of physical chemistry applied to these materials include Raman, IR, UV/Vis and EPR spectroscopy. The fact that the electrochemically synthesized materials are often adhered to conducting substrates enables a wide range of surface science (e.g. XRD and EDAX) and imaging (optical, AFM and SEM) tools to be employed in conjunction with electrochemical synthesis. In order to immobilize TCNQ-based materials onto insulating rather than conducting substrates, photochemical reduction of TCNQ into $TCNQ^{\bullet-}$ in the presence of TM cations can be used