Conducting Polymer
- Polyaniline

Last revised: 2025/02/05

Preparation

Collect the following items

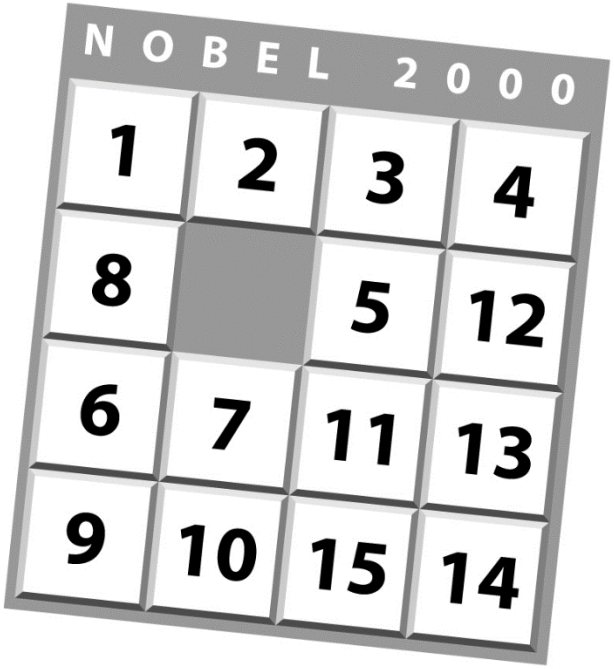
- Three 30 mL beakers (for 3 reactions)
- Two 50 mL beaker (for DI water and HCl(aq))
- Two microslides
- Two copper wires
- Two binder clips
- One filter paper strip (2 cm x 4 cm)
- One conducting glass (ITO glass)
- One connecting wire w/ two alligator clips
- One set of multimeter w/ connecting wire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

From your personal equipment

- 100 mL beaker, 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
    - Conductivity test
    - Electrochromic property



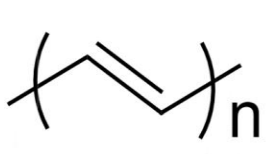
http://www.ch.ntu.edu.tw/nobel/

- **Lab techniques:**
  - DC power supply
  - Multimeter

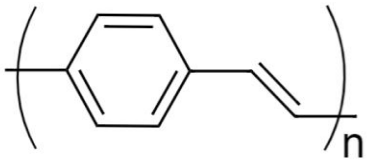
Demonstration video on YouTube NTUChemistrylab

Conducting Polymer

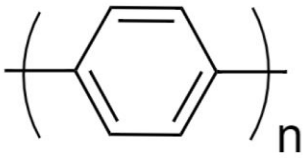
- Various conducting polymers and chemical structures



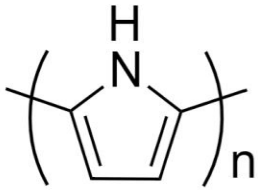
Polyacetylene (PA)



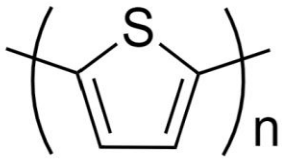
Poly-*p*-phenylene vinylene (PPV)



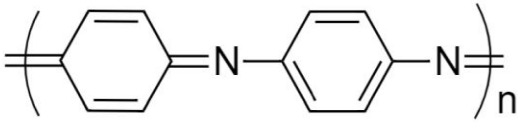
Poly-*p*-phenylene (PPP)



Polypyrrole (PPy)

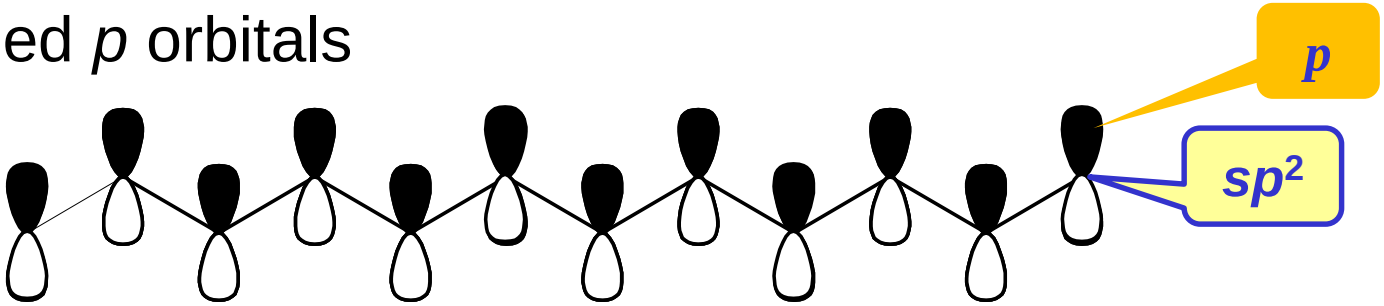


Polythiophene (PTs)



