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# Viral-templated gold/polypyrrole nanopeapods for ammonia gas sensor

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# Abstract

One-dimensional gold/polypyrrole (Au/PPy) nanopeapods were fabricated using a viral template: M13 bacteriophage. The genetically-modified filamentous virus displayed gold-binding peptides along its length, allowing selective attachment of gold nanoparticles (Au NPs) under ambient conditions. A PPy shell was electropolymerized on the viral-templated Au NP chains forming nanopeapod structures. The PPy shell morphology and thickness were controlled through electrodeposition potential and time, resulting in an ultra-thin conductive polymer shell of 17.4  $\pm$  3.3 nm. A post-electrodeposition acid treatment was used to modify electrical properties of these hybrid materials. The electrical resistance of the nanopeapods was monitored at each assembly step. Chemiresistive ammonia (NH<sub>3</sub>) gas sensors were developed from networks of the hybrid Au/PPy nanostructures. Room temperature sensing performance was evaluated from 5 to 50 ppm<sub>v</sub> and mixture of reversible and irreversible chemiresistive behavior was observed. A sensitivity of 0.30%/ppm<sub>v</sub> was found for NH<sub>3</sub> concentrations of 10 ppm<sub>v</sub> or less, and a lowest detection limit (LDL) of 0.007 ppm<sub>v</sub> within the same concentration range and a calculated LDL of 0.005 ppm<sub>v</sub>.

# 1. Introduction

With complex, often hierarchical geometries and molecular recognition capability, biomaterials serve as versatile scaffolds. In particular, the characteristic length scale of these natural templates is compatible with nanomaterials assembly, and the large surface-to-volume ratio of resultant nanostructures is desirable for applications that necessitate increased surface interaction, diffusion, and chemical reactivity. Indeed, bio-assisted assembly has demonstrated utility in a number of catalysis [1-3], energy storage [4-6], and chemical sensing [7-9] applications.

Because one-dimensional (1-D) nanomaterials are the lowest dimensional materials able to sustain effective electronic transport, specific attention has been given to high aspect ratio biological templates. As example, gold and silver metal nanowires have been assembled with DNA, virus-like particles, and nucleoprotein filaments [10-12] and ZnO semiconducting nanorods have been constructed using the tobacco mosaic virus [13]. Bio-assisted assembly is a relatively low cost alternative to conventional top-down nanofabrication techniques for 1-D nanomaterials. Moreover, bio-templates offer long-range assembly and site-specific placement, both of which can be challenging for some chemically assisted self-assembly techniques.

Although most research has focused on synthesis and assembly of inorganic metal and semiconductor building blocks [14-17], more recent studies have begun to investigate the heterogeneous integration of conductive polymers with biological templates [18-20]. Conductive polymers display a unique blend of material properties. Like more conventional polymeric materials, they are mechanically flexible and can be processed at low temperatures; however, their distinctive  $\pi$ -conjugation also endows them with electrical conductivity similar to semiconductors or even metals. In addition, the doping levels of these unique materials can be modified via surface charge transfer or redox reactions with a variety of reducing (e.g. NH<sub>3</sub>, H<sub>2</sub>S, CH<sub>4</sub>) or oxidizing (e.g. NO<sub>2</sub>) gases under ambient conditions, making them suitable room-temperature chemiresistive materials. Although conductive polymer-based nanowires have been produced via bioscaffolding [21-23], the electrical and chemiresistive gas sensing properties of these materials have yet to be widely explored.

In this work, linear arrays of viral-templated metal nanoparticles (NPs) were combined with a conductive polymer coating to form chemiresistive inorganic/organic nanopeapods. A genetically-modified M13 bacteriophage with an gold-binding peptide (VSGSSPDS [24]) displayed on each of its pVIII capsid proteins, was used to assemble chains of Au nanoparticles (NPs). This filamentous virus was about 880 nm in length and 6.5 nm in diameter [25], thus

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creating an excellent guide for assembly of high aspect ratio nanowire-like structures. The addition of Au NPs to the viral protein coat conferred sufficient electrical conductivity to the biotemplate to allow electropolymerization of the conductive polymer, polypyrrole (PPy), along its length, forming Au/PPy nanopeapods. The electrodeposition parameters including deposition potential and time were varied resulting in a range of morphologies from a thin conformal shell to a thick continuous film with microscale features. To study the effect of PPy doping on nanopeapod electrical and chemiresistive behavior, PPy shell conduction was modified using an acid treatment post-electrodeposition. The current-voltage (I-V) characteristic of these hybrid viral-templated structures was measured before and after electropolymerization, as well as following acid treatment. NH<sub>3</sub> detection was chosen as a means to evaluate the potential of these hybrid materials for chemiresistive gas sensing applications. The chemiresistive response of the Au/PPy nanopeapods was measured at gas concentrations up to 50 ppm<sub>v</sub>. These metal-semiconductor, bio-templated nanomaterials formed sensitive gas detectors, performing well within this concentration range.

