

Acid Electrolytes Effect on In-Situ Growth and Morphology of Polymer Nanowires in Microelectrode Devices

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ABSTRACT

We investigated five acids—(1) formic acid, (2) acetic acid, (3) perchloric acid, (4) hydrochloric acid and (5) nitric acid—as an electrolyte for a direct one-step, *in-situ* electrochemical growth of conducting polyaniline (CPA) nanowires onto patterned microelectrode devices (MEDs). The effect of these acid electrolytes on the growth and morphology of CPA nanowires generated from its monomer aniline solution in acid electrolytes are reported. We investigated acid electrolyte solutions with varying concentrations (0.2–1.0M) and monomer aniline solutions (concentrations: 0.1–1.0M). The growth of CPA nanowires was not observed in either formic or acetic acid electrolyte solutions at any monomer aniline and acid electrolyte concentrations. Neither formic nor acetic acids facilitated electro-polymerization processes. This may be due to their weak acid behavior. Growth of CPA nanowires was observed from all inorganic (perchloric, hydrochloric and nitric) acids with aniline concentrations of 0.1–0.6M and electrolyte concentrations of 0.2–0.6M in various degrees. High quality CPA nanowires with diameters ~50–150nm and length $\geq 2\mu\text{m}$ and high surface-area porous nanonetwork morphologies were obtained from 0.2–0.4M aniline solutions in 0.2–0.4M nitric and 0.2–0.6M perchloric acid electrolyte solutions. These high quality CPA nanowires will facilitate their use in chemical sensor and biosensor applications with improved detection capability.

Keywords: conducting polymers, electrochemical growth, nanowires, acid electrolytes, nanoframework morphology

1 INTRODUCTION

Conductive polymer (CP)-based nanostructured materials in thin films and nanowires have been utilized in numerous chemical sensor and biosensor applications [1-3]. Their beneficial attributes include: lightweight, large surface area, adjustable transport properties, chemical specificity, low cost, ease of processing, tunable conductivities, material flexibilities, and readily scalable production [1-4]. These nanomaterials have thus become prime candidates for replacing conventional bulk materials in micro- and nano-electronic devices and sensors [1-5]. CPs show the following features: (1) conjugated backbone allows for the flow of electrons, (2) able to maintain

polymer-associated physical characteristics, (3) usable in a wide range of applications including sensors and biosensors, (4) high environmental and thermal stability, (5) straightforward synthesis, (6) low-cost materials and/or monomers, and (7) conductivity can increase by over 10 orders of magnitude upon exposure to analyte gases via the change in ionic species, charge carrier and transport mechanism [1-5]. However, CP nanowires' dimension (diameter and length) and morphology play a critical role in their sensing performance. Although CP nanowires have been grown by different methods using different electrolytes, their uniform and reproducible growth is still a challenge [1-5]. To understand and overcome this challenge, we conducted a systematic studies on *in-situ* growth of CP nanowires, especially conducting polyaniline (CPA) nanowires on patterned microelectrode devices (MEDs) using a patented template-free, site-specific electrochemical process [1a] in different organic (formic and acetic) and inorganic (perchloric, hydrochloric and nitric) acid electrolyte solutions.

In this paper, we report the growth and morphologies of CPA nanowires upon using various organic and inorganic acid electrolytes and varying concentrations. We also report the effect of the concentration of electroactive aniline monomer on the growth of CPA nanowires.

2 MATERIALS AND METHODS

2.1 Materials

Both organic and inorganic acids such as (1) formic acid (HCOOH), (2) acetic acid (CH₃COOH), (3) perchloric acid (HClO₄), (4) hydrochloric acid (HCl) and (5) nitric acid (HNO₃) were purchased from Sigma-Aldrich (St. Louis, MO) and were used as received. Electroactive aniline monomer of CPA nanowires was also purchased from Sigma-Aldrich and was used after purification by distillation. Different acid electrolyte solutions of different concentrations (0.2–1.0M) were prepared by adding appropriate amount of acid in deionized (DI) water. The aniline monomer solutions (concentrations: 0.1–1.0M) were prepared in different acid electrolyte solutions.

