Proton-Conductive Gas Sensor: A New Way to Realize Highly Selective Ammonia Detection for Analysis of Exhaled Human Breath

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Materials

Polyvinyl alcohol (PVA, Mw ~67000) was purchased from Aladdin. Polyvinylpyrrolidone (PVP, Mw ~1300000) was purchased from Sinopharm Chemical Reagent Co. Ltd. Polyacrylamide (PAM, Mw ~3000000) was purchased from Beijing Chemical Corp (Beijing, China). The water used throughout all experiments was purified through a Millipore system.

Fabrication of sensor based on ceramic substrate

In order to investigate the electrical behavior of PVA, PVP and PAM films during the ammonia detection process, the aqueous solutions of three nonconjugated polymers at the concentration of 1 wt% were drop-coating on the commercial ceramic substrate (9 mm * 4 mm, 0.5 mm in thick) with the volume of 10 μL. The structure of sensors was shown in Figure S1. The ceramic substrates were made of aluminum oxide on which four pairs of graphitic interdigitated electrodes were printed. The obtained sensors were dried at 60 ºC for the following measurement. The nonconjugated polymers were also drop-coated on the commercial QCM substrates by using 2 μL solutions of three nonconjugated polymers at the concentration of 0.1 wt% to investigate water and ammonia molecular adsorption process. QCM substrates consist of AT-cut quartz crystal (8 mm diameter) with a fundamental frequency of 10 MHz and silver electrodes (5 mm diameter) were covered on both sides.

Measurement of ammonia sensors

The current signals in this work were recorded by applying a 1 V DC potential across the electrodes, and measuring the resulting current by a CHI660E electrochemical analyzer (CH Instruments, Inc., Shanghai). The complex impedance plots were recorded by a Keysight E4990A impedance analyzer with a sinusoidal voltage of 1 V without DC-bias in a frequency range from 20 Hz to 20 MHz. The frequency shift of the QCM were monitored by a frequency meter (53131A, Agilent), a self-made oscillator circuit was utilized to drive the coated QCM.

The desired concentration of the test gas was obtained by the static liquid gas distribution method, which was calculated by the following formula (1),

$$\mathrm{c} = \frac{22.4 \times f \times \beta \times V_1}{M \times V_2} \times 10^6 \quad (1)$$

where c (ppm) is the target gas concentration, *f* is the solution concentration, β (g/mL) is the density of the liquid, V_1 (mL) is the volume of liquid, V_2 (L) is the volume of the chamber, and M (g/mol) is the molecular weight of the liquid.

The humidity environments were obtained by pre-controlling the humidity of the test chamber using a constant temperature & humidity incubator (Shanghai ESPC Environment Equipment Corporation, China).

Table S1. Water adsorption capacities (g/g) of PVA, PVP and PAM under 97% RH and their ammonia adsorption capacities (g/g) for 100 ppm ammonia in 97% RH.

	PVA	PVP	PAM
Water adsorption capacity (g/g)	0.58	1.18	1.64
Ammonia adsorption capacity (g/g)	0.09	0.13	0.23

Table S2. The typical concentrations of biomarkers in exhaled human breath.

Biomarker	Disease	Healthy person	Patient	Ref.
Hydrogen sulfide	Halitosis	<1.0 ppm	1.0-2.0 ppm	[S1]
Ethanol	Lung cancer	23-868 ppb	27-5380 ppb	[S2]
Acetone	Diabetes	0.3-0.9 ppm	>1.8 ppm	[S3]
Toluene	Lung cancer	1.0-20.0 ppb	10.0-100.0 ppb	[S4]
Formaldehyde	Breast Cancer	~0.3 ppm	>1.2 ppm	[S5]
Nitric oxide	Asthma	0.2-1.0 ppm	>1.0 ppm	[S6, S7]
Isopropanol	Lung cancer	0-135.0 ppb	81.2-329 ppb	[S8]

Table S3. The different film thicknesses of the PVP sensors.