# 2. Experimental details

## 2.1. Viral-directed assembly of gold (Au) nanoparticle (NP) chains

Following an approach similar to Joo et al. and Haberer et al. [26, 27], gold-binding M13 bacteriophage were used to template chains of Au NPs. This filament-shaped biological support displayed a peptide fusion on the N-terminus of each pVIII major coat protein which conferred Au affinity and was essential for assembly. The fabrication procedure for these materials is illustrated in Figure 1. Three-terminal planar platinum microelectrodes were lithographicallydefined on a silicon substrate coated with an insulating layer of thermal oxide. These microelectrodes were composed of 15 pairs of working electrodes that were 50 µm wide and 3 µm apart surrounding a 500 µm diameter circular counter electrode with concentric ring reference electrode. The substrate with pre-fabricated electrodes was cleaned sequentially with acetone, isopropyl alcohol, and deionized water. Additionally, a 30 s oxygen plasma treatment was performed to ensure complete removal of organic contaminants, enhance surface hydrophilicity, and achieve non-specific adsorption of the biological support. The substrate was immersed in a 3 x  $10^8$  pfu  $\mu$ L<sup>-1</sup> solution of bacteriophage for 10 min, washed with 0.7% Tween-20 in Trisbuffered saline (50 mM Tris-Cl, 150 mM NaCl, pH 7.5) and rinsed with deionized water. The substrate, with phage templates attached, was incubated in gold colloid solution at a concentration of 5 x  $10^{13}$  particles  $\mu$ L<sup>-1</sup> (5.6±0.84 nm diameter, BBI Solutions) for 1 hour, rinsed with deionized water, and dried. A commercial gold electroless deposition reagent (Nanoprobes GoldEnhance<sup>TM</sup>

LM) was used for 3 min to increase the diameter of the assembled Au NPs and form continuous chains.



Figure 1. Viral-templated Au NP assembly and Au/PPy nanopeapod gas sensor formation. (a)  $O_2$  plasma treatment of pre-patterned Pt three-terminal microelectrodes. (b) Adsorption of M13 bacteriophage template with Au affinity onto microelectrodes. (c) Selective binding of Au NP seeds to template. (d) Electroless deposition to enlarge NP seeds and form electrically connected chains of Au NPs. (e) Electrodeposition of PPy shell onto Au NP chains to produce nanopeapods.

## 2.2 Electropolymerization and acid treatment of polypyrrole (PPy)

The conditions for PPy deposition on viral-templated Au nanowires were adapted from Chartuprayoon et al. [28]. A solution of distilled 0.5 M pyrrole (Sigma Aldrich) and 0.2 M lithium perchlorate (LiClO<sub>4</sub>, Sigma Aldrich) in aqueous media was prepared, then purged with high purity nitrogen gas (99.999 %) for 1 hour to eliminate dissolved oxygen. The previously described planar, microelectrodes were used in a three-terminal configuration in a 700 µL cell for electropolymerization. The deposition potential was applied to the working electrode with a potentio-/galvano- stat (SP200, Bio Logic, Inc.). Cyclic voltammetry was performed between -0.6 and 0.6 V vs Pt reference electrode with a fixed scan rate of 20 mV s<sup>-1</sup>. Electropolymerization on viral-templated Au NPs to form Au/PPy nanopeapods was subsequently monitored via chronoamperometry. Deposition potentials of 0.55, 0.65, 0.75 and 0.80 V vs Pt reference electrode were investigated using a fixed deposition time of 160 s. A deposition potential of 0.55 V was chosen for further study using deposition times between 20 and 200 s. Acid treatment was performed to study the effect of PPy doping on the electrical properties and chemiresistive behavior of the hybrid nanopeapod materials. Following a previous report by Low et al. [29], the

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as-prepared Au/PPy nanopeapods were immersed in 1 M hydrochloric acid (HCl, Fisher Scientific) for 5 min, rinsed in deionized water, and dried with air [29, 30].

