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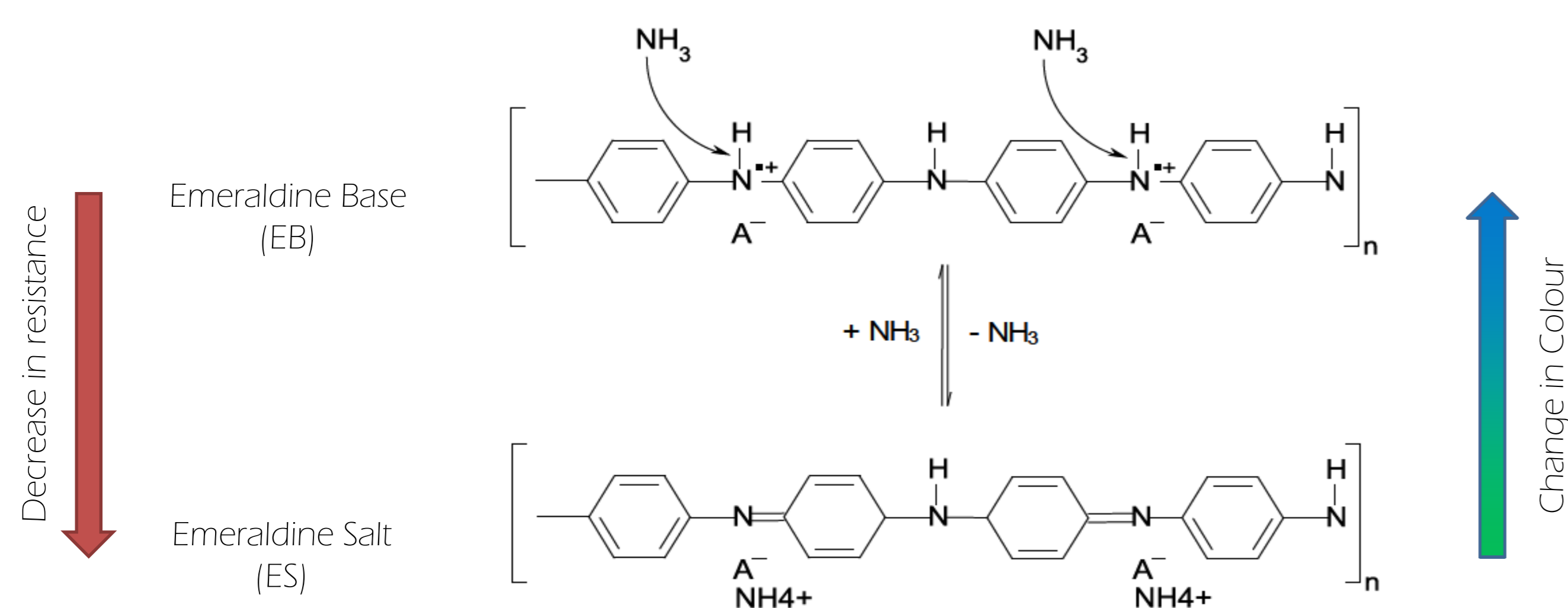
Flexible Ammonia Sensor Based on Polyaniline/Carbon Black Composites Operating at Elevated Temperatures