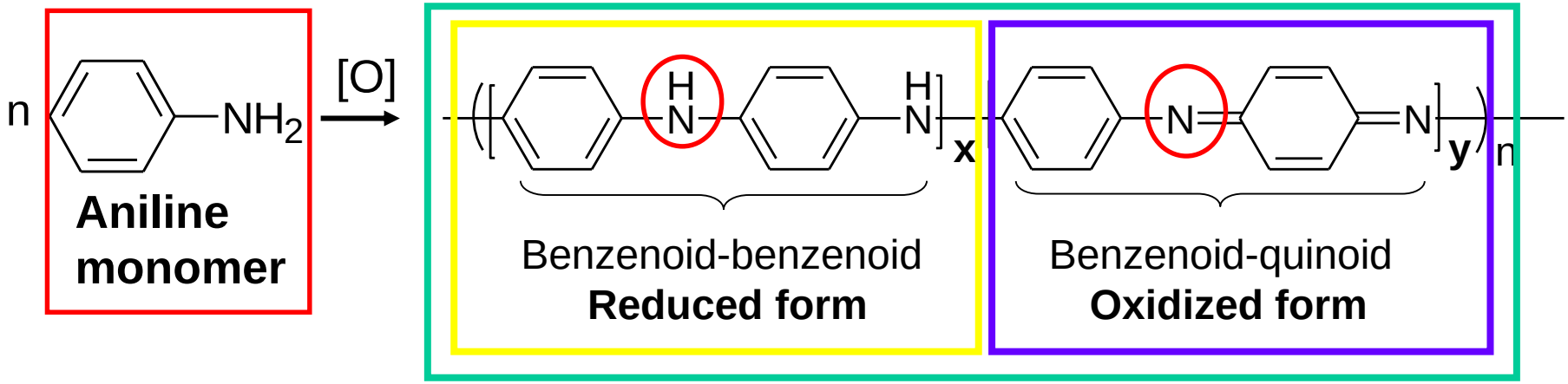
Polyaniline (PANI)

