



General Chemistry Laboratory

Conducting Polymer - Polyaniline



Preparation

Collect the following items

- Three 30 mL beaker (for 3 reactions)
- Two 50 mL beaker (for DI water and HCl(aq))
- Two microscope slides
- Two copper wires
- Two binder clips
- One filter paper strip (2 cm x 4 cm)
- One connecting wire w/ two alligator clips
- One set of multimeter w/ connecting wire
- One LED
- One conducting glass (ITO glass)
- One stop watch (distributed by TA)

From your personal equipment

- 100 mL beaker, wash bottle, glass rod and tweezers
- DC power supply w/ connecting wire (underneath lab bench)



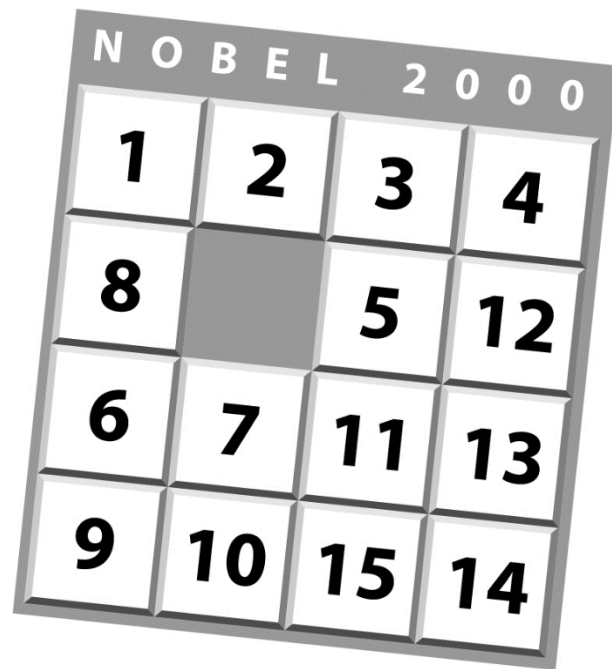
Objective and Principles

■ Objective:

- Synthesize polyaniline (PANI)
 - Chemical synthesis
 - Electrochemical synthesis
- Examine its performance
 - Conduction test
 - Electrochromic property

■ Lab techniques:

- DC power supply
- Multimeter
- [Demonstration video on Youtube NTUChemistrylab](http://www.ch.ntu.edu.tw/nobel/)

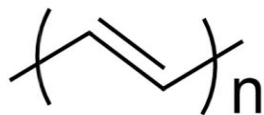


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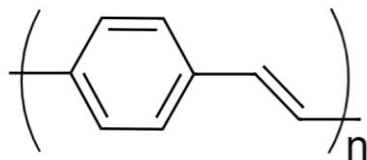


Conducting Polymer

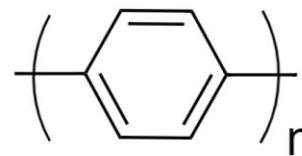
- Various conducting polymers and chemical structures



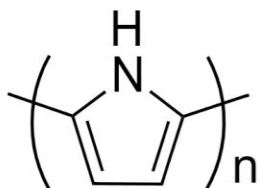
Polyacetylene (PA)



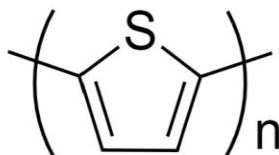
Poly-*p*-phenylene vinylene (PPV)



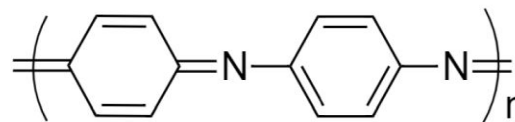
Poly-*p*-phenylene (PPP)



Polypyrrole (PPy)

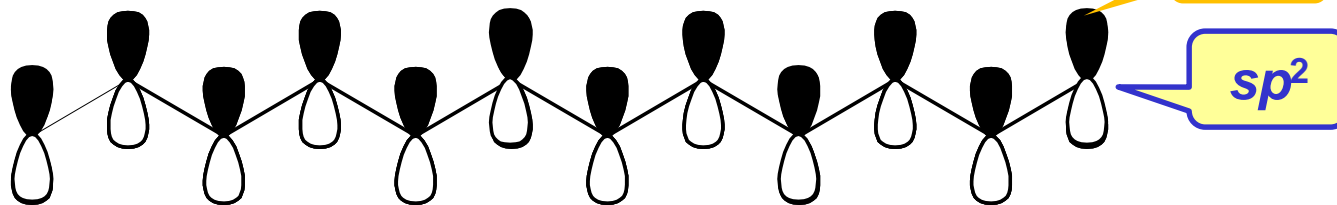


Polythiophene (PTs)



