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One-pot fabrication of uniform polypyrrole/Au nanocomposites and investigation for gas sensing

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ABSTRACT

A facile one-pot strategy is developed to fabricate polypyrrole (PPy)/Au nanocomposites, in which Au nanoparticles with an average size of ca. 4.2 nm are uniformly dispersed on PPy. The morphology, structure, and composition of the products were characterized by transmission electronic microscopy, X-ray powder diffraction, X-ray photoelectron spectroscopy and thermogravimetric analysis. Lysine plays a crucial role in the formation of uniform PPy/Au nanocomposites. Importantly, the PPy/Au nanocomposites have demonstrated great potential for detecting ammonia gas at room temperature, showing enhanced sensor performances in comparison to pure PPy as a result of the funtionalization of Au nanoparticles on PPy. The possible sensing mechanism is also discussed.

1. Introduction

Organic–inorganic nanocomposites are receiving growing research interests in recent years. Their unusual synergic activity that is unavailable from their single components can provide novel or enhanced functionalities for various applications like chemical sensors, electrocatalysts, magnetics and optics [1–5]. In particular, composite nanomaterials composed of conducting polymers such as polypyrrole (PPy), polyaniline (PANi), and polythiophene (PTh) and noble metals (Ag, Au, Pt, etc.) have attracted even more attention by virtue of combining their unique features such as high conductivity and environmental stability of conducting polymers [1–3,6] and electronic, optical and catalytic activities of noble metals [7–9]. Such nanocomposites are an advanced system rather than a simple mixture, because the individual components can be intimately hybridized on a molecule level with strong electronic interaction between each other, thus showing enhanced physical–chemical properties [1,2].

To date, various strategies including block copolymers assisted synthesis [10,11], interface polymerization [12], ionic liquid [13], surfactant-mediated approach [14], hydrothermal method [15], and direct synthesis using aniline or pyrrole and aqueous $HAuCl_4$ solution [16–18] have been developed to fabricate nanocomposites. In view of the above-mentioned works, it is noted that noble metals@conducting polymers with a typical core–shell structure are most frequently synthesized, probably because the polymer shells are useful in protecting metal nanoparticles from aggregation [19] or tuning Raman scattering properties [20] of the metal cores for novel applications at the nanoscale. However, for a better application such as catalyst or chemical sensor, it is reasonable that the noble metals should be directly exposed to the reactants to fulfill their catalytic activity, since core–shell nanoparticles may decrease or lose its catalytic function due to envelopment by the polymer shells. Very recently, Pt nanoparticles have been supported on PPy nanowires [21] and PANi nanofibers [22], which are highly attractive for fuel cell applications. In addition, a uniform dispersion of noble metals on the support is also crucial for improving their performance [5,22–24], as it can efficiently enhance the active contact area between noble metals and support and reactants. The uniform loading of small Au nanoparticles on various metal oxide supports have realized by using lysine as both the linker and capper agents by virtue of their amino groups [25–28], which could absorb on the surface of Au nanoparticles to hinder their growth into large particles.

In this contribution, we report a facile one-pot approach for the fabrication of PPy/Au nanocomposites. This procedure allows us to in situ decorate PPy particles with highly uniform dispersion of Au nanoparticles with a small size of ca. 4.2 nm. Control experiments