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



Polyaniline

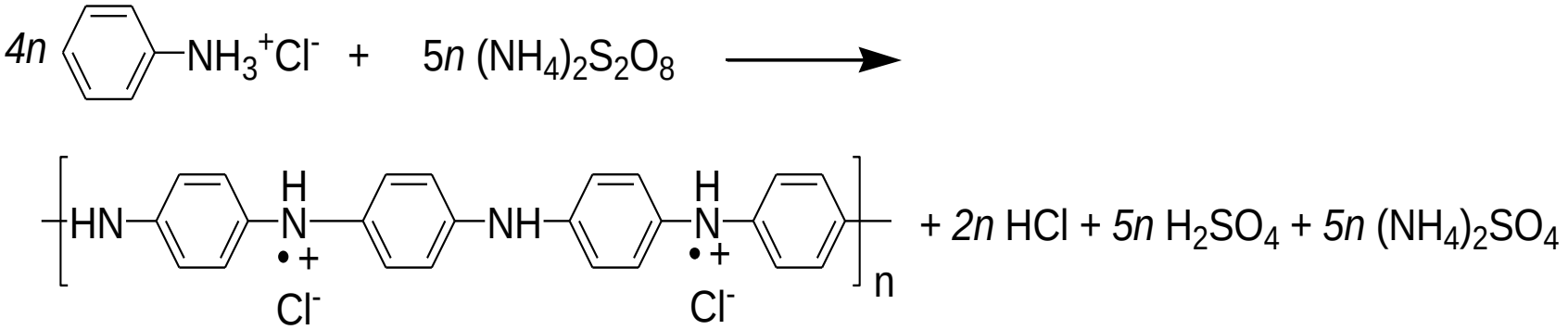
- Oxidative polymerization of aniline



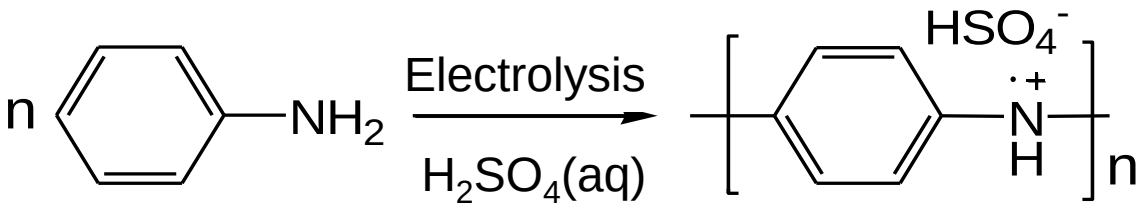
Polyaniline	Degree of oxidation	Color
Leucoemeraldine, LE (Reduced form)	y = 0 (all benzenoid form)	White
Emeraldine base, EB (Alternating)	**x > 0, y > 0 (benzenoid/quinoid)**	**Green/Blue**
Pernigraniline, PNB (Oxidized form)	x = 0 (All quinoid form)	Purple

Synthesis of Polyaniline

- **Chemical oxidative polymerization**
  - **Aniline hydrochloride** + ammonium persulfate

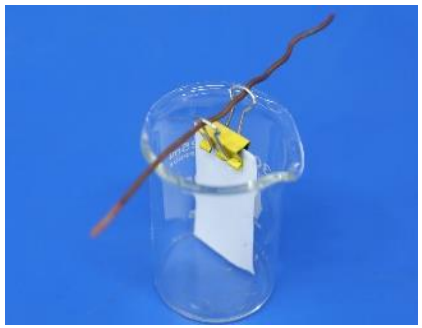


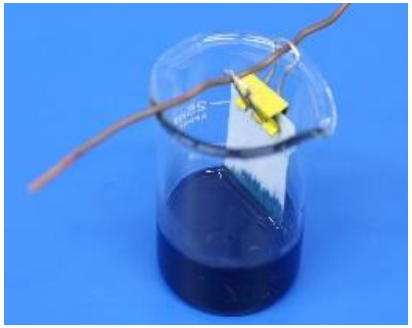
- **Electrochemical oxidative polymerization**
  - **Aniline sulfate** as electrolyte
  - Polymerize on ITO glass that connected to the **positive pole** of DC power supply