	PVP-1	PVP-2	PVP-3	PVP-4
Film thickness (μm)	13	20	42	55

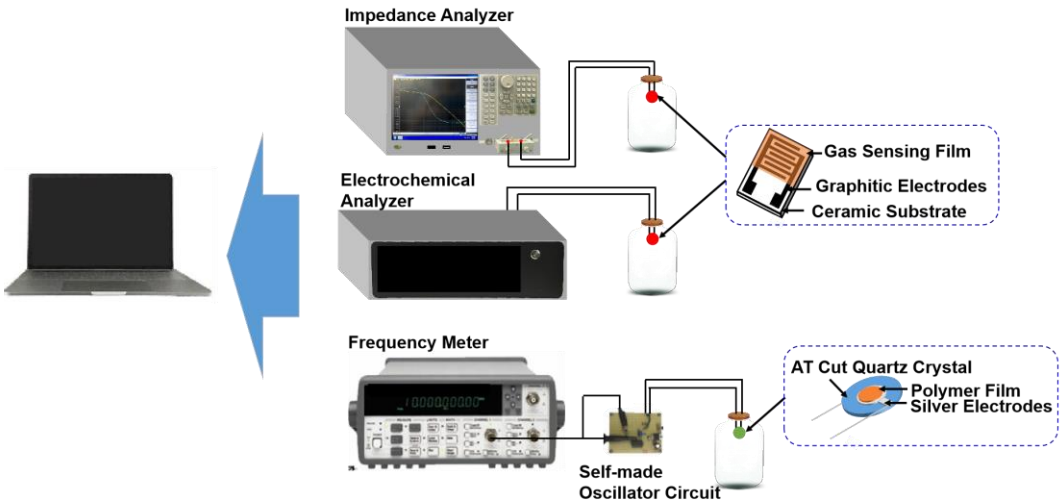

Figure S1. The schematic measurement system and device structure.

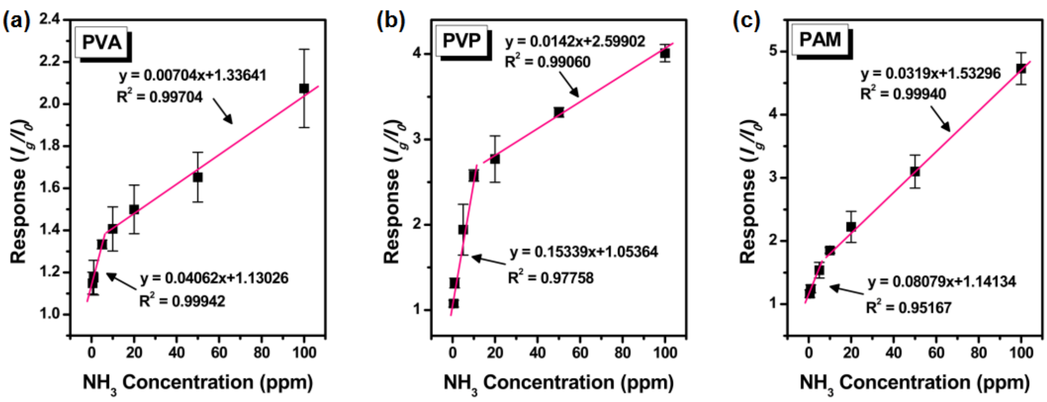

Figure S2. Linear fitting curves of the relationship between response (I_g/I_0) of (a) PVA, (b) PVP and (c) PAM sensors and ammonia concentration.

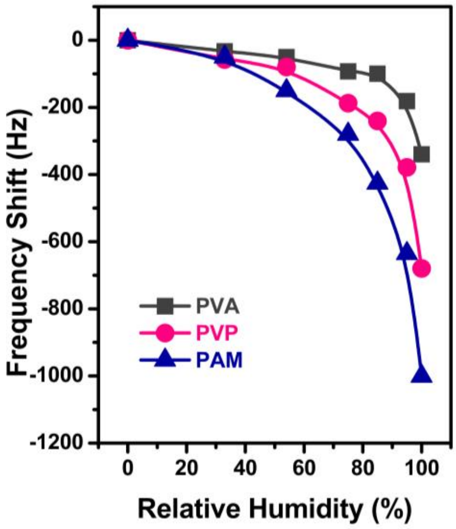

Figure S3. Frequency shift-RH curves of QCM coated by PVA, PVP and PAM films.