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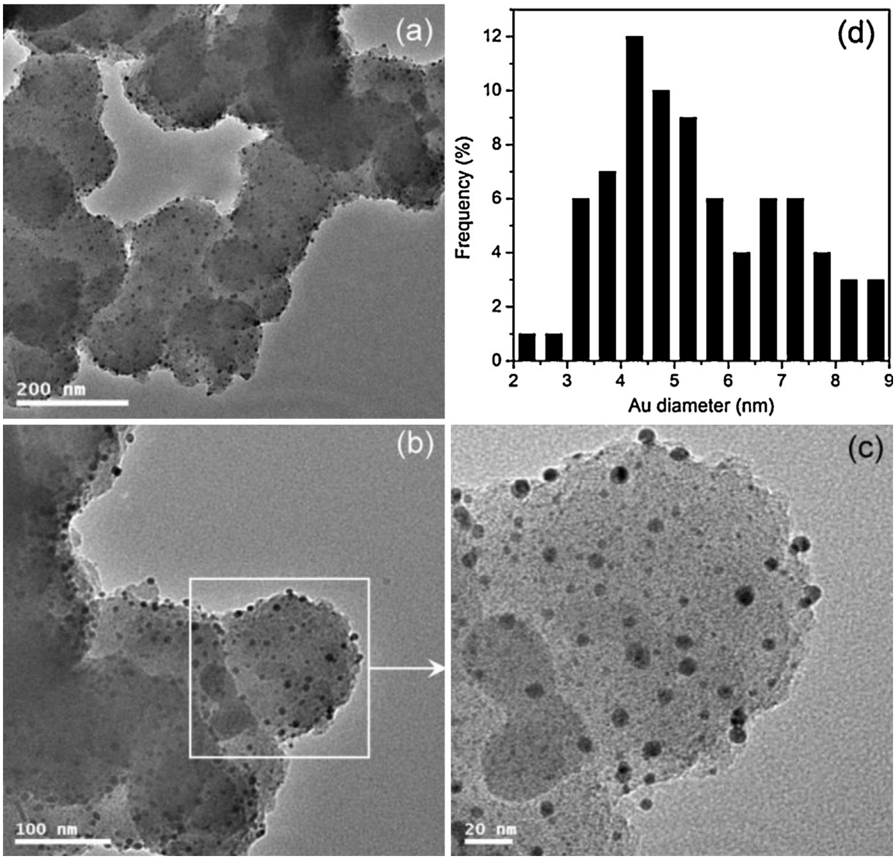

Fig. 1. (a–c) TEM images of the prepared PPy/Au nanocomposites and (d) size distribution of Au nanoparticles evaluated from panel (c).

demonstrate that lysine plays a crucial role for the formation of desired product with uniformly dispersed Au nanoparticles. To demonstrate its application, we have investigated the nanocomposites for gas sensing using NH_3 as a probe molecule. Preliminary results show that the PPy/Au nanocomposites demonstrate much better response than pristine PPy.

2. Experimental

2.1. Chemicals

All the chemicals such as anhydrous ferric chloride ($FeCl_3$) $NaBH_4$, lysine, $HAuCl_4{\cdot}4H_2O$ and absolute ethanol are of analytical grade and used as received. Pyrrole monomer was distilled under reduced pressure prior to use. Distilled water was used throughout the experiments.

2.2. Synthesis of PPy/Au nanocomposites

In a typical synthesis, 0.05 mL of pyrrole monomer was injected into 10 mL of H_2O, followed by the addition of anhydrous $FeCl_3$ (molar ratio of $FeCl_3$: pyrrole = 2.4:1) [29] to initiate the polymerization of pyrrole. After reacting for 3 h, 3 mL of 0.01 M lysine and 3 mL of 0.01 M $HAuCl_4$ aqueous solution were added, followed by fast addition of 5 mL of 0.01 M $NaBH_4$ (excess) to ensure complete reduction of Au. The reaction is continued for another 0.5 h under stirring. The product was centrifuged and washed with water and ethanol for 4 times, and then dried at 60 °C overnight.

2.3. Characterizations and gas sensing test

The products were characterized by means of powder X-ray diffraction (XRD, Rigaku D/max-2500, Cu Kα, $\lambda = 1.5418$ Å), transmission electron microscope (TEM, Philips FEI Tecnai 20ST, 200 kV), X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD spectrometer, Al Kα X-ray monochromator) and thermogravimetric analysis (TGA). Gas sensing tests were performed on a commercial HW-30A Gas Sensing Measurement System (HanWei Electronics Co., Ltd., Henan, China) at room temperature (21 °C) at a relative humidity of 36%. Prior to sensing test the gas sensor has been dried at 50 °C and subsequently aged on HW-30A for two days at room temperature. Ammonia gas (high-purity 99.999%) was injected into the testing chamber on HW-30A by a syringe. The sensor response is defined as the ratio of R_g/R_a, where R_g and R_a are the electrical resistance of the sensor in test gas and in air, respectively. The sensor resistance was read directly from the computer linked to HW-30A. Details of the sensor fabrication, photograph, schematic configuration and gas sensing test principle (Fig. S1) of HW-30A can be seen in our previous publications [30,31].