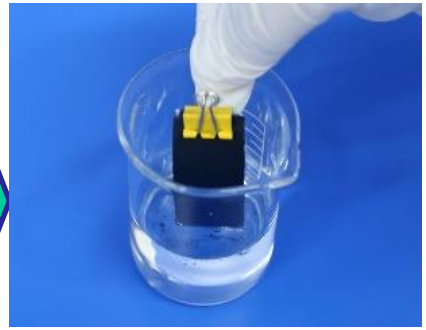


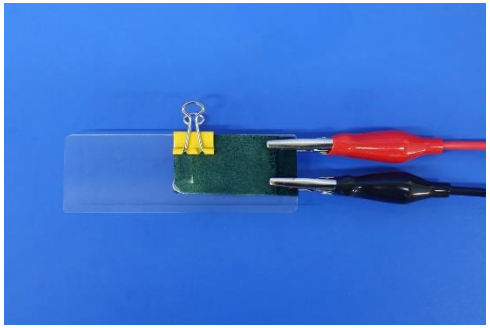
Step 1: Chemical Synthesis of PANI

- **Synthesize emeraldine salt, ES**









Polymerization

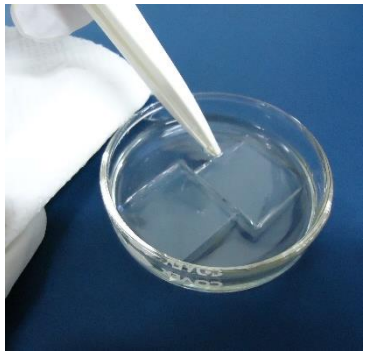
Rinse

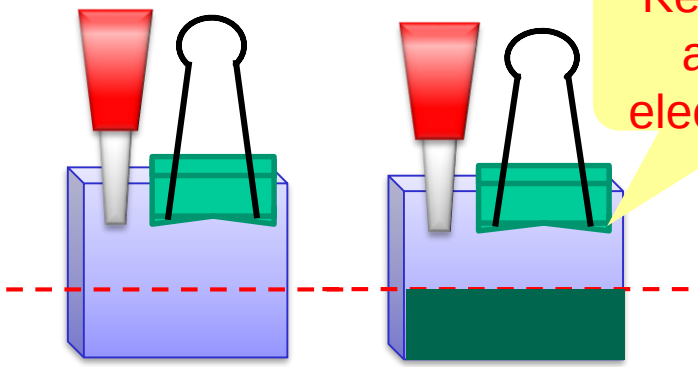
Dry and fix

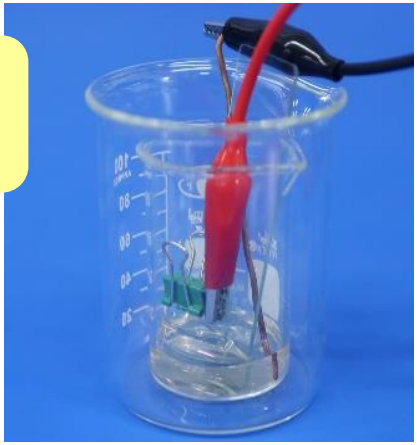
- Hang a filter paper strip in a 30 mL beaker
- Add 5 mL aniline hydrochloride $C_6H_5NH_3Cl$ and 5 mL ammonium persulfate $(NH_4)_2S_2O_8$
- Stir with a glass rod to mix the soln
- Polymerize for ca. 5 min
- Observe color change

- Take paper strip out
- Record the color of polymer
- Dip into pH 2.5 HCl(aq) to rinse
- 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 – Setup the Electrolytic Cell



