# Gas permeable silver nanowire electrode for realizing vertical type sensitive gas sensor

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## ARTICLE INFO

## ABSTRACT

We successfully demonstrated a Poly (3-hexylthiophene) (P3HT) diode gas sensor with silver nanowires as a gas permeable top electrode. The silver nanowires dispersed in isopropyl alcohol (IPA) were used to form a top electrode by a simple drop-casting method. The meshes between nanowires enable gas molecules pass through the electrode and diffuse into the underlying organic sensing layer to dope or dedope the organic semiconductor. Here, the proposed sensor successfully detects ammonia down to 30 parts-per-billion (ppb), which is sensitive enough in many applications including breath ammonia monitoring as a point-of-care application.

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## 1. Introduction

In recent years, solid state gas sensors have been a focus of research for their various applications, including breath analysis for disease monitoring, detection of humidity, air quality control, industrial process control, and hazardous gases detecting [1,2]. As a result, the demand to develop reliable solid-state gas sensor with low-cost process and high sensitivity is growing. Up to now, significant progress has been achieved to improve gas sensor performance. Incorporating various nanostructures into gas sensor is one of the powerful strategies to produce highly sensitive sensors by providing a high surface to volume ratio [3–6]. High surface to volume ratio enhances the interactions between sensing layer and the target gas, thus leads to an improved sensitivity. Among various kinds of nano-structure, nanowire structure is particularly attractive because nanowires can easily form a mesh structure to facilitate the current conduction. Zhang and co-workers

demonstrated indium oxide ($In_2O_3$) nanowire devices for the detection of nitrogen dioxide ($NO_2$) down to parts-per-billion (ppb) levels [7]. Wang et al. also utilized poly-aniline nanowires to form a resistive sensor with polymer nanoframework to successfully detect 0.5 ppm ammonia [8].

When most reported nanowire-based sensors utilize nanowire to serve as the active sensing layer, in this work, we introduce a different concept to utilize the metallic nanowire to realize a sensitive gas sensor. The metallic nanowire is used as a gas permeable top electrode to cover an organic sensing layer and form a vertical diode. The electrode with nanostructure allows gas molecules to penetrate the electrode and to interact with the charges in the underlying sensing diode. Previously, vertical type gas sensors with a porous top electrode were reported to exhibit very high sensitivity. A 10-ppb detection limit to nitric dioxide is realized by using vertical silicon nanowire sensor with a porous top electrode [9]. A detection limit lower than 20 ppb to ammonia is also successfully demonstrated by using vertical organic diode with a top porous electrode [10]. When vertical type gas sensor appears to deliver highly sensitive response, a low-cost reliable process to

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fabricate the porous top electrode is still under developed. In previous reports, the porous electrode is formed by utilizing self-assemble nanospheres to serve as the hard mask during metal deposition. After metal deposition, the nanospheres are dissolved or removed by tap and the nanometer pores in metal layer are formed. The critical step is the packing of nanospheres before metal deposition. The nanosphere packing requires subtle process control.

Here, in this work, the gas permeable top electrode is formed by a one-step coating of metallic nanowires. The underlying organic sensing film does not need to have any structure and is formed by a spin coating method. In the proposed process, no lithography process is required. The proposed sensor with such an extremely simple process exhibits a detection limit lower than 30 ppb to ammonia, which is promising for future commercialization. It is also expected that, by replacing the material of the organic sensing layer, the proposed sensor can be extended to detect other kinds of gas molecules.

## 2. Experimental

The fabrication process was shown in Fig. 1. The indium tin oxide (ITO) patterned glass substrate was cleaned with $O_2$ plasma treatment after rinsed in deionized water. Then, a 200-nm-thick cross-linkable poly (4-vinyl phenol) (PVP) layer was spin-coated on ITO patterned glass substrate and annealed at 200 °C for 1 h. The PVP in active region was then removed by $O_2$ plasma etching to determine the active region as 1 mm$^2$, as shown in Fig. 1(c). Poly(3-hexylthiophene) (P3HT), a kind of p-type semiconductor, dissolved in chlorobenzene (2.5 wt%) was spin-coated and annealed at 200 °C for 10 min to form a 200-nm-thick sensing layer. Finally, the silver nanowires dispersed in isopropyl alcohol (IPA) were drop-casted on the P3HT with substrate heated at 60 °C. The silver nanowires are purchased from ECHUANG. The density of nanowires casted was controlled by the concentration of nanowires in IPA. Specifically, three concentrations (1.25 wt%, 0.625 wt%, and 0.3125 wt% of silver nanowires in IPA) are used to generate AgNWs with high, medium, and low densities. The intercrossed silver nanowires (AgNWs) act as a gas permeable top electrode and enable ammonia molecules to pass through the electrode and diffuse into P3HT sensing layer, as shown in Fig. 1(f).

