

Student worksheet

Polyaniline Synthesized Conducting Polymer for Applicable Use in Touch Gloves

Introduction:

This lesson will introduce you to polyaniline, a conducting polymer. You will explore how nanofibers significantly improve the processing of polyaniline and its performance as a conventional application involving polymer interactions with its environment (i.e. inorganic and organic uses). The lesson shows just one example how polyaniline has great technological potential due to its physicochemical characteristics (i.e. lightweight, conductivity, mechanical flexibility), and for its inexpensive methods for synthesis. For this lesson, the instructor or you will synthesize polyaniline, which will be used with cotton cloth to create “gloves” that are conductive for use with a smartphone during the wintertime.

Touch screen capable gloves can be expensive to buy and usually do not work very well in relation to their cost. Researchers have been exploring the use of conducting polymer fibers, such as polyaniline, to provide an alternative and inexpensive way to create touch screen gloves. In this lesson, you will use synthesized doped polyaniline solution to make inexpensive gloves that will have the ability to interact with the capacitive touch screen.

Essential Question:

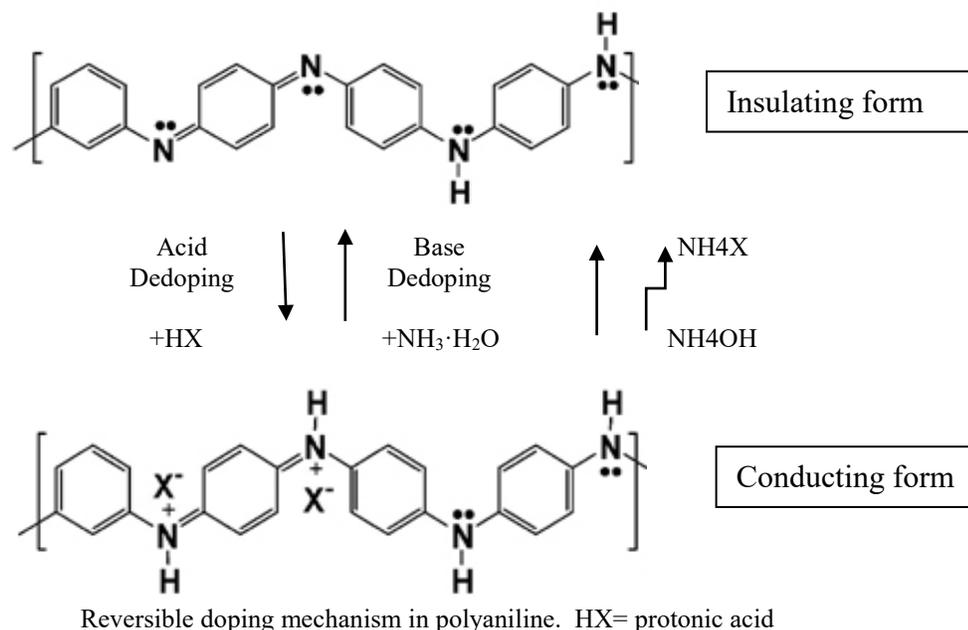
Will a conducting polymer, such as polyaniline, provide the ability for a non-conducting pair of winter gloves to interact with the capacitive touch screen of a smartphone?

Brief History on Discovery of Conducting Polymers:

A tremendous amount of research has been carried out in the field of conducting polymers since 1977 when the polymer polyacetylene was discovered to conduct electricity. The 2000 Nobel Prize in Chemistry awarded to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa recognized the discovery of conducting polymers and over 25 years of progress in this field. In recent years, there has been growing interest in research on conducting polymer nanostructures (i.e., nano-rods, -tubes, -wires, and -fibers) since they combine the advantages of organic conductors with low-dimensional systems. A low-dimensional system typically is at the nanoscale, 1-100nm, and occur where at least one of the three dimensions is intermediate between the characteristics of atoms/molecules and the characteristics of the bulk material. At this level, interesting physicochemical properties occur that may have potentially useful applications.

For example, the conductivity of polyaniline depends on its ability to transport charge carriers along the polymer backbone and between polymer chains. Chemical interactions with polyaniline that alter either of these carrier processes affect its conductivity. Dopants are used to change these properties. A dopant is a trace element (impurity) that is inserted into a substance

(in low concentrations) to change the material's electrical properties. Dedoped polyaniline chains are nearly neutral and without charge carriers to transport charges. This is responsible for the low conductivity of dedoped polyaniline. Protonation, or the addition of a proton, of the imine nitrogens by exposure to acid will introduce positive charge carriers to the polymer chain and increase the conductivity of the polyaniline.



