Supplymentary Materials: The use of conductive polymers embedded macro porous PEI and ionic liquid form of PEI cryogels for potential conductimetric sensor application to CO_2

Sahin Demirci [1], Nurettin Sahiner [1,2,3,*]

[1] Canakkale Onsekiz Mart University, Faculty of Science and Arts, Department of Chemistry & Nanoscience and Technology Research and Application Center (NANORAC), Terzioglu Campus, Canakkale, 17100, Turkey
[2] Department of Chemical and Biomolecular Engineering, University of South Florida, Tampa, FL, 33620, USA
[3] Department of Ophthalmology, Morsani College of Medicine, University of South Florida, 12901 Bruce B. Downs Blvd, MDC21, Tampa, FL 33612, USA
* Correspondence: sahiner71@gmail.com, nsahiner@usf.edu

Supporting Information

1. Synthesis of macro porous PEI and PIL PEI cryogels

The epoxy-amine reaction at cryogenic conditions was used for the synthesis of PEI cryogels as reported earlier by our group [11]. In brief, certain amount of PEI solution (1 mL, 50% in water) was placed into 9 mL of DI water containing vial, and vortexed for 2 min and placed into deep freezer for 3 min for chilling. Next, GDE (10% mole based on the repeating unit of PEI) was added into the solution as crosslinker and vortex mixted and then quickly placed into plastic straws (~8 mm diameter). Then, these plastic straws were placed in a freezer at -18 °C for 16 h to complete cryocrosslinking of PEI chains. The synthesized PEI cryogels were cut into cylindrical shapes, and washed with DI water 5 times, and dried in an oven at 50 °C.

The preparation of PIL forms of PEI cryogels was carried out by employing anion exchange reactions [11]. PEI cryogels were anion exchanged using of sodium dicyanamide (Na+[N(CN)2]-), ammonium hexafluorophosphate (NH4+[PF6]-), sodium tetrafluoroborate (Na+[BF4]-), and potassium thiocyanate (K+[SCN]-) respectively after protonation of PEI cryogels. For this purpose, 1.0 g PEI cryogels were treated with 200 mL 1 M HCl for 4 h at room temperature and then washed with DI water three times. The aqueous solutions of anion source were prepared in beakers separately with 1.5-fold excess of anions based on repeating unit of PEI by dissolving corresponding amounts in 50 mL DI water. Then, PEI cryogels were placed in the ionic liquid anion solution and exchange reactions were carried out for 24 h under 200 rpm mixing rate at room temperature.

2. In situ preparation of conductive polymers within PEI cryogels

2.1. In situ synthesis of PANi

The known weight of washed and dried PEI cryogels were placed into a beaker with 10 mL ANi for 30 min to load ANi into the PEI cryogels. The ANi-loaded PEI cryogels were then weighed again and the amount of ANi loaded into PEI cryogels was determined. Then, the ANi-absorbed PEI cryogels were placed in APS solution in 1 M HCl at 1:1.25 mole ratio of APS:ANi. The polymerization reaction of ANi continued for 15 min at room temperature at 250 rpm mixing rate. Then, the prepared PEI/PANi cryogel composites were washed 3 times with ethanol-water mixture, dried in an oven at 50 °C, and stored in an air tight container for further use.

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2.2 In situ synthesis of PPy

The synthesis of PPy within PEI cryogels was also carried out according to the literature with some modifications [**12, 13**]. For this purpose, 0.5 g of cleaned and dried PEI cryogels were placed into 10 mL Py to load the Py monomer into PEI cryogels under constant stirring at 250 rpm for 30 min. The Py-loaded PEI cryogels were placed into 200 mL 0.5 M $FeCl_3$ solution in DI water at room temperature under 500 rpm mixing rate for 2 h for the polymerization of Py monomer within PEI cryogels. Then, the prepared PEI/PPy cryogel composites were washed with ethanol-water mixture (50:50 by volume) 3 times, and dried in an oven at 50 ^{o}C. Dried PEI/PPy cryogel composites were stored in an airtight container for further use.

