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Electrochemically mediated atom transfer radical polymerization of acrylonitrile and poly(acrylonitrile-*b*-butyl acrylate) copolymer as a precursor for N-doped mesoporous carbons

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ABSTRACT

The synthesis of polyacrylonitrile (PAN) with precisely defined morphology is essential to obtain a polymer precursor for the preparation of high-value carbon-based materials. PAN homopolymers with very narrow molecular weight distribution were prepared by electrochemically mediated atom transfer radical polymerization (*e*ATRP) of acrylonitrile. The redox properties of the Cu complexes used as *e*ATRP catalysts were first investigated. Convenient polymerization conditions were identified by varying the applied potential, initiator nature, monomer and catalyst loading, and targeted molecular weight (MW). PAN with high MW, 9.1×10^4 g mol^{-1}, was obtained in only 3 h. A shorter PAN was extended with butyl acrylate to prepare a well-defined PAN-*b*-PBA copolymer, which was subjected to annealing and pyrolysis. The obtained copolymer-templated nitrogen-enriched nanocarbon was characterized by BET, TEM and Raman spectroscopy. The material showed an exceptionally high nitrogen content, together with a remarkable activity toward O_2 reduction and 40% selectivity for H_2O_2 production.

1. Introduction

Polyacrylonitrile (PAN) is a fundamental polymer precursor for preparing carbon-fiber composites and mesoporous carbons [1,2]. High-molecular-weight (high-MW) PAN, with precise architecture, is necessary to produce fibers with high mechanical and chemical resistance [3,4]. Concerning porous carbons, block copolymers (BCPs) with defined morphology, composed of PAN and a sacrificial block, serve as a template for high surface area nanocarbons, containing easily accessible redox-active N-sites [5–7]. These copolymer-templated nitrogen-enriched nanocarbons (CTNCs) showed exceptional efficiency as catalysts for oxygen reduction reaction (ORR) [8] and hydrogen evolution reaction [9], as sorbents of CO_2 [10], Cr(VI), and U(VI) [11], and as electrodes for supercapacitors [6,7], and dye synthesized solar cells [12].

To produce high-performing carbon materials, pre-determined MWs and microstructure must be achieved during AN polymerization, thus excluding the use of conventional radical polymerization. Atom transfer radical polymerization (ATRP) is the primary technique for the preparation of polymers and copolymers with defined compositions and architectures [13–15]. In ATRP, a redox couple $[\mathrm{Cu^{I}L}]^+$/$[\mathrm{XCu^{II}L}]^+$ tunes the equilibrium between active radicals and halogen-capped dormant species (Scheme 1). The mechanism of the reaction has been extensively investigated [16,17], also with the aid of electron spin resonance spectroscopy to detect paramagnetic species formed during the reaction [18–20]. Radical concentration is constant and very low, thus reducing the likelihood of termination events and enabling a controlled growth of functionalized polymer chains.

Nevertheless, first ATRP studies on AN showed poor chain-end functionality [21,22]. It was proposed that Cu catalysts react with growing PAN chains *via* an outer sphere electron transfer, thus reducing radicals to carbanions, thereby broadening the molecular weight distribution (dispersity, *Đ*) and leading to loss of halide chain-end functionality. These side reactions are detrimental to the polymerization process, preventing the possibility of reaching high MWs and building block copolymers through chain extension. In ATRP, the amount of Cu catalyst can be drastically decreased, by continuously regenerating the active catalyst, $[\mathrm{Cu^{I}L}]^+$, from [X-

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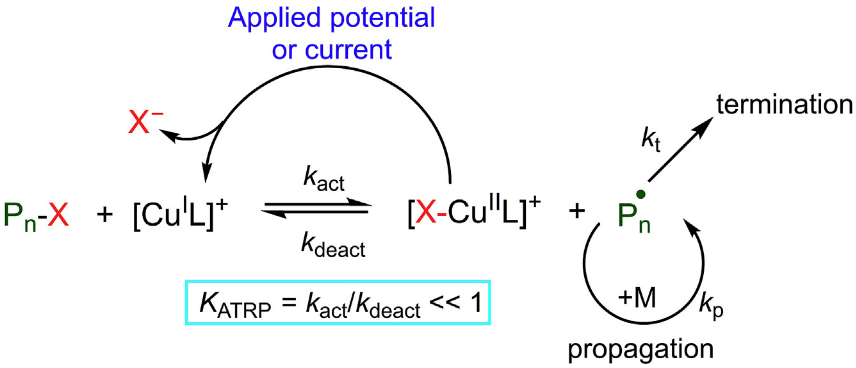

Scheme 1. Mechanism of ATRP with electrochemical regeneration of the activator complex (*e*ATRP).

$Cu^{II}L]^+$ that accumulates during termination reactions [23]. Low catalyst loadings dramatically decreased the extent of side reactions in ATRP of AN [24]. Moreover, diminishing Cu content is beneficial for CTNC production, whereby the residual metal might mask the electrocatalytic activity of the material [25]. Therefore, PAN homopolymers and copolymers were successfully obtained by using various radical initiators and/or reducing agents for Cu^I regeneration [24–29].