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2013.06.063.

3. Results and discussion

3.1. Characterization

The morphology of the PPy/Au nanocomposites has been observed by TEM. Fig. 1a–c shows the representative TEM images. It is observed that a large amount of Au nanoparticles with a uniform size and dispersion are attached on PPy surface. Fig. 1d displays the size distribution histogram of Au nanoparticles estimated from

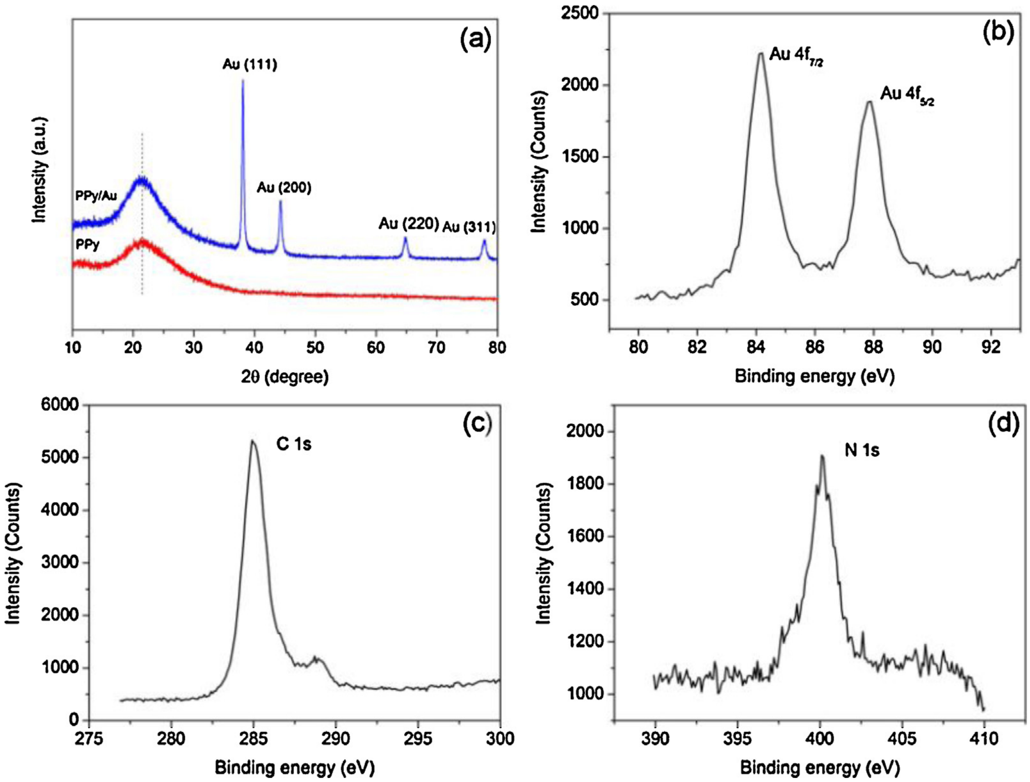

Fig. 2. (a) XRD patterns of PPy/Au nanocomposites and pure PPy and XPS spectra of PPy/Au hybrid materials: (b) Au 4f, (c) C 1c and (d) N 1s.

Fig. 1c, showing that these Au nanoparticles have a narrow size distribution in the range of 2.1–8.8 nm, with an average size of ca. 4.2 nm. To further confirm the existence of Au in the nanocomposites, XRD characterization has been performed. The XRD pattern is displayed in Fig. 2a, showing five diffraction peaks. The weak broad diffraction peak around 15–30° is ascribed to interchain spacing of PPy [30]. Four additional diffraction peaks at 38.3°, 44.6°, 64.7°, and 77.5° are ascribed to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of face-centered cubic (fcc) Au.