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Introduction

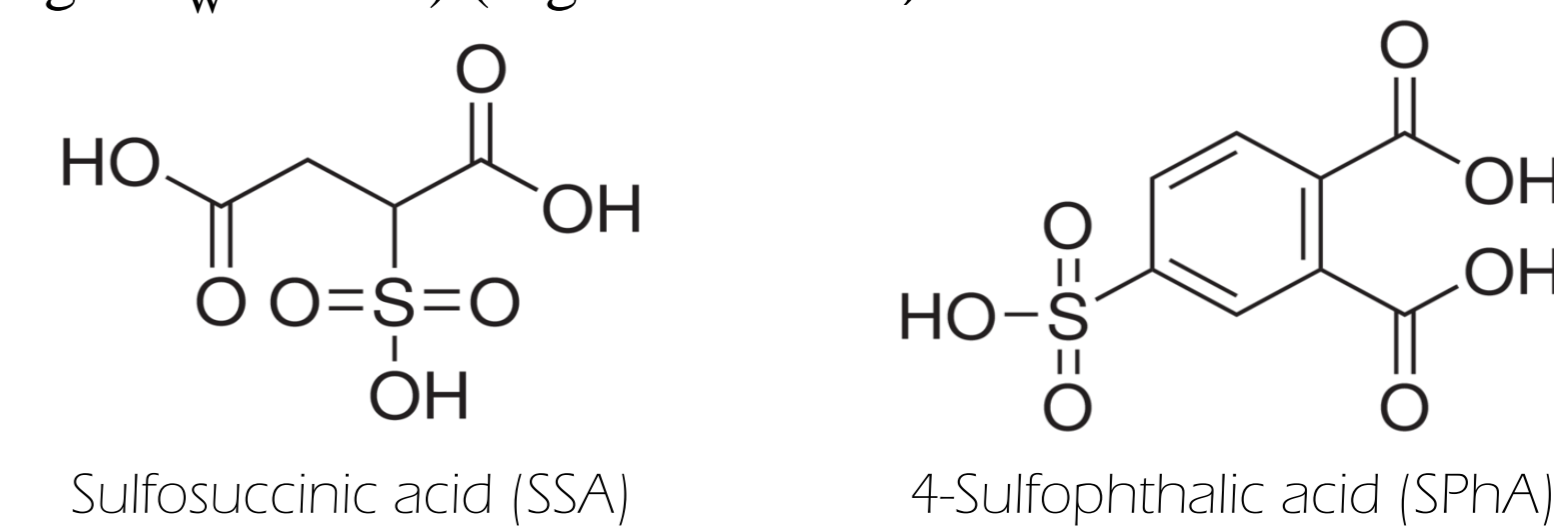
- Electrically conducting polymers (CPs) are attractive candidates for gas sensors → they offer great design flexibility, ease of fabrication, low-cost, low-power consumption and tunability [1]
- Polyaniline (PANI), a well-known CP, has reversible doping behavior through acid/base interactions; e.g., ammonia (NH₃) reversibly deprotonates emeraldine salt (doped form of PANI), converting it to emeraldine base (undoped form) with a significant decrease in conductivity (→chemiresistive behaviour).



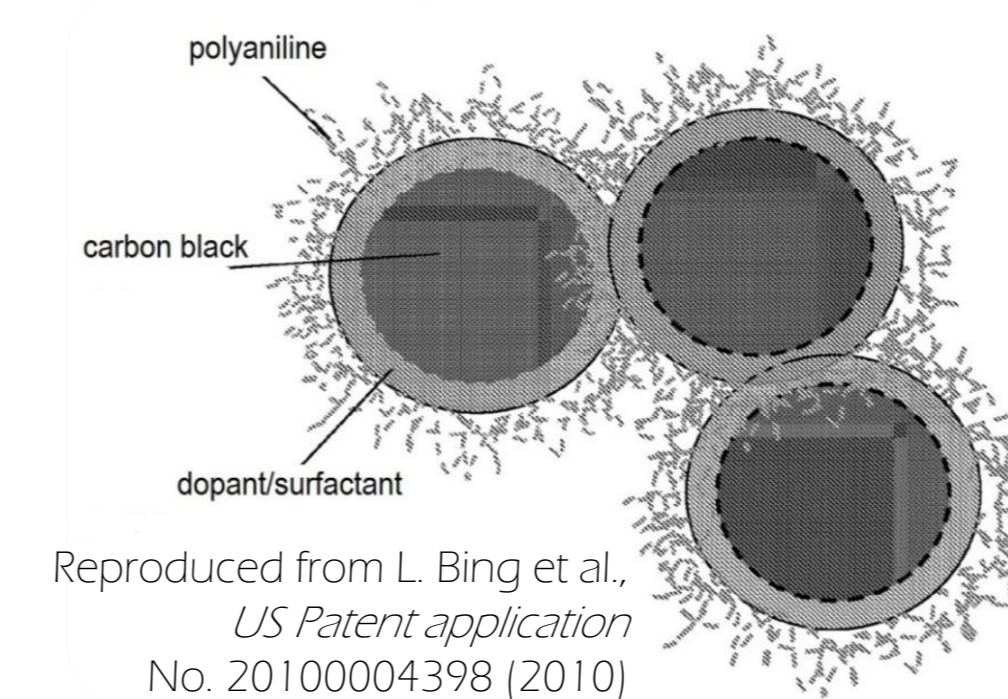
- Problem #1: Enhanced sensitivities are needed in order to meet the requirements of real-time sensing application!
✓ Solution: **Employing carbon-based/PANI composite concept** [2]; **solution processable PANI gives us the possibility to incorporate carbon black particles into polymeric complex → realizing hybrid chemiresistors.**
- Problem #2: The sensor recovery is poor!
✓ Solution: **Operation at elevated temperatures can improve desorption of NH₃ molecules from the sensor film, hence improving the recovery time** [3].
- Problem #3: Lack of solution processability [3,4], has limited implementation of ES in high-throughput sensor fabrication methods, i.e., printing!
✓ Solution: **The solution processability of PANI (particularly in its conducting state) may be improved, taking advantage of 'counter-ion induced processability' concept through a novel method: using multifunctional dopants** [5].