### 2.3 Characterization of device morphology and electrical behavior

Scanning electron microscopy (SEM, Philips, XL30 FEG) was used to characterize viraltemplated Au NP chains and Au/PPy nanopeapods. Size, size distribution, and morphology of templated NPs and nanopeapods were examined.

The room temperature electrical behavior of each device was found via two-terminal measurements before and after PPy electropolymerization, as well as following HCl treatment. The voltage was swept from -0.3 to 0.3 V using a source meter (Keithley 2636A).

## 2.4 Evaluation of ammonia (NH<sub>3</sub>) gas sensing performance

The NH<sub>3</sub> gas sensing capabilities of the Au/PPy nanopeapods before and after acid treatment were examined using a chamber with gas inlet and outlet for controlled gas flow. The carrier gas (dry air) and NH<sub>3</sub> concentration were regulated by a mass flow controller (Alicat Scientific Incorporated). The total gas flow rate was kept at 200 sccm. The fabricated nanopeapod devices were placed in this sensing chamber and a constant bias of 0.15 V was applied. A stream of dry air was flowed over the devices for 8 hours to obtain a stable baseline resistance before exposure to NH<sub>3</sub> gas. Sensing evaluation was completed by first subjecting the devices to NH<sub>3</sub> gas flow for 15 min, then purging the chamber with dry air flow for 30 min. An NH<sub>3</sub> concentration between 5 and 50 ppm<sub>y</sub> was used for each cycle. During sensing, the resistance of each device was monitored and recorded as a function of time using a Lab-VIEW program. The device response for a particular  $NH_3$  concentration was defined as percentage change in resistance (R) with respect to the baseline resistance (R<sub>o</sub>), which was calculated as  $(R - R_o)/R_o \times 100$ . The sensitivity and lowest detection limit were evaluated. Sensitivity was defined as response per ppm<sub>v</sub> of the analyte gas or slope of the linear region of device operation. The lowest detection limit was determined as the minimum concentration that leads to a signal three times higher than the inherent noise of the sensor.

# 3. Results and discussion

## 3.1 Morphology of viral-templated Au NP chains

Scanning electron microscopy (SEM) was performed to observe the morphology of viraltemplated Au NPs. As shown in Figure 2 (a), following Au electroless deposition, NP chains approximately 1  $\mu$ m in length were visible within the 3  $\mu$ m gap between Pt electrodes. These highly anisotropic, nanowire-like structures were randomly arranged, forming a network. As shown in the higher magnification image in Figure 2 (b), each nanowire was composed of linearly connected Au NPs, resembling beads or peas, with an average diameter of  $35 \pm 3$  nm , which is consistent with previous reports of NP chains formed using similar assembly conditions [31]. TEM images that depict the size of the Au NPs before electroless deposition are shown in Supplementary Data, Figure S1. In addition, histograms of the Au NP size before and after electroless deposition are provided in Supplementary Data, Figure S2.



Figure 2. Morphology and arrangement of viral-templated Au NP chains (a) at low magnification spanning the gap between Pt working electrodes and (b) at high magnification revealing the random placement of NPs along the template and the tenuous physical connections between neighboring particles.

200 nm

## 3.2 Electropolymerization of polypyrrole (PPy)

A cyclic voltammetry (CV) curve for the selected PPy electrodeposition chemistry is shown in Figure 3. A significant current increase was observed near 0.5 V indicating pyrrole radical formation through oxidation [32]. Based on the CV result, four electrodeposition potentials above 0.5 V were explored to study the electropolymerization thickness and morphology on viral-templated Au NPs (i.e., 0.55, 0.65, 0.75 and 0.8 V vs Pt reference electrode). The morphology of the electropolymerized PPy was strongly dependent on applied potential. Using an electrodeposition potential of 0.55 V, nearly conformal deposition thickness was dependent on the local electrical connection between neighboring NPs. Gaps between Au NPs hindered deposition, either inhibiting deposition completely or slowing deposition until PPy growth overcame the spatial separation. Electropolymerization potentials greater than 0.55 V resulted in non-conformal growth in which PPy film spanned several Au NP chains and larger circular features, unrelated to the viral-templated material, were observed as in Figure 5.



Figure 3. Cyclic voltammetry (CV) profile of PPy electropolymerization on Pt microelectrode at a scan rate of 20 mV s<sup>-1</sup>



Figure 4. Morphology of Au/PPy nanopeapods formed using a PPy electrodeposition potential of 0.55 V for 160 s. PPy deposition was conformal to Au NP chains.