The reversibility of the doping mechanism in polyaniline is the underlying property that makes polyaniline useful in many applications as sensors (gas, pH, etc). Due to their low cost, room temperature sensitivity, ease of deposition onto a wide variety of substrates, and the chemistry of structural modifications, polyaniline and other conducting polymers promise new materials and devices with many applications. Current areas of application include drug delivery, display devices, photovoltaic cells, polymer LEDs and micro/nano electronics. Finally, an advantage of polymeric materials, such as polyaniline, is that they can be synthesized and processed on a large scale at relatively low cost.

Vocabulary:

Low dimensional system: a low dimensional system is a system where the motion in one or more directions is severely restricted. Here, the moving particles effectively behave as if they are in two dimensions (ex.: 2D electron gas), one dimension (nanowire), or even zero dimensions (a quantum dot). Definition from <https://www.cityu.edu.hk/phy/low-dimensional-systems>

Protonation: transfer of a proton to (a molecule, group, or atom), so that a coordinate bond to the proton is formed. The addition of a proton to an atom, molecule, or ion, forming the conjugate acid.

Deprotonation: also referred to as dehydronation, is the removal (transfer) of a [proton](#) (or [hydron](#), or hydrogen cation), (H^+) from a [Brønsted–Lowry acid](#) in an [acid-base reaction](#). The species formed is the [conjugate base](#) of that acid. Definition from <https://en.m.wikipedia.org/wiki/Deprotonation> .

Dopant: a substance used to produce a desired electrical characteristic in a semiconductor. A **dopant**, also called a **doping agent**, is a trace of impurity element that is introduced into a chemical material to alter its original electrical or optical properties. The amount of dopant necessary to cause changes is typically very low. See <https://en.wikipedia.org/wiki/Dopant> for more information.

There are two methods for synthesizing polyaniline as discussed below. This activity uses the Rapid Mixing Method.

Method 1. Chemical Synthesis of Polyaniline Using the Interfacial Polymerization Method

Interfacial polymerization is performed in an aqueous/organic biphasic system with aniline dissolved in an organic solvent along with the oxidant, ammonium peroxydisulfate, dissolved in an aqueous acid solution. Nucleation centers can be seen appearing to drop between the two layers. To see the resultant layers visit: <https://www.youtube.com/watch?v=HF0a5AOIskw> and <https://www.youtube.com/watch?v=9ZpPUS23sT8>. This method produces uniform polyaniline nanofibers with diameters below 100 nm (Figure 3). The process of polymerization can be readily scaled to make kilogram quantities.

Method 2. Chemical Synthesis of Polyaniline Using the Rapid Mixing Method

Polyaniline is a precipitated product from an aqueous solution containing typical reagents such as an oxidation agent ammonium peroxydisulfate (aka persulfate), dopant acids like hydrochloric, sulphuric, nitric, perchloric, and monomer aniline. This direct route represents the classical approach to polyaniline synthesis. This route causes aniline, the monomer, to be converted directly to a conjugated polymer by a condensation process. This lesson uses the Rapid Mixing Method to create the polyaniline.

Advanced Preparation (2-3 days prior to student activities below)

Chemical Synthesis of Polyaniline (Rapid Mixing Method) - Your instructor may prepare the polyaniline in advance; if done by instructor, skip to Day 1 activities. If synthesis is to be done by students, follow procedure below and as well as all safety precautions for your lab.

Materials: To make 100 mL of solution

- 0.2 M aniline hydrochloride (purum; 2.59 g, 20 mmol) CAS# 142-04-1
- 0.25 M Ammonium peroxydisulfate (ammonium persulfate; purum; 5.71 g, 25 mmol) CAS# 7727-54-0
- 100 mL N-Methyl-2-pyrrolidone (NMP) CAS# 872-0-4 or formic acid
- (3) 100 mL portions of 0.2 M HCl
- (3) 100 mL portion of acetone
- 100 mL of distilled water
- (2) volumetric flask (200 mL)
- 4 filter papers
- funnel
- wash bottle
- beaker (250 mL) (to catch wash chemicals)
- beaker (500 mL)
- vacuum chamber (not required; may leave cloths overnight to dry)
- micropipette (100 – 1000 μ L)
- 20 mL glass vial

- lab apron
- chemical gloves
- chemical goggles

Procedure:

1. Dissolve 2.59 g of aniline hydrochloride in 50 mL of distilled water in a volumetric flask; stir well until dissolved. Keep at room temperature (~18 – 24 °C).
2. Dissolve 5.71 g ammonium peroxydisulfate in 50 mL of distilled water in a volumetric flask and stir well until dissolved. Keep at room temperature for 1 hour (~18 – 24 °C).
3. Mix both solutions in a 500 mL beaker and stir briefly. Leave at rest for 24 hours to polymerize. The polyaniline will precipitate out of solution.
4. The next day, collect the polyaniline precipitate on a filter and wash with 100-mL portion of 0.2 M HCl. Discard wash solution per lab procedures.
5. Then wash the polyaniline precipitate in 100-mL portion of acetone. Discard wash solution per lab procedures.
6. Repeat steps 4 & 5 two more times.
7. Dissolve the polyaniline in 10 mL of N-Methyl-2-pyrrolidone (NMP) or formic acid to de-dope the polyaniline. (Should be enough for 2 – 3 groups per class; enough to saturate the cotton fibers)