Materials and Methods

- Polymer: polyaniline (emeraldine base, average M_w~10000) (Sigma- Aldrich)
- Solvent: 1-methyl-2-pyrrolidone (NMP)
- Multifunctional dopants:



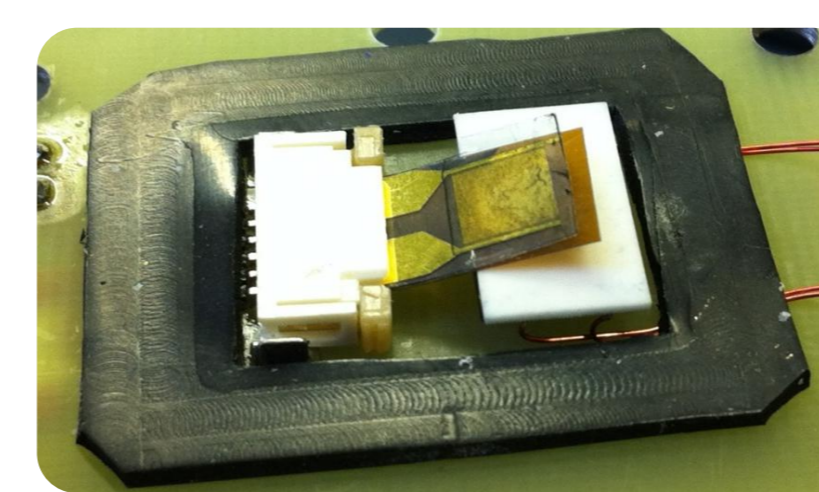
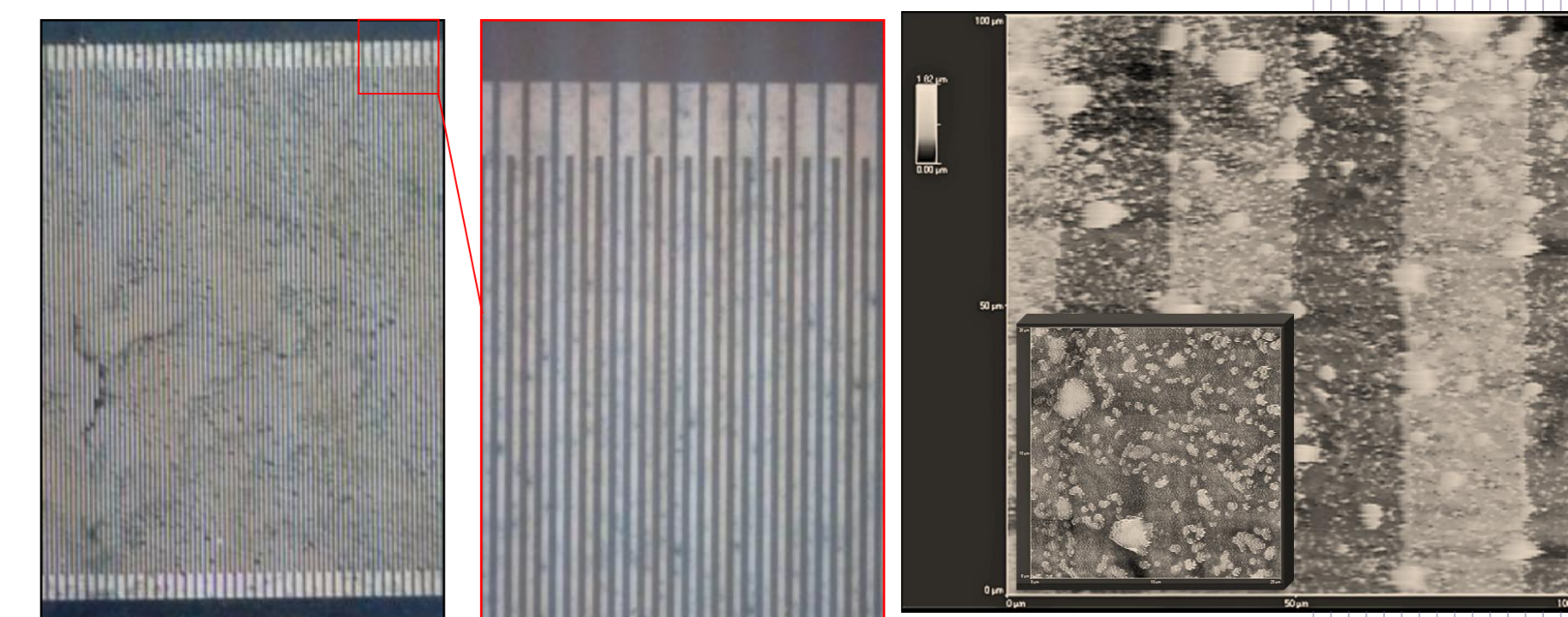
- Carbon black: PANI-modified carbon black (Sigma-Aldrich)