Figure 5. Morphology of Au/PPy nanopeapods formed using a PPy electrodeposition potential of 0.65 V for 160 s. (a) Large PPy features unassociated with the Au NPs were observed spanning the gap between electrodes. (b) Film-like morphology was observed between chains of viral-templated NPs.

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Because conformal deposition was desired, a polymerization potential of 0.55 V was selected for further experiments. The duration of electrodeposition was varied from 20 to 200 s. As shown in Figure 6, PPy shell thickness along the length of the nanopeapods increased at larger deposition times from  $7.7 \pm 2.6$  nm at 20 s to  $17.7 \pm 3.5$  nm at 200 s. The step change in PPy thickness observed between 60 s and 80 s may be caused by increased working electrode conductivity as PPy filled gaps between Au NPs. For all electropolymerization times, the PPy film deposition was conformal to the linearly arranged Au NPs. The morphology of Au/PPy nanopeapods fabricated with 20 s and 160 s electropolymerization is presented in Figure 7 (a) and (b), respectively.



Figure 6. Effect of PPy electrodeposition time on average shell thickness with associated charge.



Figure 7. Morphology and arrangement of viral-templated Au/PPy nanopeapods with electrodeposition time of (a) 20 s and (b) 160 s. Insets: high magnification images showing Au NPs encapsulated in PPy shells, scale bars are both 200 nm.

# 3.3 Electrical characteristics of Au NP chains and Au/PPy nanopeapods

The electrical characteristics of the viral-templated devices were studied using two-terminal I-V measurements. Prior to PPy deposition, the devices, composed only of Au NP chains, displayed one of two electrical behaviors within the measured potential range. The majority of the devices were Ohmic resistors, while the remaining fraction (22%) displayed non-linear behavior. Representative curves for non-linear and linear Au NP devices are shown in Figures 8 and 9, respectively. For non-linear devices, a forward-bias turn-on voltage larger than 0.3 V was observed. For Ohmic devices, the measured resistances ranged over several orders of magnitude (~ $10^4-10^{10} \Omega$ ), as shown in Figure 10, with a median value near 5.0 ×  $10^5 \Omega$ .

The electrical transport within Au NP assemblies is governed by the arrangement of nanoscale building blocks within the ensemble and typically follows a tunneling or activated hopping conduction model [33, 34]. NP size and spacing, as well as ligands or other molecules

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located within the conduction pathway directly influence electrical transport [35-39]. The viraltemplated Au NP chains are a complex, multi-component system composed of Au NPs, citrate ligands, and viruses (i.e. DNA, proteins). In this stochastically-arranged system, the NP size and spacing varied, in addition to the molecules between the NPs. The large resistance distribution of the devices composed only of Au NP chains was directly ascribed to these variations [31]. Furthermore, a multiplicity of electrical current paths were possible, each having a different energy barrier for conduction: NP to NP, NP to ligand to NP, NP to ligand to virus to NP, NP to virus to ligand to NP, and so on. Within the  $\pm 0.3$  V measured voltage range, Ohmic devices were believed to have electrical pathways with lower energy barriers for tunneling or hopping conduction than non-Ohmic devices. Moreover, the observed asymmetric or rectifying conduction behavior (comparatively large current flow in reverse bias versus forward bias) was attributed to material asymmetry (i.e. size, spacing, or composition) within the conduction path. Similar rectifying behavior has been observed in simple bilayers of gold NPs functionalized with two different ligands [40], as well as more complicated complexes of DNA and gold NPs [41].

Characteristic I-V plots for Au/PPy nanopeapods fabricated from Au NP chains with nonlinear and linear operation are shown in Figures 8 and 9, respectively. Following nanopeapod formation via PPy deposition (0.55 V, 160 s), all devices exhibited Ohmic behavior. In the devices fabricated from non-Ohmic Au NP chains, PPy deposition eliminated the small forward turn-on voltage and increased the overall current flow by filling gaps or strengthening tenuous electrical connections between Au NPs with conductive polymer, thus reducing barriers related to electrical transport (see schematic in Supplementary Data, Figure S3). Furthermore, as demonstrated in Figure 10, PPy deposition shifted the range of the resistance distribution of the devices fabricated from Ohmic Au NP chains to lower values ( $\sim 10^3 - 10^7 \Omega$ ) and slightly decreased the median device resistance to  $4.3 \times 10^5 \Omega$ . The observed resistance reduction was likely associated with increased connectivity between neighboring Au NPs due to PPy electropolymerization, as well as increased cross-sectional area with the formation of nanopeapods (see schematic in Supplementary Data, Figure S3).