2.3 In situ synthesis PTh

The earlier report was also followed for in situ synthesis of PTh within PEI cryogels [**12, 13**]. PEI cryogels weighing 0.5 g was placed into 10 mL Th, and stirred at 250 rpm mixing rate for 30 min. Next, these Th-loaded PEI cryogels were placed into 50 mL 0.3 M $FeCl_3$ solution in chloroform in a 100 mL flask with a reflux system, and stirred at 65 ^{o}C for 16 h at 500 rpm mixing rate. Then, the prepared PEI/PTh cryogel composites were washed at least 3 times with ethanol-water mixture (50:50 by volume) and dried in an oven at 50 ^{o}C. The dried PEI/PTh cryogel composites were stored in an air tight container for further use.

2.4 Instruments

Fourier Transform Infrared (FT-IR) spectra of PEI based cryogels and their PANi, PPy and PTh conductive polymer composites, and also PANi composites of PIL PEI cryogels were recorded between 650-4000 cm $^{-1}$ spectral range with 4 cm^{-1} resolutions via attenuated total reflectance attached FT-IR spectrometer (Thermo, Nicolet iS10).

The SEM images of freeze-dried PEI cryogels were obtained using an SEM (JEOL JSM-5600) with an operating voltage of 20 kV. The images were acquired after placing PEI cryogels onto carbon tape-attached aluminum SEM stubs at room temperature after coating with gold to a few nanometer thicknesses under vacuum.

The conductivities of PEI based cryogels and their PANi, PPy and PTh conductive polymer composites, and also PANi composites of PIL PEI cryogels were measured from current-voltage measurements using a computer-controlled electrometer (Keithley 2400 Source-Meter) at room temperature. Carbon tape was attached to the top and bottom of PEI based composites to connect the electrodes, and the conductivities were measured at room temperature using the slope of the Ohmic region of the I-V curves.

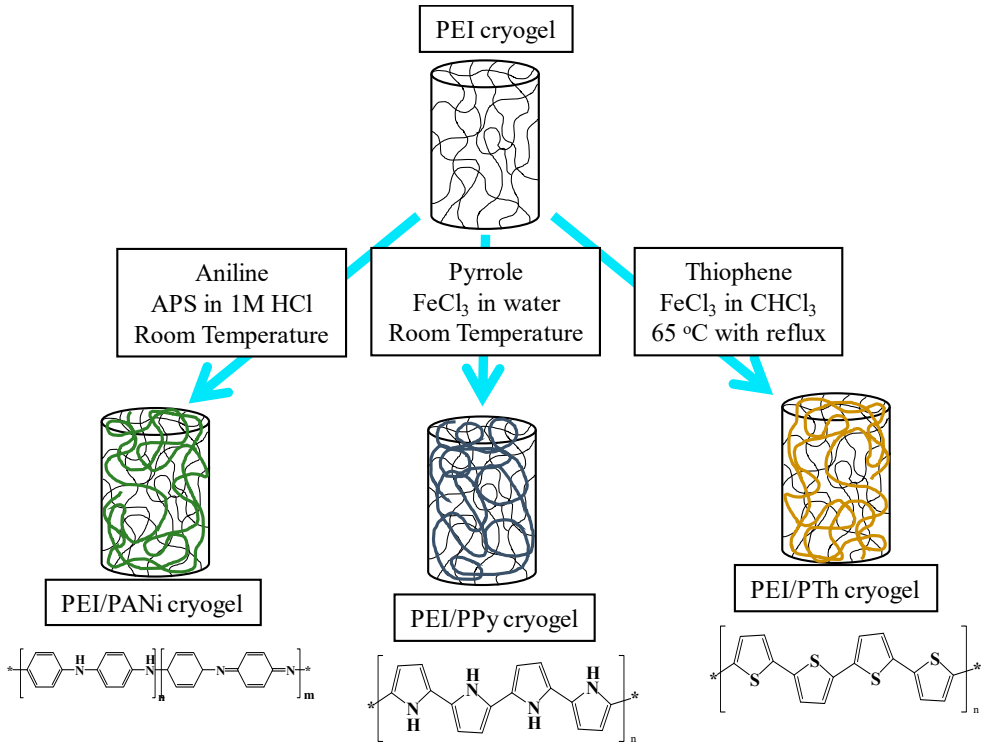

Figure S1. The schematic presentation of in situ synthesis of conductive PANi, PPy, and PTh polymers within PEI cryogels.