Polyaniline (PANI)

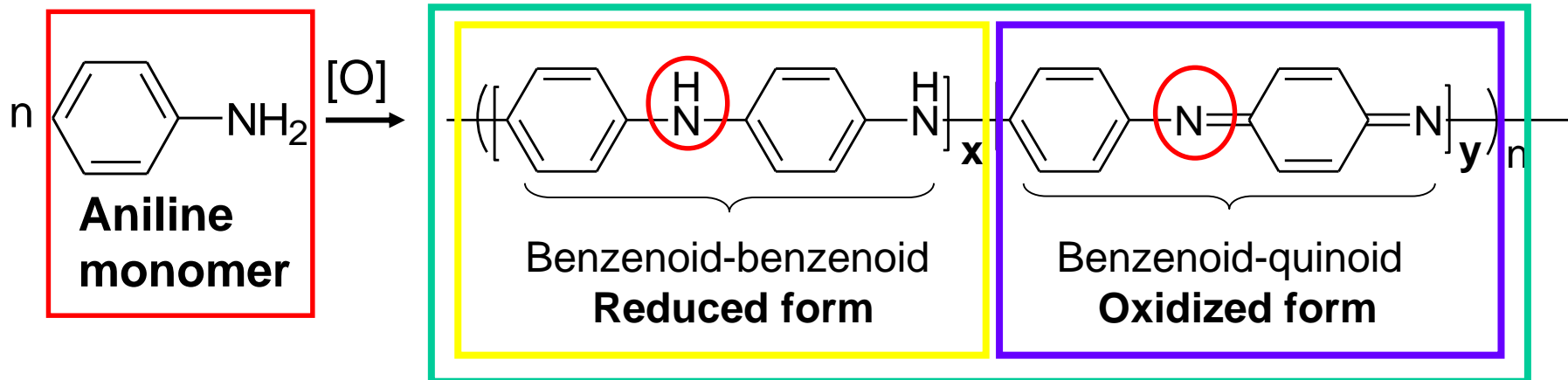
- Characterize with conjugated double bonds and multi-paralleled *p* orbitals





Polyaniline

■ Oxidative polymerization of aniline



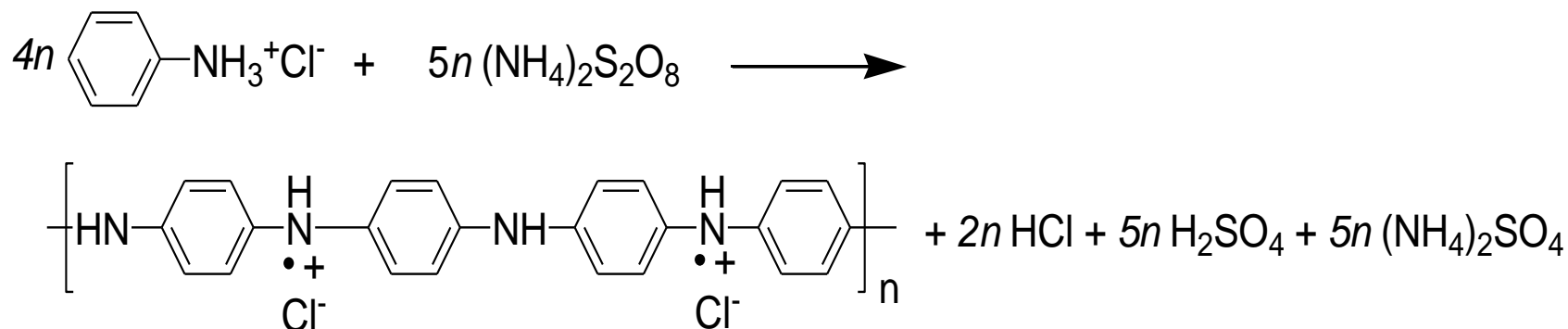
| Polyaniline | Degree of oxidation | Color |
|--|--|-------------------|
| Leucoemeraldine, LE (Reduced form) | $y = 0$ (all benzenoid form) | White |
| Emeraldine base, EB (Alternating) | $x > 0, y > 0$ (benzenoid/quinoid) | Green/Blue |
| Pernigraniline, PNB (Oxidized form) | $x = 0$ (All quinoid form) | Purple |