To further confirm the attachment of Au nanoparticles on PPy, the surface chemical composition of the prepared PPy/Au nanocomposites has been analyzed by XPS. Fig. 2b–d exhibits the high resolution spectra of Au 4f, C 1s and N 1s. The doublet with binding energy at 83.8 and 87.5 eV in Fig. 2b corresponds to metallic Au, while Fig. 2c and d shows significant signals for C 1s and N 1s, which can be ascribed to the C and N atoms in PPy. The content of Au in the nanocomposites is estimated to be around 26.7 wt.% according to the XPS analysis. The thermal stability of the PPy/Au materials has been examined by TGA. From Fig. 3, it can be observed that the PPy/Au hybrids exhibits a total weight loss of 87.3% in the temperature range of 30–523 °C, including the evaporation of adsorbed water before 150 °C and thermal decomposition of PPy matrix after 150 °C. Interestingly, the weight loss of the hybrids finally stops at 523 °C, which is a bit higher than that (510 °C) of pure PPy [30], implying that the thermal stability of PPy is enhanced due to hybridization of Au nanoparticles.

In the synthesis process, lysine has been used as the capping agent for Au [26–28,32–34]. To reveal the effect of lysine on the formation of uniform PPy/Au nanocomposites, a control experiment has been performed without using lysine. Fig. 4a–c shows the TEM image of PPy/Au materials prepared in the absence of lysine. The Au nanoparticles are observed to have a relatively large size. The size distribution histogram in Fig. 4d reveals a wide size range of 5–45 nm. Compared with Fig. 1a–c, the Au nanoparticles in Fig. 4a–c have a much larger size. Based on the above discussion, we can conclude that lysine plays an important role in the formation of small size Au nanoparticles in PPy/Au nanocomposites. This is probably due to the capping of lysine to Au nucleus initially formed on reduction. Lysine moleucles have rich amino groups, which could adsorb onto Au surface and thus effectively hinders their further growth into large particles.

3.2. *Gas sensing performance*

Conducting polymers have been reported to be good candidate for chemical sensors for a long time [3,4,35–40], because it can be operated at low or room temperature for gas detection, which is significantly superior to that (usually 200–400 °C) of metal oxides such as SnO_2 and ZnO. However, the sensing performance of conducting polymers is usually low. The performance can be improved by forming organic–inorganic composites. Noble metals such as Au, due to its exceptionally catalytic activity and electronic properties,

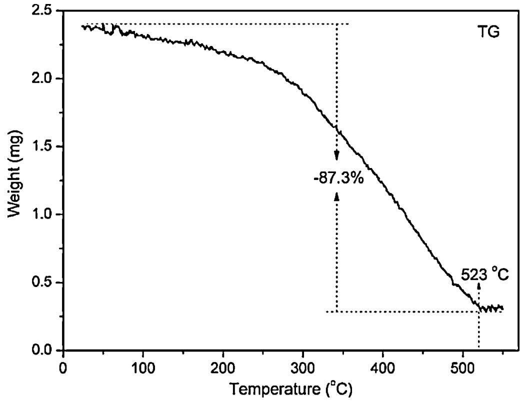

Fig. 3. TGA of PPy/Au nanocomposites.