2.2 Microelectrode Device Fabrication

Microelectrode devices (MEDs) were designed by using an AUTO CAD 2008 2D software and fabricated via

standard photolithography techniques for template-free, direct *in-situ* growth of CP nanowires. A photomask for the MEDs was first prepared at Photo-Sciences, Inc. (Torrance, CA). Using the photomask, gold-electrode MEDs were fabricated at REVTEK, Inc. (Torrance, CA) on a four-inch silicon substrate coated with 400nm thick silicon dioxide. The MEDs had a 55nm thick layer of gold on a 15nm of titanium as an adhesive layer (see Fig. 1A). The two electrode pads contained four (4) gold electrodes or “fingers”. The gold “fingertips” of each electrode had a 2 μ m gap between them. A scanning electron microscopy (SEM) image of the electrode junction is shown in Fig. 1B. Each silicon wafer usually contains several hundred MEDs. Thus, before the electrochemical polymerization of the nanowires, the MEDs were diced and separated from each other. The surfaces were thoroughly cleaned by soaking in a series of solutions and sonication [1-3]. Before the electrochemical polymerization of the nanowires, the MED surfaces were activated in a piranha solution (70% concentrated sulfuric acid, 30% hydrogen peroxide) for 10 minutes, followed by a deionized (DI) water rinse and drying in a clean nitrogen jet. A wire was bonded to each electrode pad by both soldering and using conductive silver epoxy and the wire bonding sites were encapsulated using a non-conducting epoxy layer (see Fig. 1C). An actual size of a MED compared to a penny is shown in Fig. 1D. This allowed the growth of CPA nanowires in the 2 μ m gap of the MEDs.

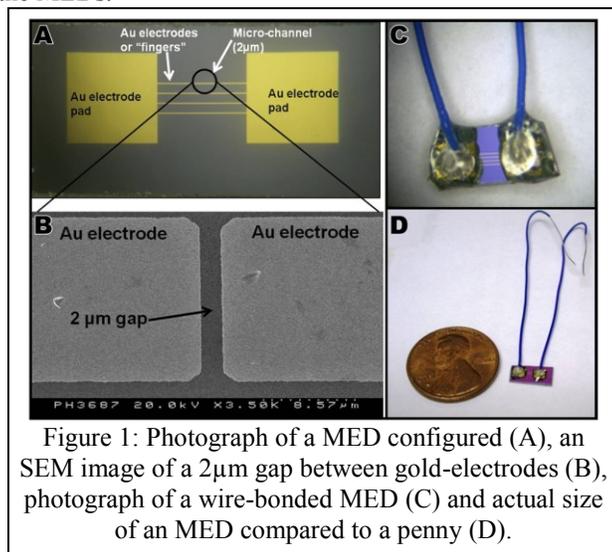


Figure 1: Photograph of a MED configured (A), an SEM image of a 2 μ m gap between gold-electrodes (B), photograph of a wire-bonded MED (C) and actual size of an MED compared to a penny (D).

2.3 Electrochemical Growth of Nanowires

CPA nanowires were grown by the template-free, site-specific electrochemical process [1-3]. We used a small volume flask filled with ~16–20mL aniline monomer solution (0.1–1.0M) in an acid electrolyte solution (0.2–1.0 M), in which a wire-bonded MED was submerged. One side of the MED acted as the working electrode. For the counter electrode, a platinum coil was used. The platinum coils had 10–12 turns and a wire diameter of 0.25mm. A

