Construction of a Polyaniline Nanofiber Gas Sensor

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Nanotechnology, the science of materials on the scale of one–billionth of a meter, is at the frontier of science today. The unique mechanical and electrical properties expressed by materials at this small length scale have been harnessed in applications for fields as diverse as computing and biotechnology (1). This laboratory introduces students to the fundamental concepts and applications of nanoscale science through a simple polyaniline nanofiber chemical sensor that can be constructed and used by both high school and college students.

Among the polymeric materials currently available, polyaniline possesses many of the properties desired for a sensor. Polyaniline is easily and inexpensively synthesized through an acid-catalyzed radical polymerization of aniline (2). The conductivity, $\sigma$, of the polyaniline can be controlled by the addition of a dopant, which results in a partly filled band and allows it to be easily switched from the “off” to the “on” state (3). In the undoped form, polyaniline is a poor conductor that consists of chains of alternating benzenoid and quinoid rings (Scheme I). Exposing dedoped polyaniline (which is an insulator) to a strong acid (e.g., hydrochloric acid, HCl) makes the polyaniline more conducting, hence decreasing its resistance, $R$ (2). The addition of base reverses this process.

Scheme I shows the conversion of the insulating emeraldine base form of polyaniline to the conducting emeraldine salt form upon exposure to HCl. This process occurs instantaneously with films in solution and within minutes in the gas phase and is fully reversible upon exposure of the films to a strong base. Acid doping and base dedoping can be cycled as many times as desired. The change in resistance from the dedoped to the doped form is large and easily measured—dedoped polyaniline is an excellent sensor for acids and doped polyaniline an excellent sensor for bases with orders of magnitude changes in resistance upon exposure to these analytes. Polyaniline can also be used to selectively distinguish between strong and weak acids. Weaker acids will not dope polyaniline as well or as quickly as strong acids (4), resulting in a change in response time from seconds or minutes extending to hours or days, accompanied by much smaller response levels.

The morphology of the polyaniline films is important for detection sensitivity. Doped polyaniline (PANI) nanofibers are water dispersible and can be readily cast into uniform conductive films. Compared to conventional, agglomerated polyaniline that forms non-uniform films, the nanofibers have additional advantages inherent to nanoscale materials—a porous structure and a large surface-to-volume ratio. These properties result in fast and effective sensors (5). In addition to the very desirable selectivity for acids and bases observed in bulk polyaniline, polyaniline nanofibers also offer sensitivity with parts per billion detection limits, excellent reversibility for base sensing (6), fast response times (7), low fabrication cost, and robustness.

Experimental

This laboratory comprises two sections: (i) the synthesis of polyaniline nanofibers and (ii) the construction and use of sensors. The first part is suitable for students at the collegiate level, but is likely to be too hazardous to be handled by anyone other than the instructor at the high school level. The latter part can be conducted by students at all levels.

Scheme I. Doping of the insulating emeraldine base form of polyaniline to the conducting emeraldine salt form of polyaniline upon exposure to an acidic gas, HCl, is reversible by dedoping with exposure to a basic gas, such as ammonia (NH$_3$).
In the Laboratory

Synthesis

Polyaniline nanofiber synthesis is based on the classical chemical oxidative polymerization of aniline (2), but instead of using the traditional homogeneous aqueous solution of aniline, acid, and oxidant, the polymerization is performed at the interface of an immiscible organic/aqueous two-phase system (8). Nanofibers of different diameters can be made by varying the doping acid used in the synthesis. For example, nanofibers synthesized from perchloric acid yield the largest diameter fibers (120 nm) while nanofibers synthesized from HCl yield the smallest diameter fibers (30 nm). This part of the lab can be performed by students if facilities are available for dealing with organic chemicals or can be done ahead of time on a larger scale by the instructor.

Sensor Construction

The second part of this laboratory is the construction of a gap sensor. The lab may be modified to match student levels and institutional needs. If a metal evaporator or sputterer is available, a layer of conductive metal, such as gold, can be evaporated or sputtered onto a slide affixed with tape placed at intervals to act as a mask. The tape can then be removed to reveal a gap between the gold electrodes. Alternatively, electrodes can be made from strips of foil or copper tape affixed to a microscope slide. Polyaniline nanofibers in aqueous solution are then dropped onto the sensor and dried.

There are many options for exposing the sensor to analytes that vary in sophistication (see the online supplement). The fundamentals of each design involve exposing the sensor to acid or base vapors while monitoring the conductivity of the sensor through a computer interface or a hand-held multimeter.