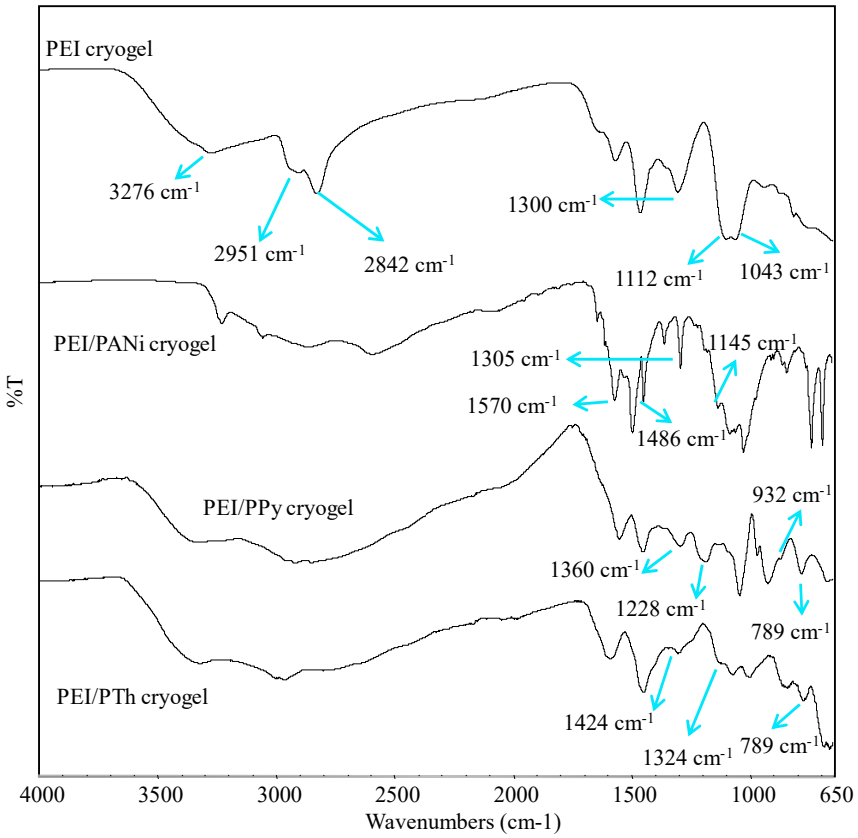

Figure S2. FT-IR spectra of bare PEI cryogel, PEI/PANi, PEI/PPy, and PEI/PTh cryogel composites.

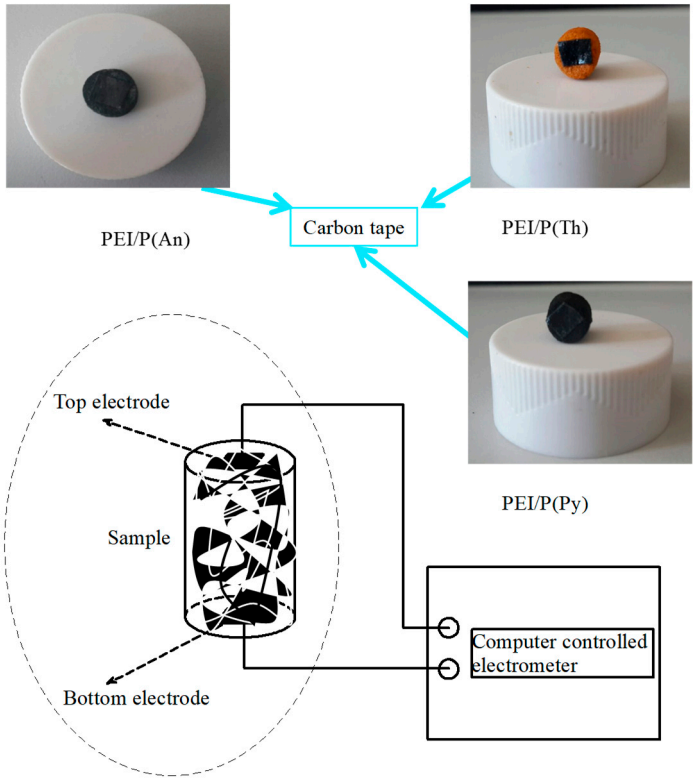

Figure S3. Digital camera images of PEI/PANi, PEI/PPy, and PEI/PTh cryogel composites and the schematic presentation of experimental setup used in electrical conductivity measurements.