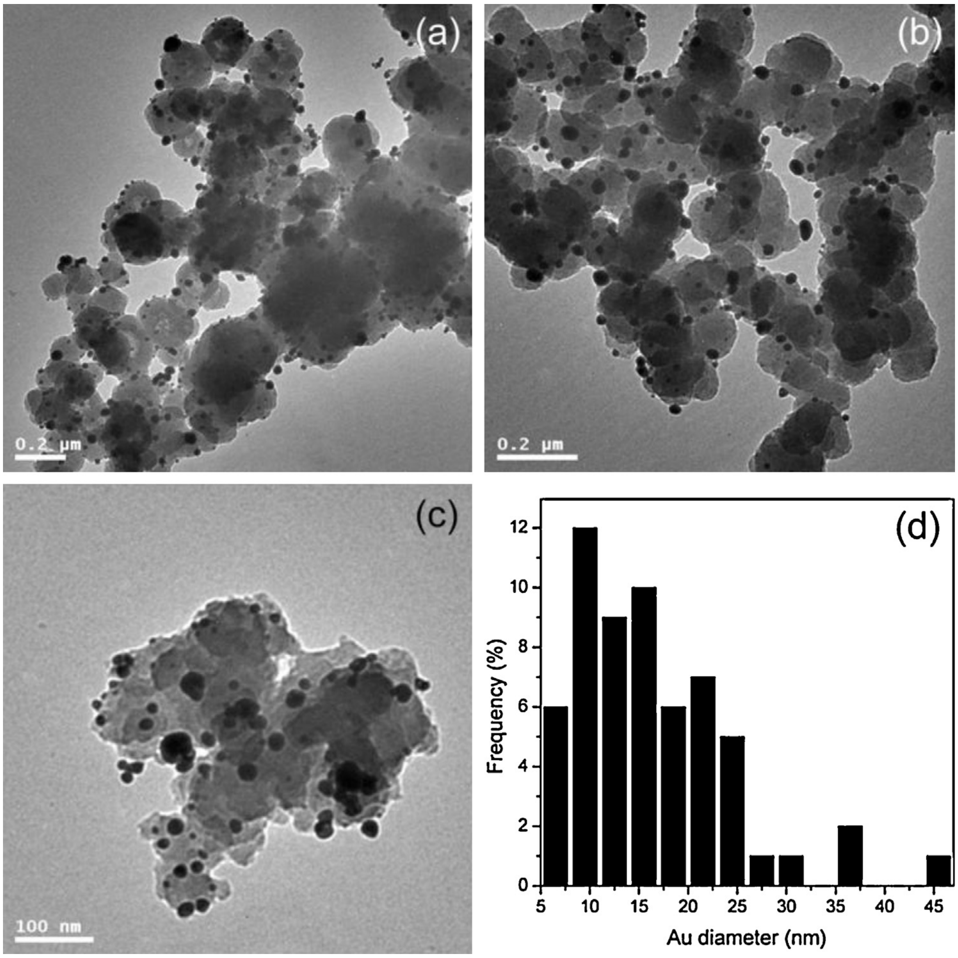

Fig. 4. (a–c) TEM images of PPy/Au materials prepared without using lysine and (d) size distribution of Au nanoparticles evaluated from panel (c).

have been often used as additives to sensitize the support materials [37,41,42].

The sensing performance of the as-prepared PPy/Au nanocomposites has been preliminarily evaluated using ammonia gas as the probe molecule. Fig. 5a and b shows the dynamic transient resistance of pure PPy and PPy/Au materials on exposure to 100 and 300 ppm ammonia gas. For both concentrations, it is observed that the PPy/Au features much higher response than that of pure PPy, although their response speed shows not very large difference. Several other gases are also tested to investigate the selectivity of the PPy/Au nanocomposites. Their corresponding sensor responses are compared in Fig. 5c, indicating that PPy/Au possesses a higher response and good selectivity to ammonia. Furthermore, it is observed that the sensor response to 300 ppm ammonia is higher than that to 100 ppm ammonia, indicating that a higher gas concentration would cause more electrons transferring in the sensing reactions and hence lager change in sensor resistance.

Humidity might have an influence on gas sensing performances. The gas sensing result at a relative humidity of 51% showed that the sensor response to 300 ppm ammonia severely deteriorate. As shown in Fig. 6, the response amplitude of PPy/Au sensor is much lower compared with that at a relative humidity of 36%. The sensor response also decreased with higher relative humidity of 51%, as shown in the inset of Fig. 6. Although the detailed reason is still not clear, this phenomenon is probably due to the interference and adsorption of water molecules onto the sensing layer. Such a performance degradation of the PPy/Au sensor might not be suitable for practical application, especially in an environment with a high relative humidity. Further efforts are needed to tackle this problem.