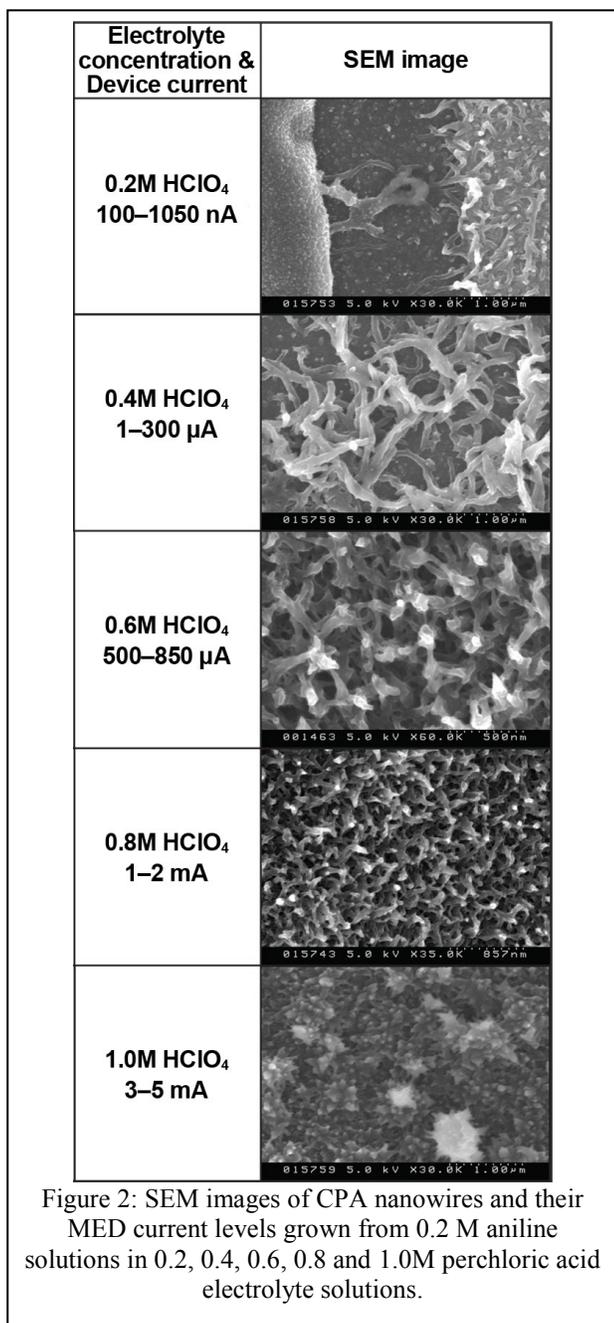
silver/silver chloride reference electrode was used to monitor the reaction voltage. The solution was purged with nitrogen for 10min prior to starting the electrochemistry. Nitrogen was constantly flowed into the flask during the experiment to maintain a neutral and non-oxidative environment above the solution. An oxidative potential was applied to one side of the electrode junction device, and ground to the platinum coil. A Princeton Applied Research model 263A-1 potentiostat was used to generate the potential difference. This oxidized the aniline monomers and triggered a chain reaction resulting in the formation of CPA nanowires.

The morphology, size distribution (diameters and lengths) and spatial arrangements of the CPA nanowires were characterized by SEM and energy dispersive X-ray spectroscopy (EDX) analysis at Photometrics Inc. (Huntington Beach, CA). The electrical properties were evaluated by measuring two-terminal current-voltage (I-V) characteristic curves using an Agilent semiconductor device analyzer (model B1500A).

3 RESULTS AND DISCUSSION

To grow CPA nanowires onto MEDs, solutions of aniline (monomer) with concentrations from 0.1M to 1.0M in 0.2, 0.4, 0.6, 0.8 and 1.0M formic acid were prepared. The site-specific electrochemical polymerization was first performed with 0.2M aniline solution in 1.0M formic acid. Similar electro-polymerization process was performed with other aniline solutions (0.4, 0.8 and 1.0M) in 0.6 and 0.8M formic acid electrolyte solutions. After the electro-polymerization process was done, the MEDs were examined under a microscope with 45x magnification. The visual examination showed no growth of CPA films or nanowires and the MEDs were as they were before the electrochemical process. This was confirmed by I-V characteristic measurements and SEM analysis. The same results were observed when using CH₃COOH electrolyte solutions. The conclusion was that organic acid is, in general, a poor electrolyte to initiate electro-polymerization for the growth of CPA nanowires.