Reproduced from L. Bing et al.,
US Patent application
No. 20100004398 [2010]

- EB was first dissolved in NMP (~ 1 wt. %), filtered through a 0.45 μm pore size PTFE membrane (Millipore);
- Multifunctional dopant was added to the solution (dopant molecule to PANI(mer) ratio = 0.5);
- Modified carbon black was added to the green solution of SSA-doped PANI to make a 20 wt% carbon black/PANI composite.

- Deposition method: Dip/Spin coating!
- Optical Microscopy & AFM images of the sensor in non-contact mode. The area scanned in AFM is 100×100 μm. (The inset shows the zoom in area of 20×20 μm):
→ Fairly uniform dispersion without using intensive mixing methods!

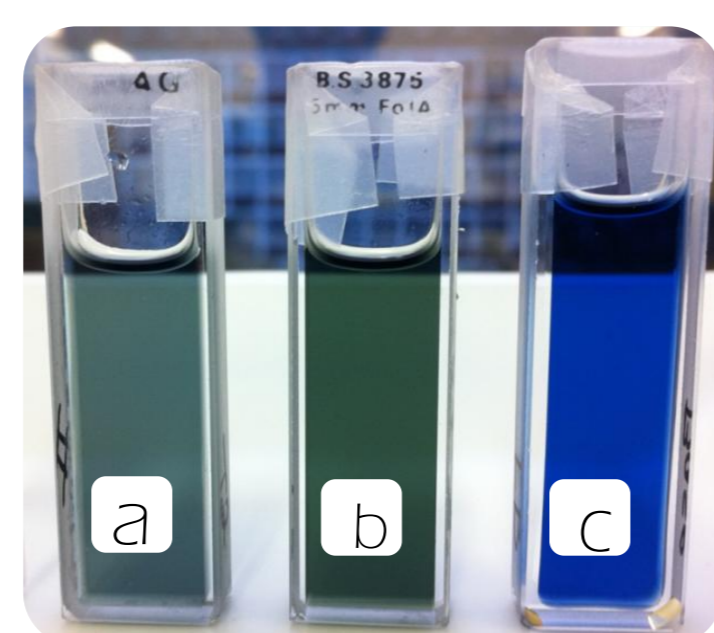
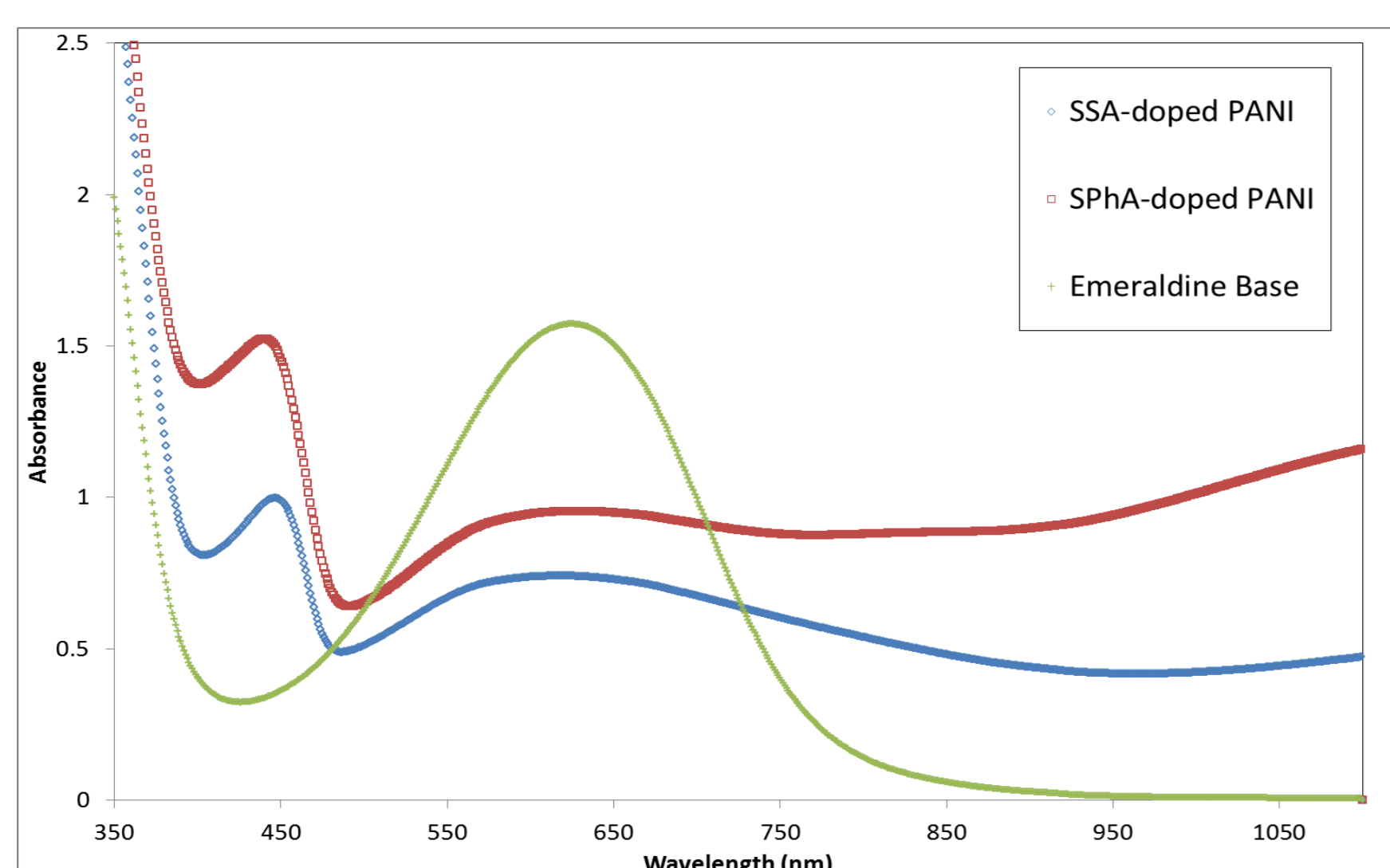


- Substrate: flexible polyimide substrates (Kapton®) with gold interdigitated electrodes (electrode gap = 20 μm)[†]
- A miniature heater was applied underneath the sensor to maintain a stable 80 °C temperature in a Teflon chamber.
- Ammonia vapour source: recalibrated permeation tube (permeation rate: ca.548 ng min⁻¹) (Fine permeation tubes).