Electrochemical stimuli (*i.e.* applied current or potential) can also be used to reduce the accumulated Cu^{II} species, with the unique advantage of avoiding by-products formation, because electrons are used in lieu of chemical reducing agents [30,31]. Moreover, the ratio between Cu^{II} deactivator and Cu^I species is fixed by the applied potential or current, thus it can be finely tuned by modulating the electrochemical stimulus. This technique, named electrochemically mediated ATRP (*e*ATRP) was applied to several monomers in organic solvents [32,33], water (at both neutral and very acidic pH [34,35]), oil-in-water miniemulsion [36] and ionic liquids [37]. However, *e*ATRP of acrylonitrile has never been reported.

In this work, well-controlled PAN homopolymers were prepared *via e*ATRP, catalyzed by Cu with tris(2-pyridylmethyl)amine (TPMA) as ligand. The high activity of the catalyst enabled relatively fast polymerizations with low catalyst loadings (≤164 ppm on molar basis with respect to monomer).

This copper complex was considered too active for ATRP of AN with Cu^0 as reducing agent and supplemental activator (SARA ATRP) [25], whereas it proved to be a good catalyst in initiators for continuous activator re-generation (ICAR) ATRP of AN, with azobisisobutyronitrile (AIBN) as radical initiator [28]. This big difference of catalyst behavior in the two ATRP techniques was attributed to different activation kinetics. The rate of ICAR ATRP depends strongly on AIBN decomposition, which is relatively slow. On the other hand, in SARA ATRP the dormant species (P_n-X) can be activated by both Cu^0 and Cu^I, the latter being generated by relatively fast comproportionation between Cu^0 and Cu^{II}. Thus, in SARA ATRP less active catalysts had to be employed, at the expense of the reaction rate, to avoid excessive generation of propagating radicals [25]. Herein, the applied potential was tuned to ensure the presence of a sufficient amount of Cu^{II} deactivator, enabling the use of such an active catalyst, and therefore shortening the reaction time.

The effect of monomer loading and nature of alkyl halide initiator (RX) were investigated. High-MW PAN ($M_n = 9.1 \times 10^4\ g\ mol^{-1}$) was prepared in only 3 h. The good retention of chain-end functionality was proved by extending a PAN-Br macroinitiator with *n*-butyl acrylate (BA), obtaining PAN-*b*-PBA copolymer with $Đ = 1.11$. *e*ATRP conditions were arranged to prepare a suitable precursor for CTNC. Indeed, PAN-based block copolymers with ~40 wt% AN were demonstrated to possess a bicontinuous morphology, which is essential to avoid the collapse of the nanostructure during the pyrolysis of the copolymer [6,10,25].

The copolymer was subjected to pyrolysis at 700 °C, preceded by an oxidative annealing step at moderate temperature (280 °C for 1 h). The annealing step is essential to preserve the PAN precursor nanostructure, which depends on phase-separation driven self-assembly, induced by the sacrificial block (*i.e.* PBA) [5]. The final material was characterized by transmission electron microscopy, Raman spectroscopy, nitrogen adsorption/desorption and elemental analysis, whereas electrochemical selectivity for H_2O_2 generation was evaluated at a rotating ring disk electrode.

2. Experimental

2.1. Materials

Anhydrous dimethyl sulfoxide (DMSO, Sigma-Aldrich, 99.9%), anhydrous *N*,*N*-dimethylformamide (DMF, Sigma-Aldrich, 99.8% or VWR, 99.8%), methanol (VWR, ACS grade, 99.8%), copper(II) trifluoromethanesulfonate ($Cu(OTf)_2$, Sigma-Aldrich, 98%), copper(II) bromide ($CuBr_2$, Sigma Aldrich, 99.999% trace metal basis), tris(2-pyridylmethyl)amine (TPMA, Sigma-Aldrich, 98%), 2-bromopropionitrile (BPN, Sigma-Aldrich, 97%), 2-chloropropionitrile (CPN, Sigma-Aldrich, 97%), ethyl *α*-chlorophenylacetate (ECPA, Sigma-Aldrich, 97%), lithium bromide (Sigma-Aldrich, 99.9%), H_2SO_4 (Fluka, 95%, TraceSELECT), commercial mesoporous carbon (C-MC, Sigma Aldrich 99.95%, <500 nm particle size, 0.342 cm^3/g total pore volume), and Nafion (5 wt% in a mixture of lower aliphatic alcohols and water, Sigma-Aldrich) were used as received.

Acrylonitrile (AN, Sigma-Aldrich, 99%), and *n*-butyl acrylate (BA, Sigma-Aldrich, >99%) were purified by passing through a column filled with active basic aluminum oxide (Al_2O_3, VWR chemicals), to remove polymerization inhibitors.

Tetraethylammonium tetrafluoroborate (Et_4NBF_4, Alfa Aesar, 99%), used as a supporting electrolyte, and tetraethylammonium bromide (Et_4NBr, Sigma-Aldrich, 99%) were recrystallized from ethanol and acetone, respectively. Tetraethylammonium chloride (Et_4NCl, Sigma-Aldrich, 98%) was first dissolved in ethanol, then precipitated with ethyl ether. The three salts were dried in a vacuum oven at 70 °C for 48 h.

2.2. Instrumentation

Electrochemical studies on the Cu catalyst and electrosynthesis of polymers were carried out in a 5-neck electrochemical cell,