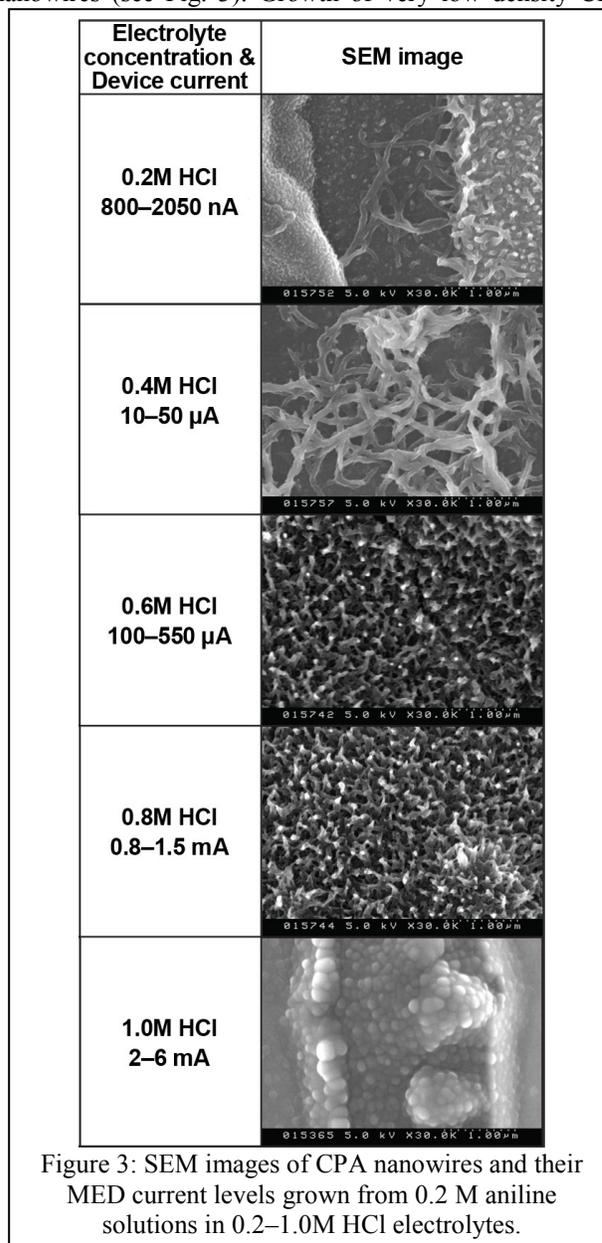
The bulk of our investigation was then focused on the three inorganic (HClO₄, HCl and HNO₃) acids-based electrolytes. Following similar setup and process, electro-polymerization of aniline monomer solutions (concentrations: 0.1–1.0M) in perchloric acid electrolytes (0.2–1.0M) was performed. The visual examination showed varying degrees of growth of CPA nanowires, which was then confirmed by SEM analysis and I-V measurements. The results are summarized in Fig. 2 showing SEM images, morphologies, nanowire dimensions and levels of MED currents. The MEDs showed a lower current level as the electrolyte concentration decreased. The concentration and density of the CPA nanowires were also proportional; increasing the HClO₄ electrolyte concentration resulted in more CPA nanowire growth. For instance, SEM images of CPA nanowires grown from the 1.0M HClO₄ electrolyte



solution showed tightly packed nanowire (film-like) morphology with low porosity. CPA nanowires grown from both 0.4M and 0.6M HClO₄ electrolyte solutions showed the formation of uniform nanowires (diameters: 50–150nm; length: ≥2μm) with highly porous network morphology. The CPA nanowires obtained from 0.8M HClO₄ electrolyte solution also showed porous network morphology. These results showed that desired high quality CPA nanowires with porous network morphology can be easily obtained from 0.2–0.4M aniline solutions in 0.4–0.6M HClO₄ electrolytes. These high quality CPA nanowires with porous network morphology would have a high 3D surface area, resulting in a greater number of reactive sites and also allowing analytes to penetrate in the network faster. These

will improve sensing capability of CPA nanowires-based chemical sensor and biosensor devices.

In a similar fashion, electro-polymerization of varying concentrations of aniline solutions (0.1–1.0 M) in 0.2–1.0M HCl electrolytes was investigated for the growth of CPA nanowires (see Fig. 3). Growth of very low density CPA



nanowires was observed for 0.2M aniline solution in 0.2M HCl electrolyte. Formation of uniform CPA nanowires (diameters: 50–150nm; length: ≥2μm) with highly porous network morphology was observed from 0.2–0.4M aniline solutions in 0.4–0.8M HCl electrolyte solutions. In 1.0M HCl case, growth pattern of CPA was globular and packed very closely (film-like morphology). Thus, the HCl electrolyte-based CPA nanowires growth and morphologies at different aniline and electrolyte concentrations follow a trend similar to that observed for HClO₄ electrolyte. Other than slightly elevated MED current levels, the general trend

of increasing CPA nanowires growth with higher HCl concentrations was maintained.