Results

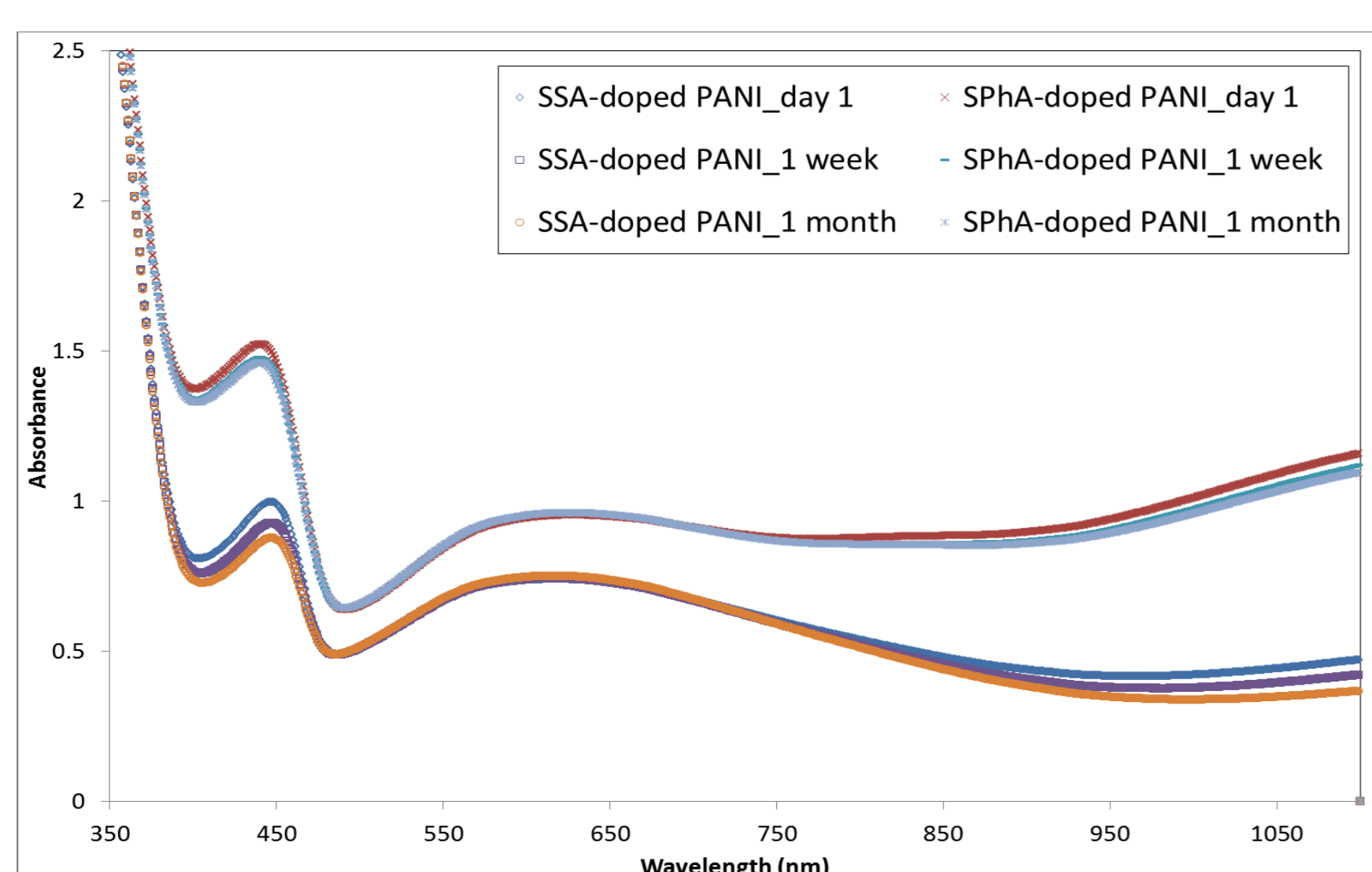
UV/Vis Spectroscopy

- A UV-visible spectrophotometer (PerkinElmer lambda 35) was used to study the doping behaviour of different polyaniline solutions.