Day 1 Student Activity:

Materials per group:

- 1 set of gloves
- 4 pieces of cotton T-shirt
- 1 20 mL glass vial
- 1 glass petri dish
- 1 multimeter
- 1 scissors
- 1 tape dispenser
- 1 lab apron
- 1 chemical gloves
- 1 chemical goggles
- Polyaniline solution (shared among groups)

Procedure:

1. Using tweezers, soak your cotton cloth pieces in the polyaniline solution until saturated.
2. Using the tweezers, place the pieces into the glass vials and ready the container for the high vacuum drying or overnight drying in a fume hood.
3. The cotton cloth pieces will be vacuumed for approximately 8 hours as NMP has a very high boiling point.

Day 2: Lab Procedures
(Make sure all cotton samples are completely dried)

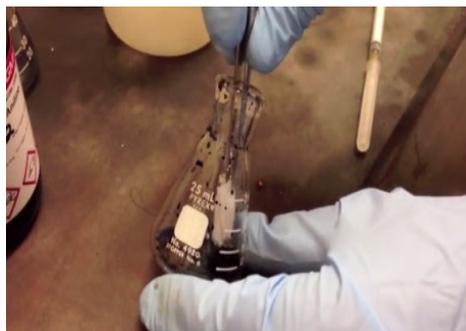
Step 1: Polyaniline was synthesized by using the Rapid Mixing Method. **(May have been done by the teacher)**



Step 2: Next, the polyaniline was dissolved in N-Methyl-2-pyrrolidone (NMP) or formic acid which de-doped the polyaniline. **(May have been done by the teacher)**



Step 3: A cotton T-shirt or similar fabric was cut up in small squares as test materials. **(May have been done by the teacher)**



Step 4: Using tweezers, dip the small pieces of fabric into the NMP solution with the dissolved polyaniline fibers. The polyaniline solution fully impregnates the fibers of the fabric upon immersion.

Step 5: Place the dipped pieces of fabric into vials and dry under high vacuum as NMP has a very high boiling point. It is best to vacuum for 8 hours to ensure the fabric is completely dry. Alternatively, dry overnight in a fume hood.





Step 6: Dip two of the dried pieces of cloth into hydrochloric acid to re-dope the polyaniline polymer. Gently dry one of the re-doped pieces of the fabric, which will cause the fabric to turn a greenish color indicating the polyaniline polymer has been re-doped. Keep another piece wet. Once doped fabric piece is dry, place the four pieces of fabric on a petri dish. One of each: untreated, treated de-doped, treated doped (wet), treated doped (dry).

Note the placement of the samples so you know which one you are testing.



Step 7a: Measure the conductivity of the 4 cotton fabric samples. Begin with the untreated cotton fiber fabric square sample as the control. Record the resistance in your data table.

Step 7b: Test the de-doped PANI-treated fabric sample. Record its resistance.



Step 7c: Test the freshly doped (wet) PANI-treated fabric. Record result.

Step 7d: Test the doped (dry) PANI-treated fabric. Record result.



Step 8: Test the material by using a set of winter gloves that were not treated with the doped PANI-treated fabric.

Step 9: Attach the dry doped fabric to the glove. Use tape to adhere the fabric to the glove. Test the winter gloves using the doped PANI-treated fabric to shows it can easily open the screen and allows the ability to interact with the capacitive touch screen. This is a crude method for showing how conducting polymers could provide an inexpensive way to create gloves that are conductive for smartphone winter time use.



Cleanup: Special care must be taken to dispose of all chemicals from the lab. Do not dispose in the sink. All lab equipment and area can be cleaned according to normal protocol.

POST-LAB ASSESSMENT QUESTIONS:

1. Why did you place the dried polyaniline-dipped cotton cloth into the hydrochloric acid?
2. What do you think would happen to the resistance if the treated cotton fabric was exposed to a base instead of a strong acid?
3. What is the resistance of the untreated cotton fabric? What is the resistance of the doped-polyaniline dipped cotton fabric?
4. What do you think would happen to the resistance if the treated cotton fabric was exposed to a base instead of a strong acid?
5. What is the chemical formula of vinegar, hydrochloric acid and ammonia? Are they acids or bases? Which is the strong acid? Why?
6. What are some uses for polyaniline as a conducting polymer?