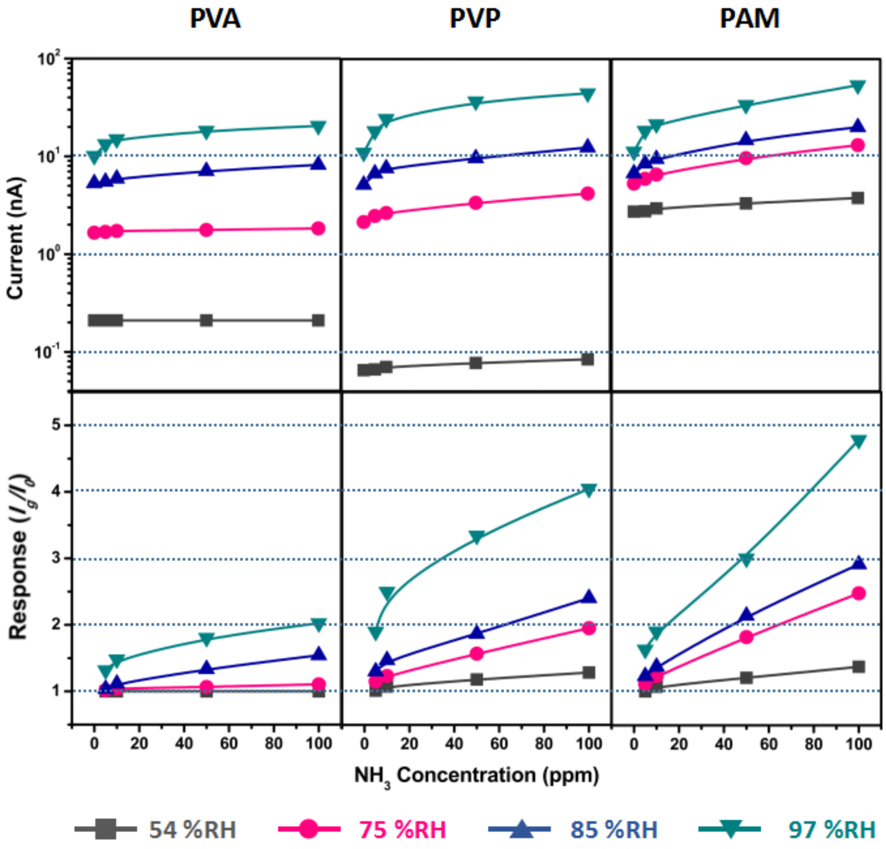

Figure S4. Current and response (I_g/I_0) v.s. ammonia concentration curves of PVA, PVP and PAM sensors under different RHs.

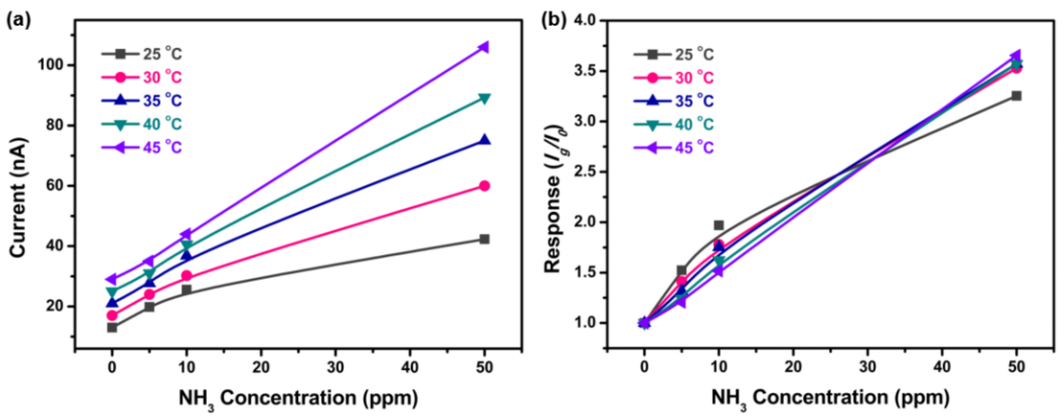

Figure S5. (a) Current and (b) response (I_g/I_0) v.s. ammonia concentration curves of PVP sensor under humid air (97% RH) at different temperatures.