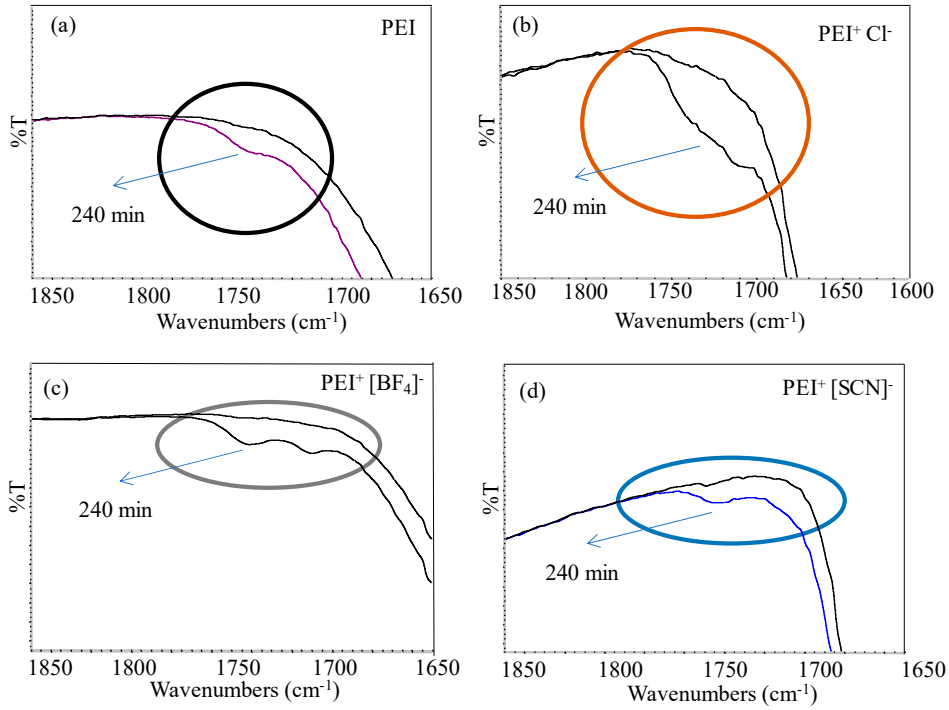

Figure S4. The FT-IR spectrua between 1650-1850 cm^{-1} wavenumber region of (**a**) bare PEI cryogel (**b**) $PEI^{+}Cl^{-}$, (**c**) $PEI^{+}BF_4]^{-}$, and (**d**) $PEI^{+}[SCN]^{-}$ PIL cryogels before and after 240 min CO_2 exposure. [200 mL/mim flow rate].

Table S1. The conductivities of bare and conductive polymer composites embedded PEI cryogel composite and the amounts polymers within PEI cryogels.

Materials	**Room Temperature Conductivities** **(S.cm^{-1})**	**Amount of Conductive Polymer (g) in 1 g of PEI Cryogel**
PEI cryogel	$6.40 \times 10^{-7} \pm 3.45 \times 10^{-8}$	-
PEI/PANi	$4.80 \times 10^{-3} \pm 5.10 \times 10^{-4}$	5.9 ± 0.4
PEI/PPy	$1.40 \times 10^{-4} \pm 2.25 \times 10^{-5}$	5.1 ± 0.1
PEI/PTh	$2.02 \times 10^{-6} \pm 3.61 \times 10^{-7}$	3.2 ± 0.3

Table S2. The effect of anion on the electrical conductivity of bare PEI cryogels and their PANi containing IL forms of composites.

Materials	Room Temperature Electrical Conductivities ($S.cm^{-1}$)	
	Bare Form	**PANi Embedded**
1-PEI	6.40×10^{-7}	4.8×10^{-3}
2-PEI^{+} Cl^{-}	1.64×10^{-4}	4.90×10^{-3}
3-PEI^{+} $[N(CN)_2]^{-}$	1.68×10^{-9}	1.32×10^{-2}
4-PEI^{+} $[PF_6]^{-}$	1.76×10^{-8}	5.20×10^{-3}
5-PEI^{+} $[BF_4]^{-}$	1.55×10^{-5}	5.01×10^{-3}
6-PEI^{+} $[SCN]^{-}$	1.09×10^{-5}	2.52×10^{-4}

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