Figure 8. Representative I-V curves for non-Ohmic, viral-templated Au NPs before and after PPy electrodeposition.



Figure 9. Representative I-V curves for Ohmic viral-templated Au NPs before and after PPy electrodeposition, in addition to HCl-treated Au/PPy nanopeapods.

A subset of the nanopeapods fabricated from Ohmic Au NP chains were briefly treated with HCl. Oxidation levels associated with p-type doping within PPy can be controlled both electrochemically and chemically. Here, HCl-treatment was used as a chemically-driven secondary doping approach to modify the oxidation level and thus the electrical behavior of the PPy nanopeapod shell post-electrodeposition. The resistance distribution of these PPy/Au nanopeapod devices is found in Figure 10. The HCl-treated devices continued to display linear behavior, as in Figure 9, however the median resistance increased by almost 2-fold. Generally, the treatment of PPy with protonic acids such as HCl increases oxidation (see e.g. recent review

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[42]), increasing doping levels and reducing electrical resistance. The conductivity increases because energy states are introduced within the bandgap due to polymer cation or polaron formation. As oxidation proceeds, doping continues to increase and resistance drops as localized cations interact to create bipolaron states farther from the band edge which eventually overlap, forming bipolaron bands. At very high oxidation levels, *overoxidation* occurs resulting in partial loss of  $\pi$ -bond conjugation, lower doping, and reduced overall polymer conductivity [43-45]. The resistance increase (rather than resistance decrease) observed for the hybrid nanopeapods suggested that the PPy shell was overoxidized by the acid treatment [43-45].



Figure 10. Resistance distribution of Ohmic, viral-templated Au NPs before and after PPy electrodeposition, as well as following HCl-treatment.

## 3.4 Ammonia (NH<sub>3</sub>) gas sensing

The chemiresistive behavior of the viral-templated materials was evaluated using NH<sub>3</sub> concentrations ranging from 5 to 50 ppm<sub>v</sub>. Representative real-time sensing responses for Au/PPy nanopeapod devices assembled with non-Ohmic and Ohmic Au NP chains, as well as HCl-dipped Ohmic Au NP chains are shown in Figure 11. The device resistance increased upon exposure to

 $NH_3$  gas and the magnitude of the response was larger for greater gas concentrations. The device resistance decreased throughout the dry air purge, exhibiting partial recovery for each  $NH_3$ exposure. While viral-templated Au NPs exhibited a small response to NH<sub>3</sub> (Supplementary Data, Figure S4), the observed sensitivity of the nanopeapods was primarily attributable to interactions with the PPy semiconductor shell. Exposure of PPy to NH3 can yield both reversible and *irreversible* changes in resistance. Adsorbed NH<sub>3</sub> molecules can act as electron donors, reducing the hole concentration through compensation, and *reversibly* de-doping (or increasing the resistance of) the polymer [46, 47]. Alternatively, nucleophilic  $NH_3$  molecules can attack the PPy carbon backbone, reducing polymer conjugation length and *irreversibly* increasing resistance [46, 48]. Typically, the most significant irreversible resistance changes occur after lengthy  $NH_3$ exposures, interaction with high  $NH_3$  concentrations, or under humid conditions [47]. The partial resistance recovery of the hybrid nanopeapods suggests that during NH<sub>3</sub> exposure, a combination of reversible and irreversible reactions occur. Similar mixed behavior has been observed for PPy by several researchers [49-54] and, in general, is a common challenge for conductive polymerbased  $NH_3$  sensors [42, 55]. Although further studies are needed to fully understand the origin of the irreversible resistance change within this material system, the use of PPy layers with large conjugation lengths and low disorder may minimize this effect [47].