The electronic conductivity of PPy conducting polymers strongly depends on their doping levels, which can be easily changed by chemical reactions with many analytes such as ammonia [37,38,43]. The chemical reactions could result in transfer of electrons from or to PPy, which causes the changes in sensor resistance. Ammonia behaves as an electron-donor and it can inject electrons to the backbone of PPy, leading to the increase of resistance of PPy sensing layer. After refreshing with air, the sensor resistance can be totally or partly recovered. The whole sensing process of PPy to ammonia can be presented by the following reactions [43,44]:

$$\mathrm{PPy}^{+} + \ddot{\mathrm{N}}\mathrm{H}_3 \rightarrow \mathrm{PPy}^{0} + \mathrm{NH}_3^{+} \quad \text{Adsorption}$$

$$\mathrm{PPy}^{0} + \mathrm{NH}_3^{+} \rightarrow \mathrm{PPy}^{+} + \mathrm{NH}_3 \quad \text{Desorption}$$

As for as-fabricated PPy/Au sensor, the enhanced sensor response should be directly related to the funtionalization of Au nanoparticles. Because when the size of Au nanoparticles is smaller than 5 nm, due to the quantum-size effect, it will become very active [7–9], and facilitates the adsorption of ammonia molecules onto PPy sensing layers in the presence of atmosphere oxygen (in our sensing test, air is used as the reference gas) [45]. On the other hand, it is known that both conducting polymers such as PPy, PANi, PTh and carbon nanotubes (CNTs) are P-type semiconductors with positive holes serving as the charge carriers [43,46–48]. In

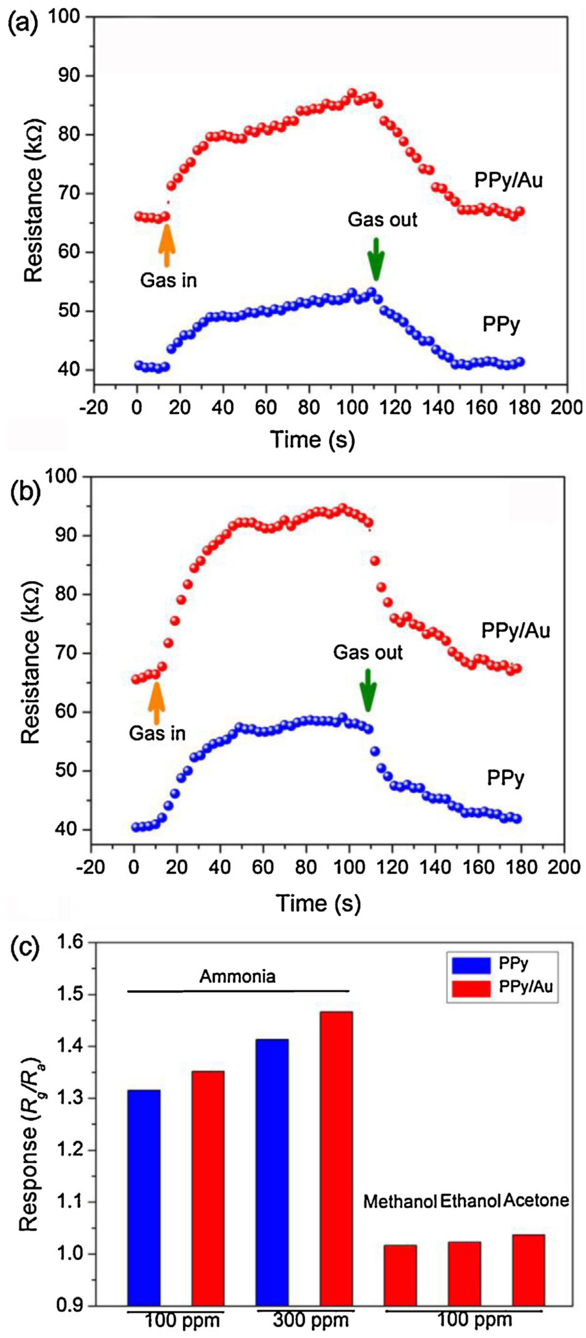

Fig. 5. Dynamic transient resistance of PPy/Au and pure PPy materials for detecting (a) 100 and (b) 300 ppm ammonia gas; (c) sensitivity of PPy/Au to various gases.