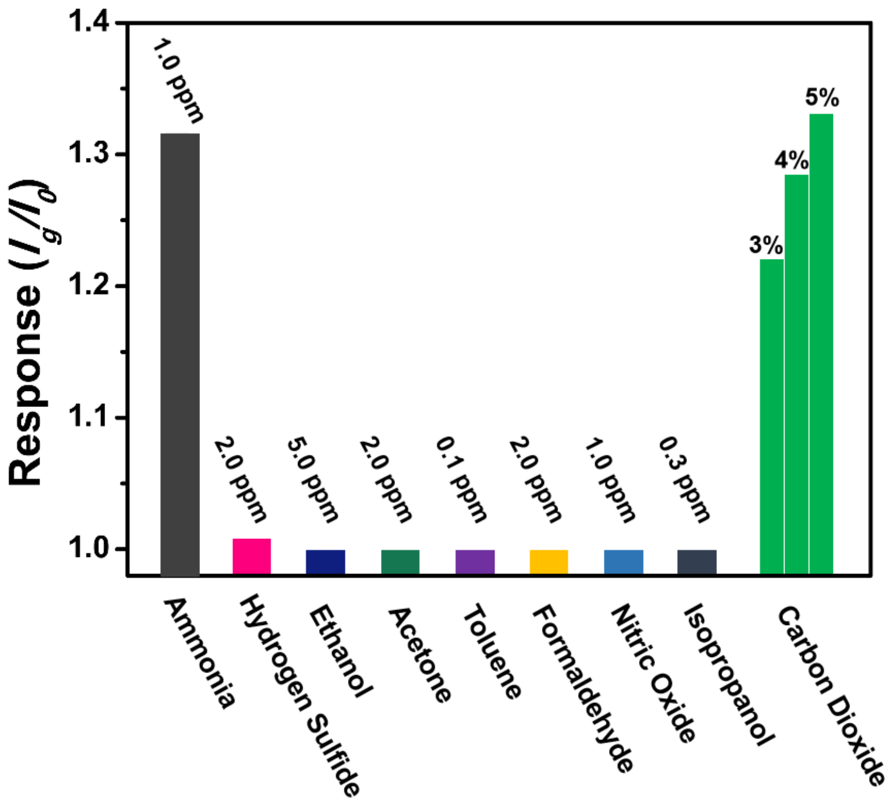

Figure S6. Selectivity of the PVP sensor in 97% RH.

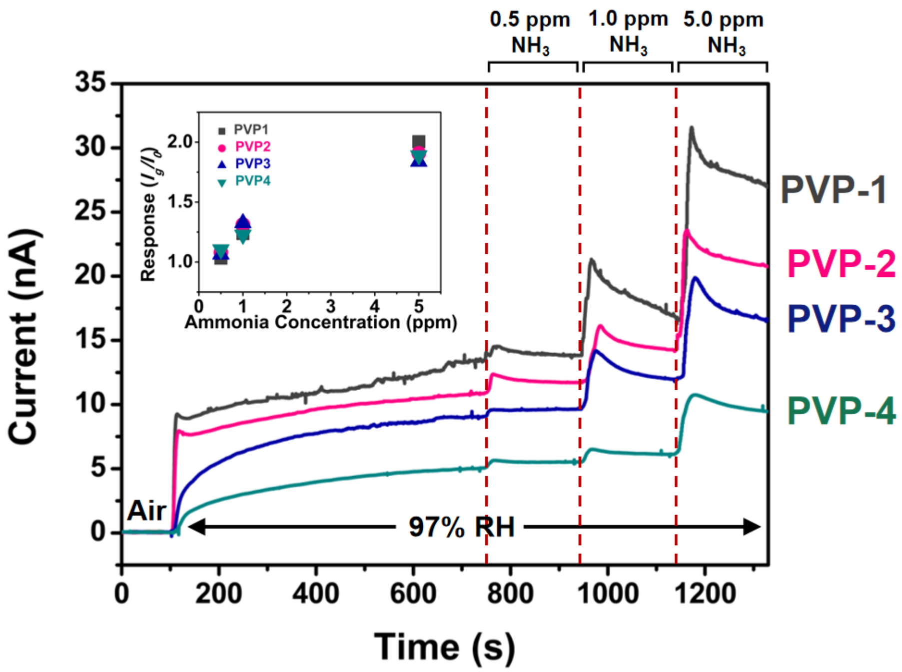

Figure S7. The current-time curves for PVP sensors with different film thicknesses in an air atmosphere, humid atmosphere and humid atmosphere with different concentrations of ammonia. The inset shows the responses of the PVP sensors to ammonia in a humid atmosphere.

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