Synthesis of Polyaniline

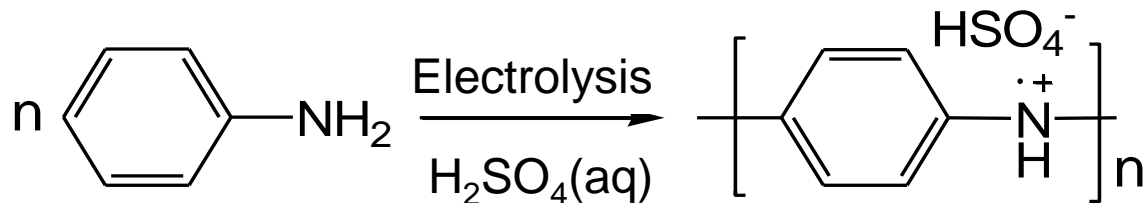
■ Chemical oxidative polymerization

- **Aniline hydrochloride** + ammonium persulfate



■ Electrochemical oxidative polymerization

- **Aniline hemisulfate** as electrolyte
- Polymerize on ITO glass that connected to positive end of DC power supply





Step 1: Chemical Synthesis of PANI

■ Synthesize emeraldine salt, ES



Make a turn



Polymerization



Wash



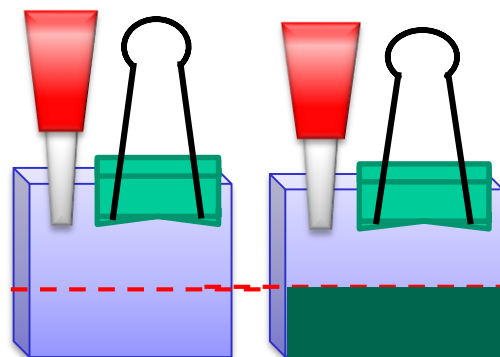
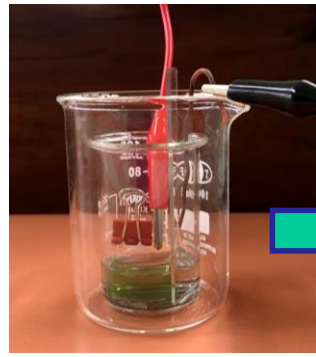
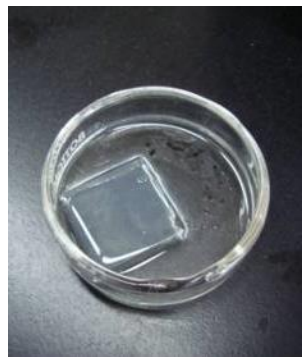
Dry and fix

- Hang a filter paper strip in a 30 mL beaker
- Add **5 mL aniline hydrochloride** $C_6H_5NH_3Cl$ and **5 mL ammonium persulfate** $(NH_4)_2S_2O_8$
- Polymerize for **3-5** min
- Observe color change

- Take paper strip out
- Record the color of polymer
- Dip into pH 2.5 HCl(aq)
- Dip into DI water to rinse
- Put it on a paper towel and blow dry with hair dryer
- Fix paper strip onto microslide to test conductivity later