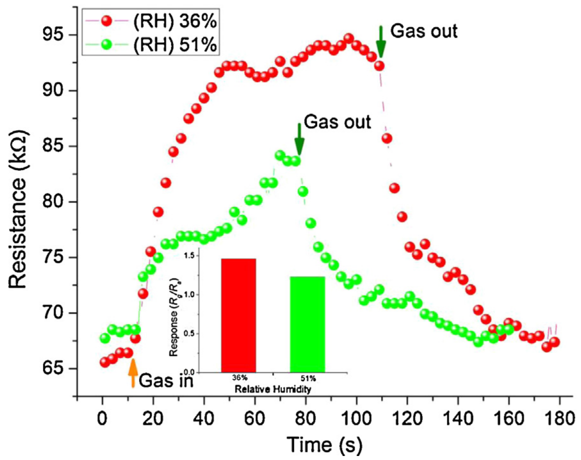

Fig. 6. Gas sensing performances of PPy/Au nanocomposite to 300 ppm ammonia at a relative humidity (RH) of 36% and 51%.

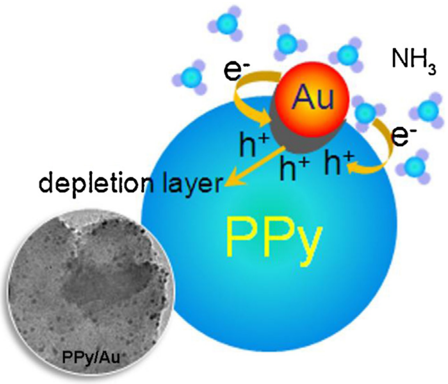

Fig. 7. Possible sensing mechanism for PPy/Au nanocomposites.

a previous work [48], Kauffman et al. showed that Au nanoparticles decorated on CNTs could increase the potential barrier at the interface by forming a "nanoSchottky". Simultaneously, a depletion layer is formed surrounding Au nanoparticles due to the consumption of positive holes as a result of electron–hole (e^-–h^+) recombination (Fig. 7), which decreases the carrier mobility through the CNTs chains. In other words, the conductance (or resistance) of the sensing layer is decreased (or increased). Considering that PPy and CNTs are analogous in their P-type conduction, a similar "nanoSchottky effect" is expected in the case of PPy/Au hybrids. This is also supported by the increased resistance (ca. 65 kΩ) of PPy/Au hybrids compared with that (ca. 40 kΩ) of pure PPy, as shown in Fig. 5a and b. And a similar result has been recently reported for CNTs after decoration by Au nanoparticles [49]. A possible sensing mechanism for the PPy/Au nanocomposites is illustrated in Fig. 7. NH_3 is usually regarded as an electron donating gas [50] or Lewis base [51], which may cause "secondary doping" of PPy by consuming the positive holes. Consequently the concentration of charge carriers in PPy is decreased, resulting in the increase of sensor resistance of the PPy/Au nanocomposites.

4. Conclusion

In summary, we present here a facile and efficient approach to fabricate a novel nanocomposites in which Au nanoparticles with a small size of ca. 4.2 nm are uniformly dispersed on PPy matrix. Control experiments reveal that lysine plays a crucial role in the successful synthesis of homogeneous PPy/Au nanocomposites. Gas sensing results demonstrate the as-prepared PPy/Au nanocomposites possess improved sensor response to ammonia compared to pure PPy. The enhanced response is ascribed to the funtionalization of Au nanoparticles on PPy, which might increase the sensing potential barrier. The synthetic procedure is also expected to be extendable to fabricate other conducting polymer/metal nanocomposites to seek novel functionalities.

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Biographies

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