Fig. 4 shows the SEM images including MED current levels and acid electrolyte concentrations of CPA nanowires grown by electro-polymerization of 0.2M aniline solution in 0.2–1.0M HNO_3 electrolyte solutions. The

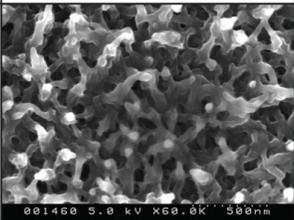
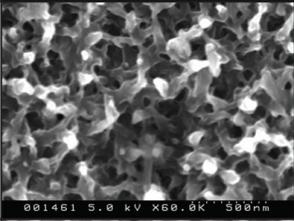
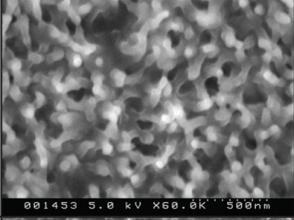
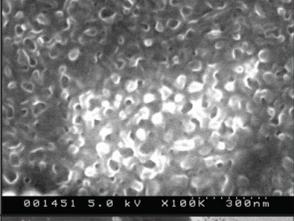
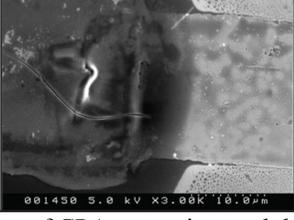
| Electrolyte concentration & Device current | SEM image |
|---|---|
| 0.2M HNO_3 100–500 μA |  |
| 0.4M HNO_3 800–2000 μA |  |
| 0.6M HNO_3 1.5–2.5 mA |  |
| 0.8M HNO_3 6–15 mA |  |
| 1.0M HNO_3 30–50 mA |  |

Figure 4: SEM images of CPA nanowires and their MED current levels grown from 0.2 M aniline solution in 0.2–1.0M HNO_3 electrolyte solutions.

HNO_3 turned out to be a much more aggressive electrolyte media than HClO_4 or HCl . CPA nanowires grown from 0.2–0.4M HNO_3 electrolyte solutions showed porous network morphology of nanowires (diameters: 50–150nm). Electro-polymerization from 0.6–0.8M HNO_3 electrolyte solutions showed CPA nanowire formation that was closer to film-like morphology, whereas complete film-like morphology of CPA was obtained from 1.0M HNO_3 electrolyte solution. In order to find any distinctive features

among these three acid electrolyte sets further study is required.

4 CONCLUSIONS

Distinctive features in growth and morphology of CPA nanowires were observed during electro-polymerization of aniline monomer from different acid electrolyte solutions. Our studies showed that nature of acid (organic/inorganic and weak/strong) and electrolyte concentration play a critical role in the growth and morphology of CPA nanowires. The organic acids did not result in any growth of CPA nanowires or films. All three inorganic acid electrolytes, in general, showed growth of porous CPA nanowires network morphologies. Therefore, uniform and porous network CPA nanowires can be used to improve chem- and bio-sensor performance.

5 ACKNOWLEDGMENTS

This research work was supported by the DOD Missile Defense Agency SBIR contract number HQ0147-14-C-7012 and the DOE SBIR Grant Number DE-SC0008210.

REFERENCES

- [1] (a) M. M. Alam and U. Sampathkumaran, “Modular Chemiresistive Sensor,” U.S. Patent 9896772, 02/20/2018. (b) M. M. Alam, “Nanowire Sensor Array-based Assay for Early Diagnosis of Alzheimer's Disease”, NIH Phase II Technical Progress Report (TPR), (Report #: TPR-0317-3100-NIH-ALZ II) (Grant #: 2R44AG046059-02A1), 03/15/2017.
- [2] M. M. Alam, M. Mushfiq, U. Sampathkumaran, E. L. Brosha and K. Goswami, “Detecting CO_2 using nanowire chemiresistive sensor for monitoring air quality in enclosed space habitat,” Proceeding of the 44th International Conference on Environmental Systems, ICES-2014-044, 771–784, 2014.
- [3] (a) M. M. Alam, J. Wang, Y. Gao, S. P. Lee and H-R. Tseng, “Electrolyte-gated transistors based on conducting polymer nanowire junction arrays,” Journal of Physical Chemistry B, 109, 12777–12784, 2005. (b) M. M. Alam, J. Wang and H-R. Tseng, “Conducting polymer nanowire-based electrochemical transistors of interest for sensor applications,” Polymeric Materials Science and Engineering, 92, 662–663, 2005.
- [4] T. A. Skotheim and J. R. Reynolds, “Handbook of Conducting Polymers, Conjugated Polymers: Processing and Applications. 3rd ed.,” CRC Press: Boca Raton, 2007.
- [5] S. Virji, J. X. Huang, R. B. Kaner and B. H. Weiller, “Polyaniline nanofiber gas sensors: examination of response mechanisms,” Nano Letters, 4, 491–496, 2004.