Step 2.1: Electrochemical Synthesis



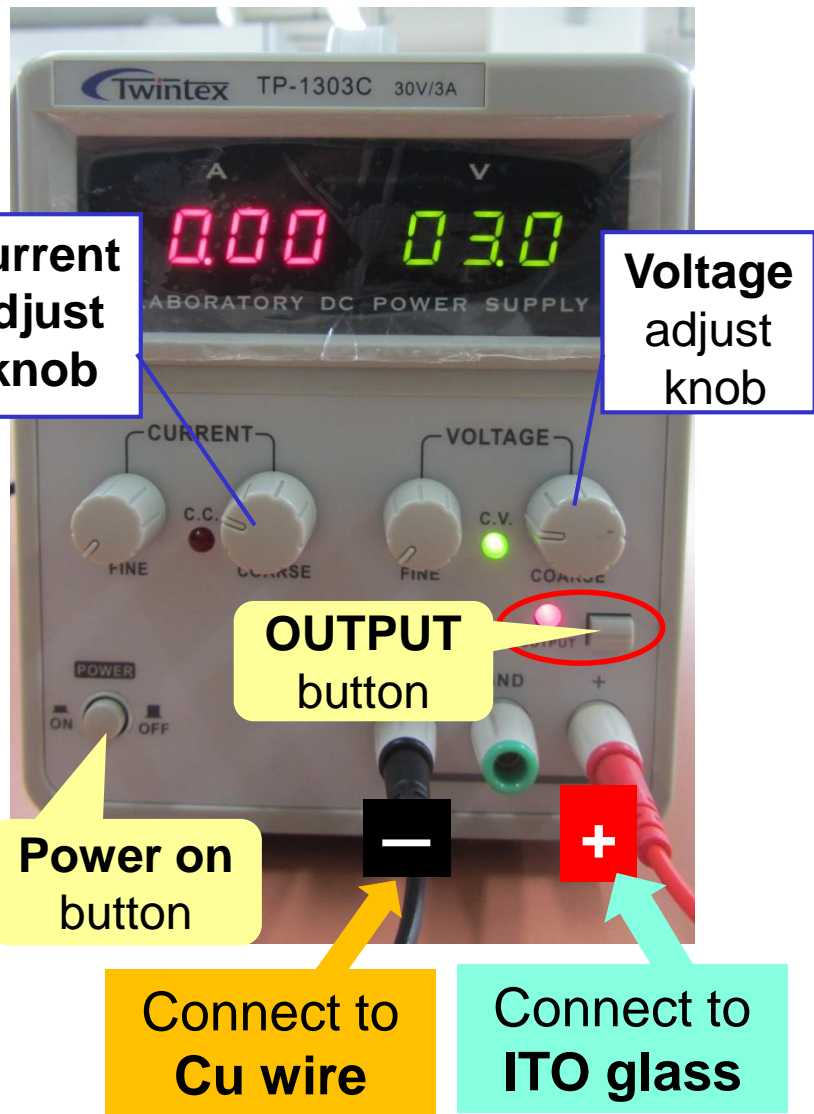
- Use tweezers to clip an ITO glass to avoid contamination
- Immerse ITO glass in 95% EtOH to clean up surface
- Wash with DI water
- Place it on a paper towels to dry
- Connect ITO glass to positive end (red), and copper wire to negative end (black) of DC power supply

- Take 5 mL $\text{C}_6\text{H}_5\text{NH}_3^+\text{HSO}_4^-$ in a 30 mL beaker as electrolytic cell
- Put ITO glass and Cu wire into cell
- Use microslide to separate two electrodes to avoid short circuit
- Place electrolytic cell in a 100 mL beaker

- ✓ Hold ITO glass w/ binder clips
- ✓ Keep clips from touching soln to avoid contamination



Step 2.2: Electrochemical Synthesis



1. Set all knob/button at **zero** before connecting to Cu wire and ITO glass
2. Power on and press **OUTPUT** button (light on)
3. Adjust voltage/current knobs to **3 V**
4. Press **OUTPUT** button again (light off)
5. Connect Cu wire/ITO glass correctly
6. Press **OUTPUT** button (light on) to electrolyze for **3 min**
7. Observe the color change



Step 2.3: Electrochemical Synthesis

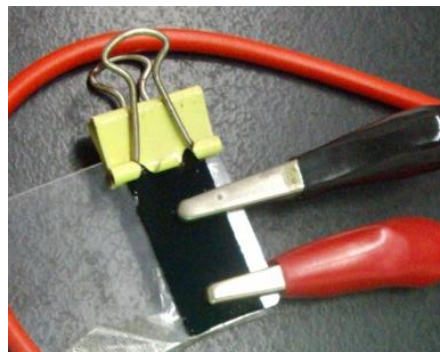
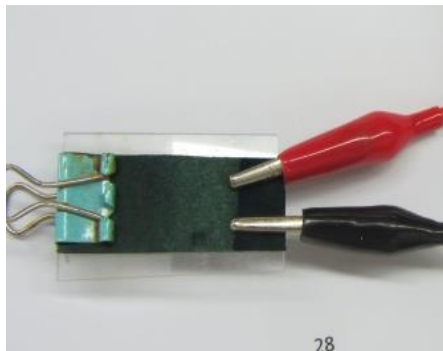