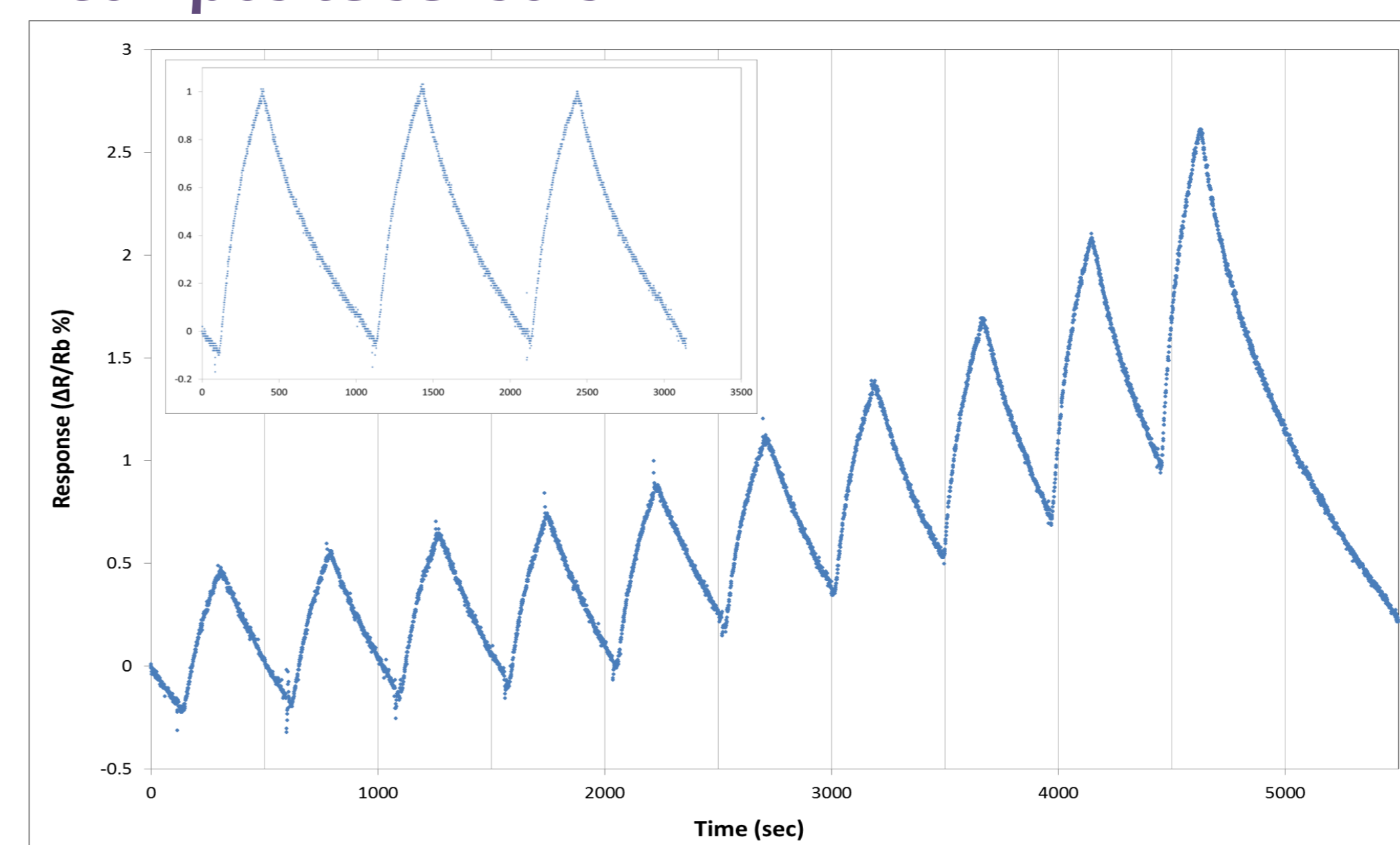
a) SSA-doped PANI
b) SPhA-doped PANI
c) Emeraldine base

- For the EB the absorption band at ca.635 nm is relate to the n-π* transition (quinoid form structure) → undoped/half oxidized PANI structure.
- For ES (either with SSA or SPhA) the absorption at ca. 435 nm is due to the presence of localized semiquinone population or the polaron absorption. The long free tail extended to near IR region may be attributed to highly delocalized free electron state of polyaniline doped with these dopants.