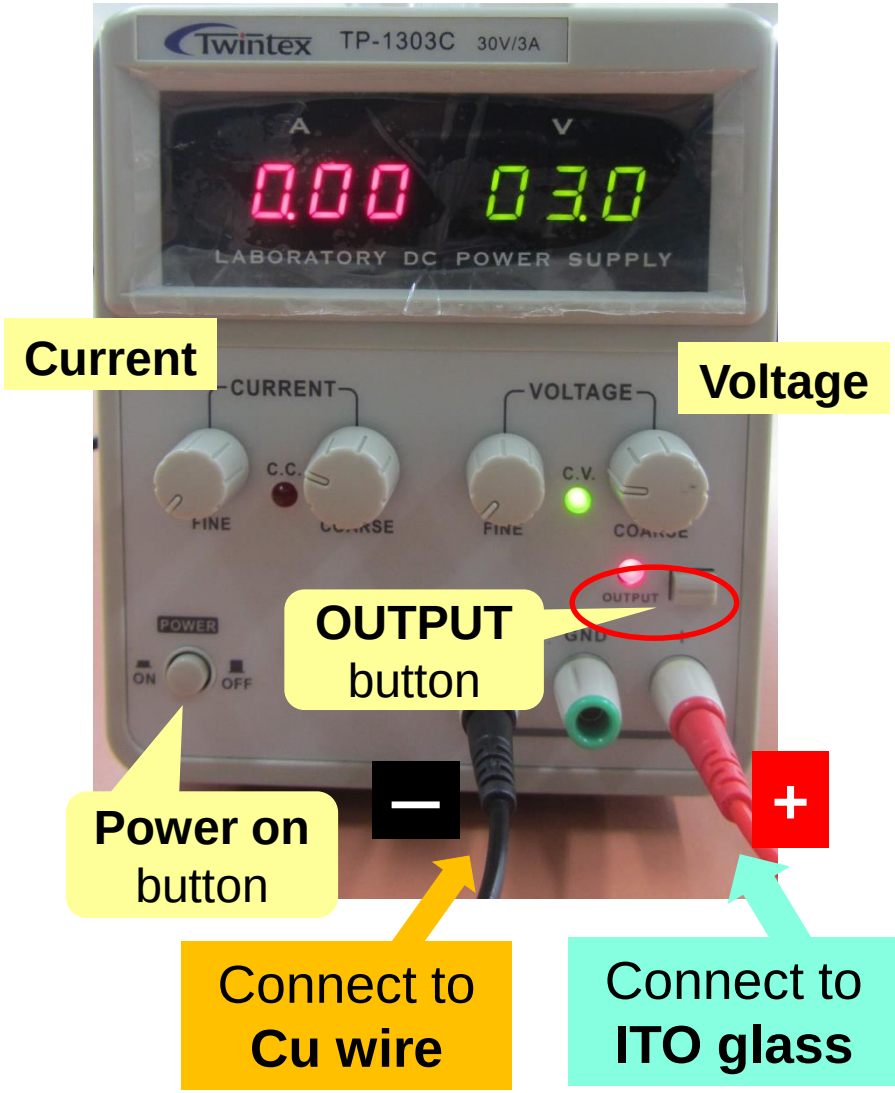




- Use tweezers to clip an ITO glass to avoid contamination
- Immerse ITO glass in 95% EtOH to clean up surface
- Rinse with DI water
- Place it on a paper towels to dry
- Connect ITO glass to positive pole (red), and copper wire to negative pole (black) of DC power supply

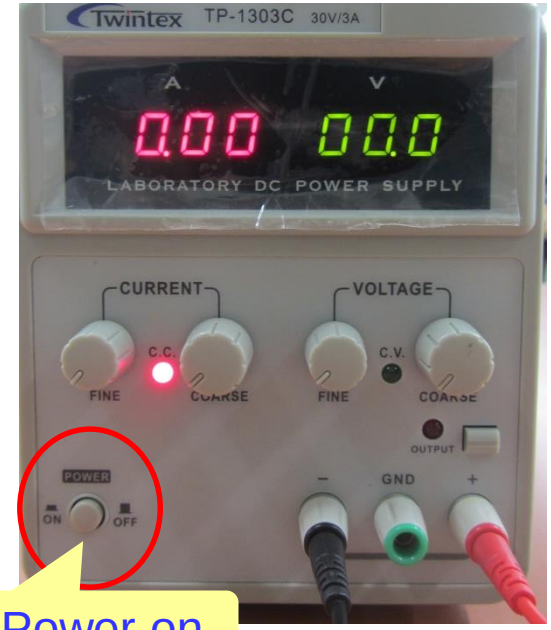
- Take 5 mL $(C_6H_5NH_3)_2 \cdot H_2SO_4$ in a 30 mL beaker as electrolytic cell
- Place electrolytic cell in a 100 mL beaker
- Put ITO glass and Cu wire into cell
- Use microslide to separate two electrodes to avoid short circuit
- Conduct the electrochemical polymerization at 3 V for 3 min

Step 2.2: Electrochemical Polymerization

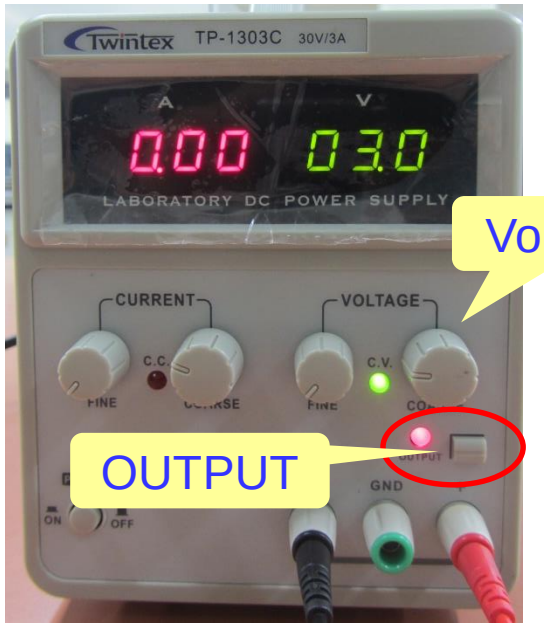


1. Set all knobs at zero
2. Power on and press OUTPUT button (light on)
3. Adjust voltage/current knobs to 3.0 V
4. Press OUTPUT button again (light off)
5. Connect Cu wire/ITO glass correctly
6. Press OUTPUT button (light on) to electrolyze for 3 min
7. Observe the color change