Attach at the end

- Immerse ITO glass in pH 2.5 HCl(aq), then DI water to wash clean
- Blow dry with hair dryer to powder like
- Apply transparent tape to PANI surface firmly by finger pulp, then peel off
- Fix the polymer tape on microslide to test conductivity



Step 3: Conductivity Test

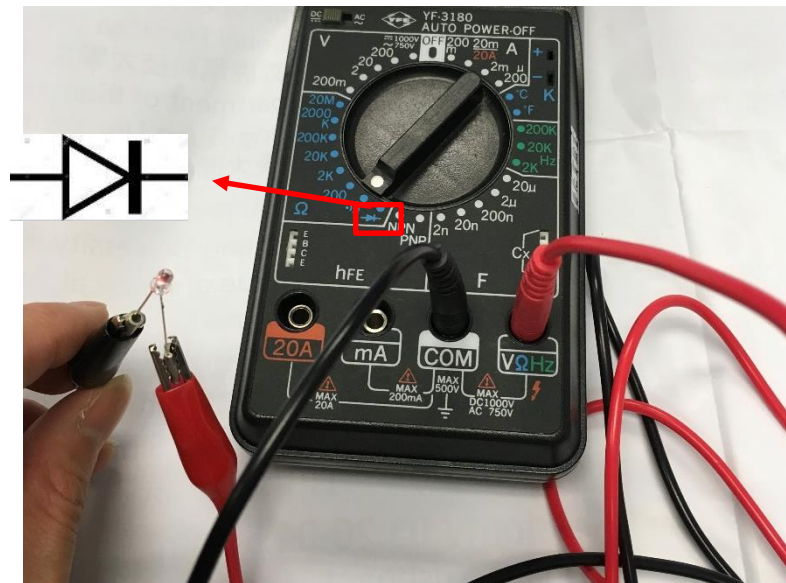
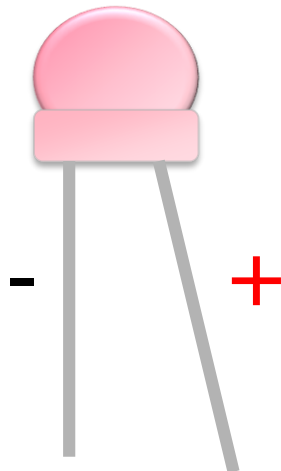


- **Fix testing sample to microslide**
 - 1) PANI on the filter paper
 - 2) PANI on the tape
- **Conductivity test**
 - 1) LED is lit or not
 - 2) Resistance test

✓ Record the distance between two clips and the depth of the clips



Step 3.1: Examine LED

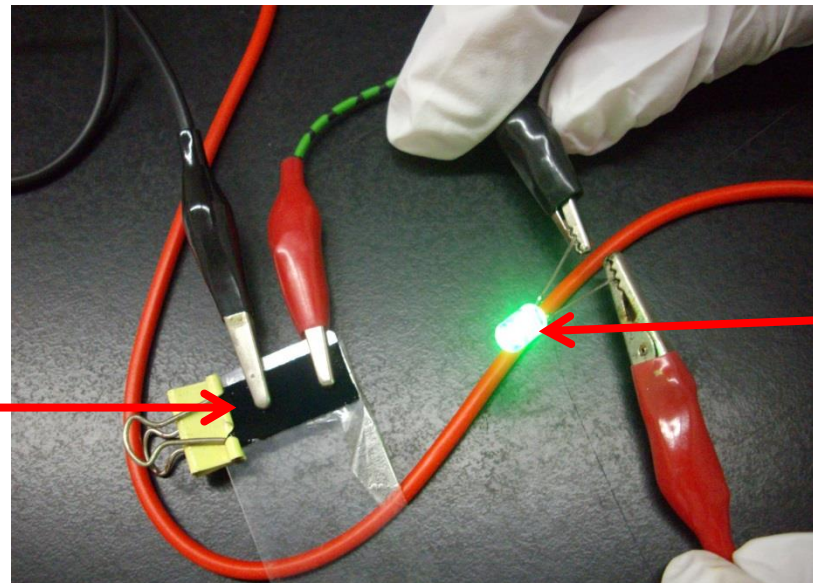
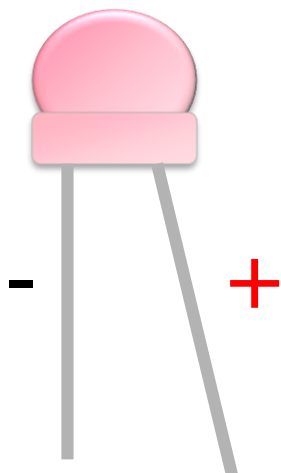