Sensing

The conductivity, $\sigma$, of pristine polyaniline increases in the presence of acid as it forms the doped emeraldine salt (see Scheme I). Upon exposure of doped polyaniline to base, the conductivity decreases owing to the conversion of the emeraldine salt form to the dedoped emeraldine base form. A variety of acids and bases may be used in this laboratory, as long as they are volatile, since it is the vapor that is being detected. The laboratory will demonstrate that the detection of acids and bases is reversible, and that the diameter of the nanofibers affects the magnitude (detection limit) and rate of the response. The concentration range of the chemical vapors used in this lab can be varied between 100 and 1000 ppm. The resistance change of the polyaniline is larger with higher concentrations. It is also possible to sense chemicals other than acids and bases, such as methanol, that cause the polyaniline chains to align thus increasing charge transfer between chains, which results in a decrease in the resistance of the polyaniline (5).

Hazards

The beauty of this experiment lies in its simplicity and safety. The purified polyaniline nanofibers are dispersed in water and the resultant aqueous dispersions are believed to be nontoxic. Aniline, however, is toxic. The MSDS lists acute exposure effects such as skin and eye irritation (from direct contact) and breathing difficulties (from inhalation of vapors). Chronic effects may include increased cancer risk, damage to unborn fetuses, or liver and central nervous system damage. Therefore aniline, if handled by students, should be monitored carefully. A possible solution to this problem would simply be to have the teachers synthesize the polyaniline nanofiber dispersions beforehand.

All acids and bases and organic solvents used in this lab are hazardous. D-limonene is arguably the safest choice among organic solvents as its only hazards are as an irritant and its combusability. General lab safety precautions should be sufficient to guard against direct exposure to these substances.

Results and Discussion

Polyaniline nanofibers respond to acid vapor by becoming more conducting and the doped form to base vapor by becoming more insulating. Figure 1 shows an example of typical response data for (A) dedoped polyaniline nanofibers exposed to 100 ppm HCl and (B) doped polyaniline nanofibers exposed to 50 ppm of ammonia.

Figure 1. Normalized resistance measured versus time upon exposure of (A) dedoped polyaniline nanofibers to 100 ppm of HCl and (B) doped polyaniline nanofibers with small (- - -) and large (–) diameters to 50 ppm of ammonia.
ppm ammonia. The normalized resistance, \( R/R_0 \) (y axis), is the time change in resistance, \( R \), divided by the initial resistance, \( R_0 \). As can be seen from the graphs, the resistance of a dedoped polyaniline film changes by orders of magnitude on exposure to 100 ppm acid and the resistance of a doped polyaniline film changes by a factor of 2 on exposure to 50 ppm base. The doping (i.e., acid) response is larger than the dedoping (i.e., base) response because the addition of even a few charge carriers rapidly increases the conductivity of the films. The complete removal of these charge carriers requires much higher base concentrations.

The sensor response is related to the nanofiber diameter; the smaller diameter nanofibers show greater response than the larger diameter nanofibers because they have a proportionally higher surface area, so they can interact with gas more efficiently than the larger diameter nanofibers (Figure 1B). Since the films are porous, however, different film thicknesses give similar responses when exposed to an analyte gas (5).

**Use and Assessment**

This laboratory introduces students to the fundamentals of sensors and the advantages of using nanoscale fibers for sensing. The University of California–Los Angeles (UCLA) has employed this experiment with great success in both undergraduate and graduate materials chemistry classes as part of the National Science Foundation’s Integrative Graduate Education Research and Training (NSF–IGERT) program known as the UCLA Materials Creation Training Program (MCTP) (9). The experiment can be easily modified for use in undergraduate education in other disciplines. For example, recently it has been successfully incorporated into soft materials oriented undergraduate courses in the Materials Science and Engineering Department at Northwestern University (10). We have also created a modified version of these experiments in collaboration with the California NanoSystems Institute (CNSI) outreach program that targets high school teachers and their students in the Los Angeles Unified School District (11).

Owing to the toxicity of aniline monomer, the hazards accompanying polyaniline nanofiber synthesis are generally too great for a high school classroom, so the instructor should prepare the nanofibers. High school students can still benefit from building the sensors from pre–fabricated nanofibers. The connections to the high school curriculum correspond with discussions on acids, bases, and sensors along with conductivity, resistance, and circuits. This laboratory also exemplifies the link between basic introductory classroom science and current nanotechnology. Students are introduced to the idea that high surface area nanomaterials can show enhanced materials performance. The polyaniline nanofibers have also been used to detect toxic gases relevant to Homeland Security and are being employed to develop handheld “sniffing” detectors.

This lab has now been taught to over 100 high school science teachers in the Los Angeles Unified School District. Feedback from high school teachers has been extremely positive. Students are engaged and inspired by the idea of building a sensor and for the most part, understand the relationship and emerging promise of nanotechnology.

**Literature Cited**


**Supporting JCE Online Material**


Abstract and keywords

Full text (PDF)

Links to cited URLs

Supplement

Student handouts

Instructor notes