For  $NH_3$  concentrations of 10 ppm<sub>v</sub> or less, the average sensitivity of the devices based on non-Ohmic Au NP chains was about 2.5 times the sensitivity of devices fabricated with Ohmic Au NP chains. Moreover, the lowest limit of detection of the non-Ohmic devices (0.004 ppm) was 1.75 times smaller than that of the Ohmic devices (0.007 ppm). As mentioned previously, the non-Ohmic Au NP chains were believed to have higher energy barriers related to electrical transport via tunneling or activated hopping conduction than Ohmic Au NP chains. These barriers were significantly reduced by PPy deposition, as evidenced by the removal of the forward bias turn-on voltage and the overall increased current flow. Thus, the conductive polymer shell played a more sizable role in the electrical transport of the non-Ohmic devices than the Ohmic devices (see Supplementary Data, Figure S3). For this reason, in the non-Ohmic devices, de-doping of the PPy shell through NH<sub>3</sub> adsorption resulted in a larger percentage increase in resistance and overall greater sensitivity. The average sensitivity of the HCl-treated nanopeapod devices fabricated with Ohmic Au nanowires was more than 4-fold that of the untreated devices and the calculated lowest limit of detection (0.005 ppm) was reduced by 28%. The notable enhancement in sensitivity was ascribed to the increased Debye length of the acid-treated PPy shell. The Debye length or screening length, which is inversely proportional to the square root of the doping concentration, is the distance over which the adsorption of a reducing gas molecule such as NH<sub>3</sub>

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depletes the carrier concentration (see Supplementary Data, Figure S5). In nanoscale materials, the Debye length is comparable to the dimensions of the conduction pathway such that charge screening can have a significant impact on material resistance. The more lightly doped and more resistive HCl-treated materials were believed to have longer screening lengths which resulted in larger resistance changes and, thus, larger gas sensing responses. For all devices, saturation resistances were not attained within the NH<sub>3</sub> exposure interval, therefore the response times were determined to be greater than 15 min and recovery times could not be measured.



Figure 11. Room temperature, real-time sensing responses are shown for viral-templated Au/PPy nanopeapods assembled from (a) non-Ohmic and (b) Ohmic Au NP chains, in addition to (c) HCl-treated nanopeapods.

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Although the response of the HCl-treated nanopeapod devices was lower than some sensors composed of electropolymerized PPy nanowires 50 nm in diameter (20% response near 10 ppm<sub>v</sub> NH<sub>3</sub>) [56], it was comparable or higher than a number of other PPy-based nanowire devices. Specifically, PPy nanowires electrodeposited on a sacrificial nickel nanowire template displayed a sensitivity of only 0.314% ppm<sub>v</sub><sup>-1</sup> in the 1-10 ppm<sub>v</sub> concentration range [54]; high aspect ratio, chemically oxidized PPy particles produced about a 4% response at 50 ppm<sub>v</sub> [57]; and individual, 300 nm diameter PPy nanowires achieved a 6% response at almost 40 ppm<sub>v</sub> [58]. Moreover, the calculated average lowest detection limit for the HCl-treated nanopeapods (0.005 ppm<sub>v</sub>) was significantly lower than the 0.4 and 40 ppm<sub>v</sub> NH<sub>3</sub> measured by Kim et al. [54] and Hernandez et al. [58], respectively.

The noteworthy sensing performance of the PPy/Au nanopeapods may be credited to the low thickness of the PPy shell along the length of the nanopeapods and/or the presence of Au/PPy interfaces throughout the device. The average thickness of the electropolymerized PPy along the length of the nanopeapods was 17.4 nm. The Debye length in this thin coating was likely a considerable fraction of the total PPy thickness, enabling a correspondingly large modification of material resistivity and device resistance with NH<sub>3</sub>. Furthermore, the incorporation of Au NPs within the backbone of the gas sensor may have contributed to enhanced sensing performance through catalytic effects or localized free carrier depletion due to nanoscale Au/PPy Schottky junctions. Indeed, increased NH<sub>3</sub> sensing response has been reported for a number of hybrid Au NP-conductive polymer materials including nanocomposites of chemically-polymerized PPy and Au NPs [59]; layers of PANI NPs loaded with smaller Au NPs via an osmosis-based method [60]; and Au/PANI nanocomposite fibers [61].

# 4. Conclusion

The synthesis of inorganic/organic hybrid Au/PPy nanopeapods has been demonstrated using a M13 filamentous virus. A genetically modified bacteriophage was used to assemble linear chains of Au NPs on its pVIII major coat proteins. These NPs were subsequently coated with a PPy shell using electropolymerization. Tuning of electropolymerization conditions was used to control PPy shell morphology and thickness. NH<sub>3</sub> chemiresistors fabricated from the viral-templated nanopeapods displayed a blend of reversible and irreversible chemiresistive activity. Sensing performance comparable to or better than many PPy-based nanowire devices was observed. The enhanced device performance has attributed to both the ultra-thin PPy layer and the potentially catalytic effects of the Au NPs. This bio-assisted assembly platform for nanopeapods can be used

to fabricate nanostructures with a variety of "shell" materials for additional chemiresistive applications.

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