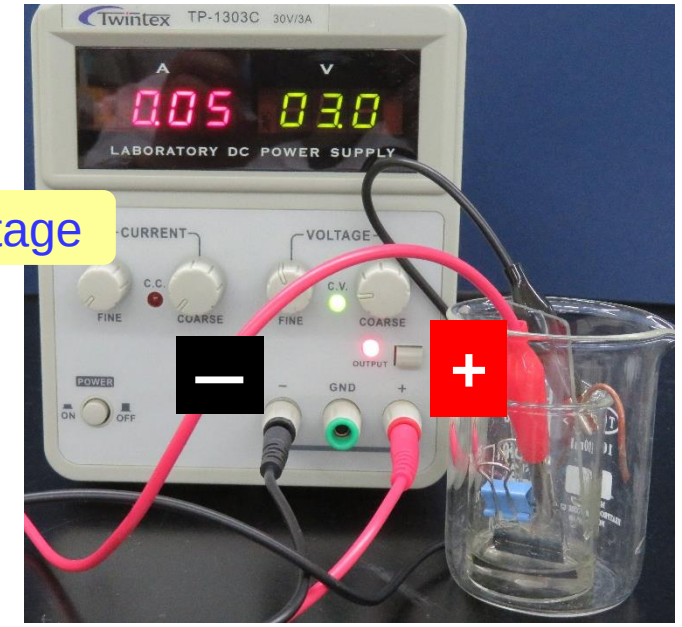
Step 2.3: Electrochemical Synthesis – DC Power Supply



- ✓ Set all knobs at zero
- ✓ Press power on

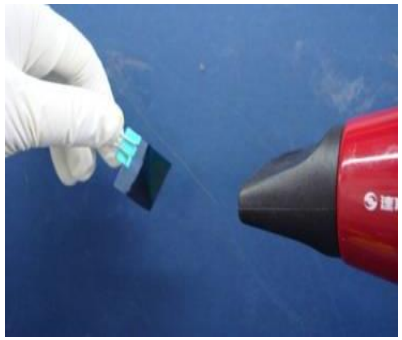
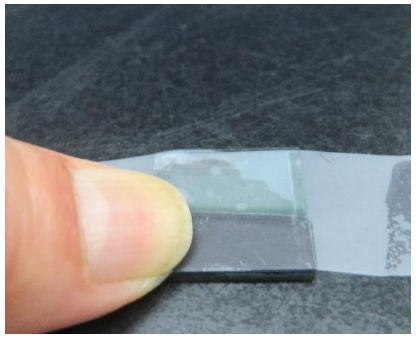
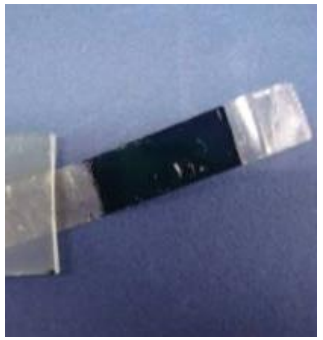


- ✓ Press OUTPUT button (light on)
- ✓ Adjust voltage/current knobs to 3.0 V
- ✓ Press OUTPUT button again (light off)



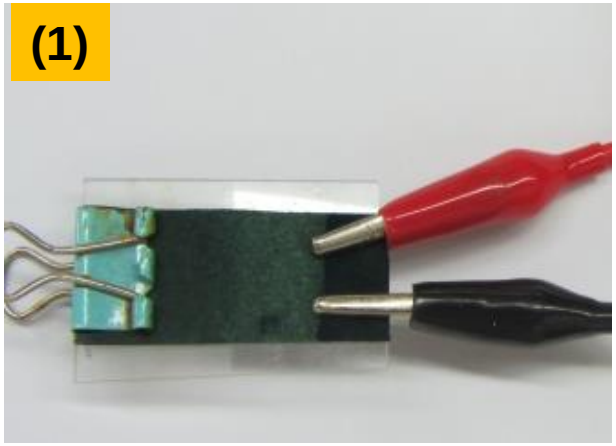
- ✓ Connect Cu wire and ITO glass correctly
- ✓ Press OUTPUT button (light on) to electrolyze for 3 min
- ✓ Observe the color change

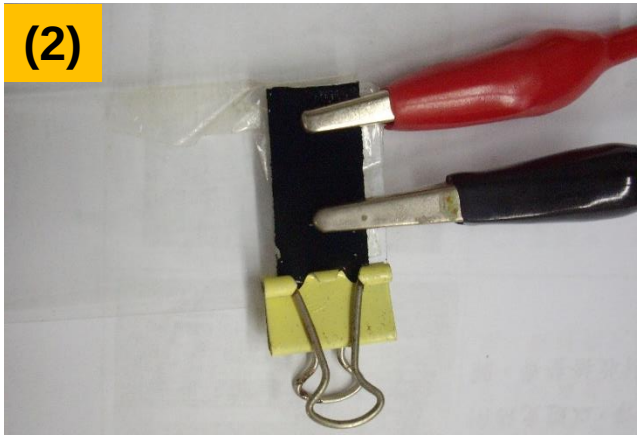
Step 2.4: Product of Electrochemical Polymerization