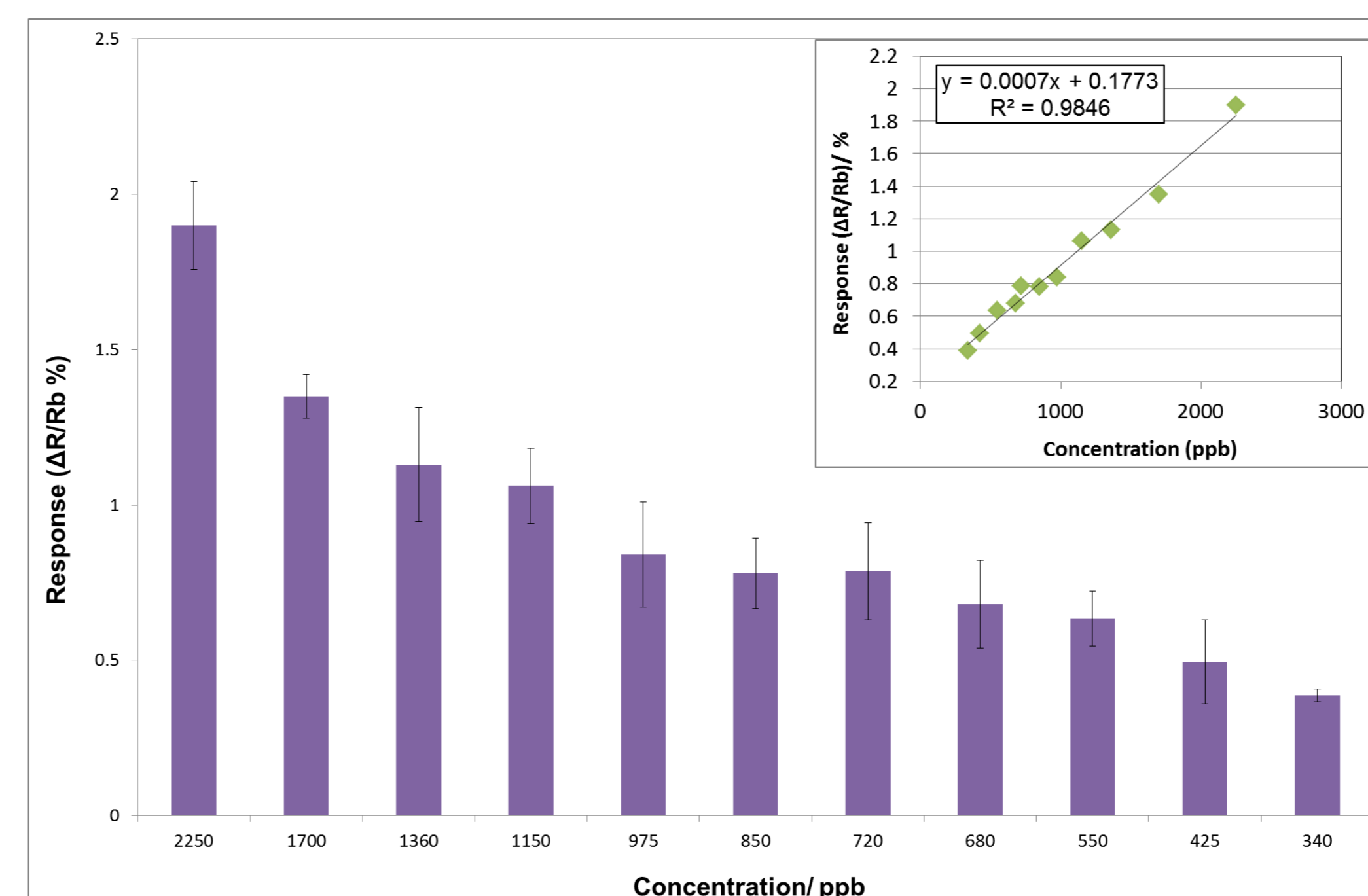


- Solutions were stable at least for 1 month; only slight changes in UV/Vis spectra were observed in this period. (practically the solutions can be stored for several months without any visible precipitation)
- These solutions can be used for depositing very low-resistant layers of PANI using solution deposition methods, such as spin coating and spray coating, as well as printing methods, such as inkjet printing.

Ammonia sensing behaviour of flexible PANI/carbon black composite sensors



- Sensor response toward an ascending sequence of ammonia concentrations (425, 550, 680, 720, 850, 975, 1150, 1360, 1700, 2250 ppb) (exposure time=3 min, recovery time=5 min, T_{sensor}= 80 °C).
- Inset shows reproducibility of response toward 550 ppb ammonia (exposure time=5 min, recovery time=12 min)



- Maximum response of the sensor toward a series of concentrations of ammonia. Error bars are representative of the standard deviation of maximum sensor response at each concentration.
- Inset shows the linearity of response over concentration range studied here (exposure time=3 min, T_{sensor}= 80 °C)

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Acknowledgment

This work was supported by FlexSMELL-FP7-PEOPLE-ITN-2008-238454.

[†]We would like to thank our FlexSMELL partner at IMT labs in EPFL university for providing the substrates used in this study.

Conclusions

- Multifunctional dopants protonate emeraldine base, make it soluble in the aprotic solvents such as NMP; homogenous solutions were stable for several months.
- Solution processability of PANI through the employment of multifunctional dopants gives us enormous flexibility in order to design novel hybrid sensors.
- Ultra sensitive ammonia sensors were made by depositing SSA-doped PANI/carbon black composite on flexible polyimide substrates with interdigitated gold electrodes; sensor response was fast and reproducible; the sensors showed a linear response behaviour in the range of concentrations tested here.
- Sensing operation at elevated temperatures (here 80 °C) can improve response recovery and stability of CP-based sensors..