✓ If LED is not lit, it may be broken

- Examine LED before using it to test the conductivity
- Connect LED to multimeter
 - **Black: Short leg (-) of LED to COM port**
 - **Red: Long leg (+) of LED to Ω port**
 - **Dial: Turn to diode check (\rightarrow)**



Step 3.2: LED Emission to Show Conductivity

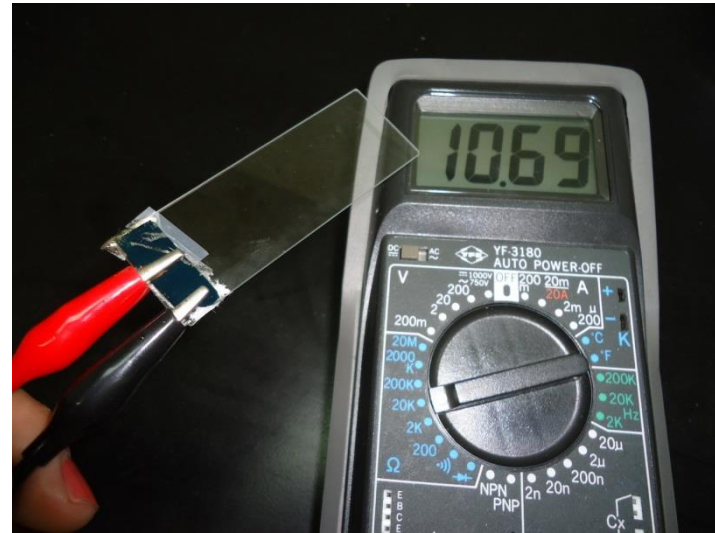
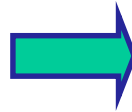


✓ Start applying voltage under 2 V

- Connect PANI sample with LED to DC power supply in series
- Turn on power supply and adjust (fine) voltage to observe the emission of LED



Step 3.3: Resistance Test



Multimeter

- **Anode (black)** to the COM port
- **Cathode (red)** to the Ω port
- Switch function mode to “ Ω ”
- Examine resistance from maximum scale, i.e. 20M, to lower scale, such as 2000K
- If LCD shows “1”, it means over scale

Measure resistance

- Fix alligator clips onto PANI films
- Record the resistance and distance/width of two clips





Step 4: Electrochromism Test



- **LE** (all reduced form) appears **colorless**
- **EB** (mixed) appears **green/blue**
- **PNB** (all oxidized form) appears **purple**

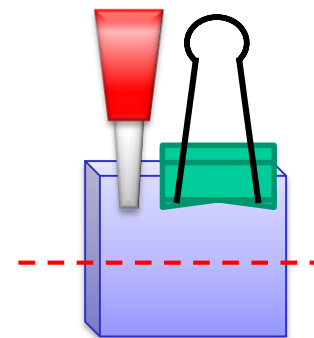
- Take **5 mL** of 20% NaCl in 30 mL beaker
- Connect ITO glass to negative end and **Cu wire** to positive end (**red**)
- Separate both electrode by a microslide
- Apply **0.5-1.0 V** voltage to reduce PANI on ITO glass
- Observe and record the color change

✓ The layer of PANI on ITO should not be too thick



Additional Notes

- Wear NBR gloves to avoid contacting with toxic aniline
- Microslide is easily broken that should be handled with care
- Connect ITO glass with the correct electrode
- Connect alligator clips onto ITO glass directly
- Use a microslide to separate cathode and anode





Clean-Up and Check-Out

- Recycle ITO glass, microslide, Cu wire, and chemical waste
- Wash the beaker with the remaining HCl (pH = 2.5)
- Wash binder/alligator clips with DI water and wipe dry to avoid rusting
- Turn off multimeter and DC power supply; return the connecting wires
- Clean up the lab bench and check personal equipment inventory (have an associate TA sign the check list)

- This is a **Brief Report** experiment:
 - Member A/B: **Hand in prelab report to TA**
 - Member B/A: **Hand in prelab/lab note/report together to TA**

- Groups on duty shall stay and help clean up the lab