- 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

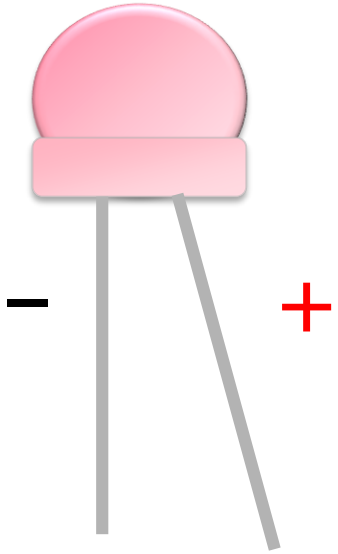


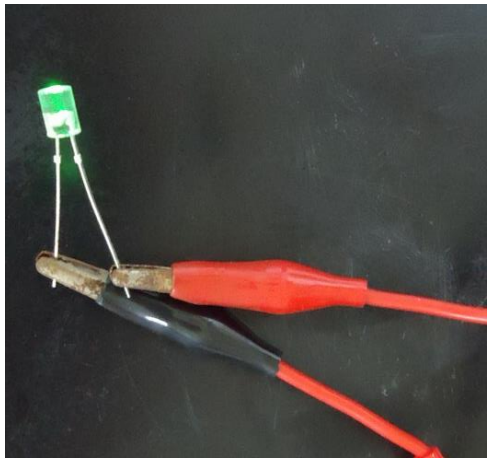


- **Fix two testing samples to microslides**
  1) PANI on the filter paper
  2) PANI on the tape
- **Two conductivity tests**
  1) LED is lit or not
  2) Resistance measurement

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

Step 3.1: LED Function Test

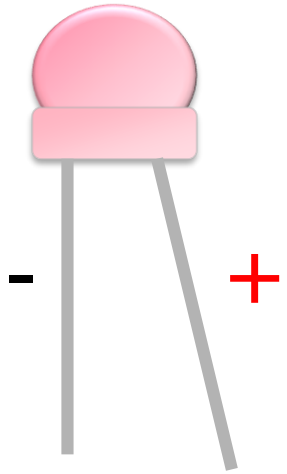


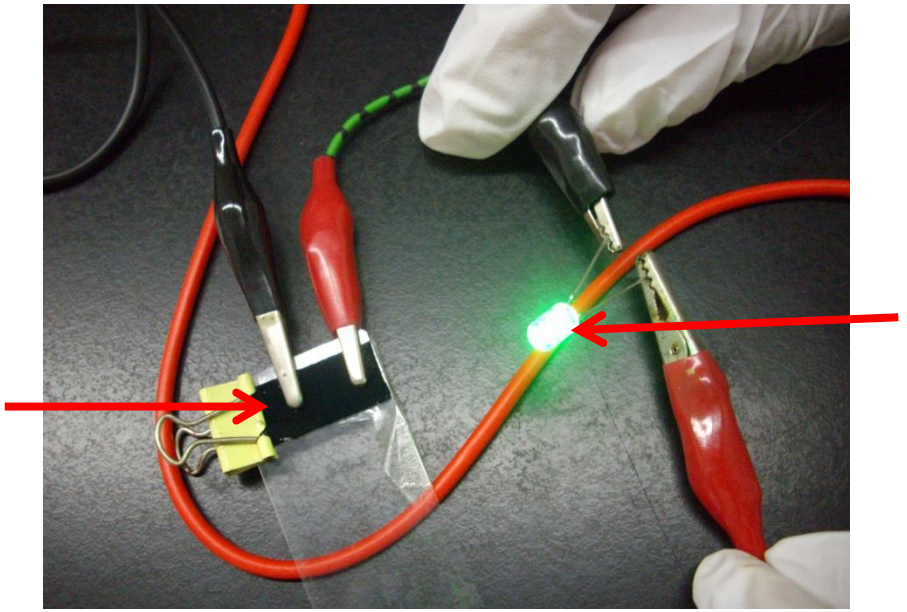


- Connect the longer pin of the LED (+) to the positive pole of the DC power supply
- Connect the shorter pin of the LED (−) to the negative pole of DC power supply
- Turn on the DC power supply with a voltage of 2 V to test the emission

✓ If LED is not lit, it may be broken, replace a good one

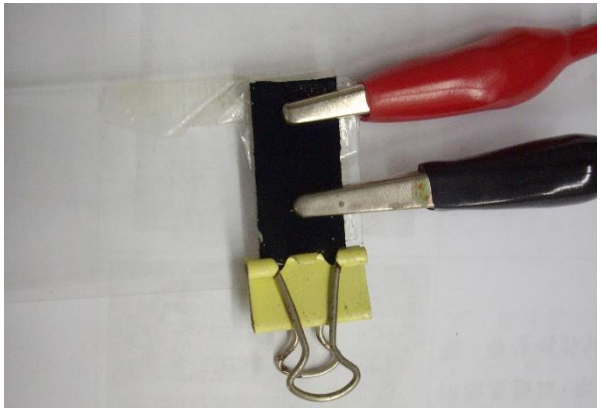
Step 3.2: Conductivity Test - LED Emission





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

Step 3.3: Conductivity Test - Resistance Measurement



Connection of multimeter

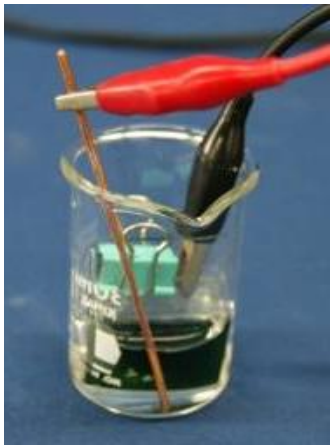
- Fix alligator clips onto PANI films
- Anode (black) to the COM port
- Cathode (red) to the Ω port
- Switch function mode to “Ω”

Measure resistance

- Examine resistance from maximum scale, i.e. 20M, to lower scale, such as 2000K
- Record the scale and resistance (i.e. 20K,10.69 kΩ) and distance/width of two clips

✓ If LCD shows “1”, it means over scale

Step 4: Electrochromism Test



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

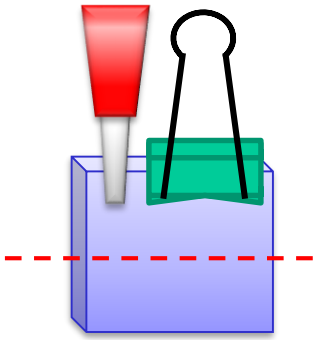
- Take 5 mL of 20% NaCl in a 30 mL beaker
- Connect ITO glass to negative pole and Cu wire to positive pole (red) of DC power supply
- Place two electrodes into NaCl solution and separate by a microslide
- Apply 0.5-1.0 V voltage to reduce PANI on ITO glass
- Observe and record the color change

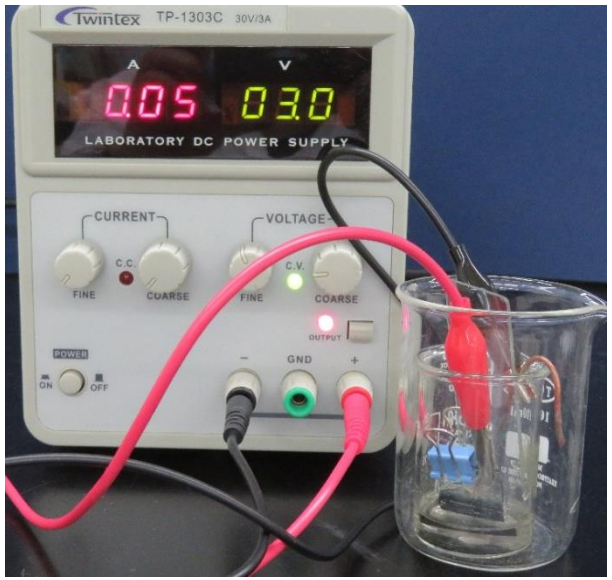
✓ The layer of PANI on ITO should not be too thick

✓ Keep the voltage lower than 1.0 V to avoid side reaction

Additional Notes

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





Clean-Up and Check-Out

- Wash binder/alligator clips with DI water and wipe dry to avoid rusting
- Recycle ITO glass, microslide, Cu wire, and chemical waste
- Wash and brush the beakers with the remaining HCl (pH = 2.5)
- 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:
  - **Hand in prelab/lab note/report together to TA**

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