To investigate the gas sensing response, the devices were mounted in a microfluid sensing chamber with electrical feed through and gas inlet/outlet. The pure nitrogen flow kept by a mass-flow controller was served as background ambience during the detection. An electrical syringe pump system was used to inject the ammonia into a tube where ammonia mixed with background nitrogen before entering the sensing chamber. The concentration of ammonia was controlled by adjusting the injection speed of the syringe pump. Keithley Source Meter (model 2400) was used to measure the current–voltage relationship of the sensor.

## 3. Results and discussion

The work function of silver nanowire is reported to be around 4.0–4.2 eV [11–13] and the highest-occupied molecular orbital (HOMO) of P3HT is about 5 eV, hence there may be a Schottky barrier between AgNW and P3HT. Accordingly, in the proposed sensor, the intertwined silver nanowires act as the cathode. Oxygen plasma treated ITO with a work function about 5 eV acts as the anode [14]. P3HT is sandwiched between ITO and AgNW to form a Schottky diode while an Ohmic contact can be obtained in the ITO/P3HT interface. The energy band diagram of the proposed sensor is shown in Fig. 2. The current as a function of applied voltage of the AgNW-covered P3HT diode is shown in Fig. 3(a). In forward bias condition, holes are injected from ITO into P3HT and are collected by AgNW electrode. In reversed bias condition, hole injection from AgNW into P3HT is limited and the current is low. The injection barrier may be due to the Schottky barrier between AgNW and P3HT [15]. The electric characteristics in Fig. 3(a) verify that silver nanowires are feasible to serve as the electrode in this work. As applying forward bias voltage, the current turns on within 1 V. The scanning electron microscope (SEM) images of the AgNW-covered P3HT
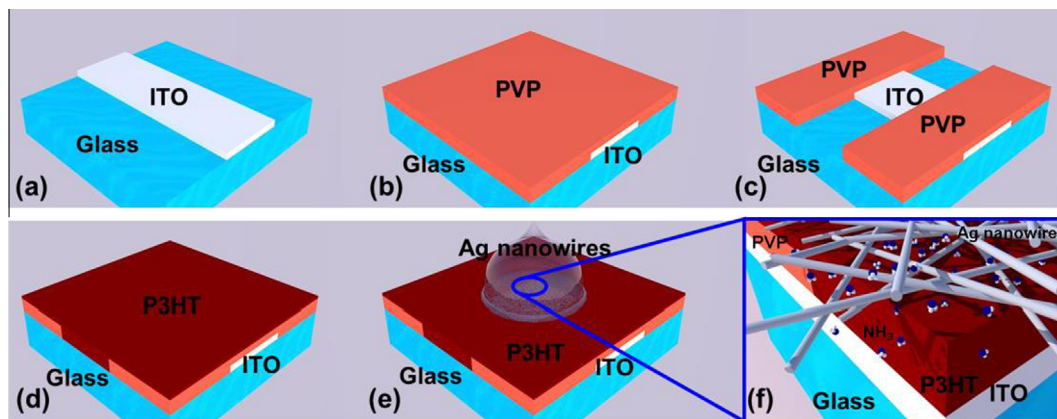


**Fig. 1.** Schematic illustration of process steps for fabricating the P3HT diode: (a) Glass substrate with patterned ITO. (b) Spin-coating PVP on substrate. (c) $O_2$ plasma etching to define active area. (d) Spin-coating P3HT. (e) Drop-casting Ag nanowires (AgNW). (f) Schematic illustration of $NH_3$ sensing.
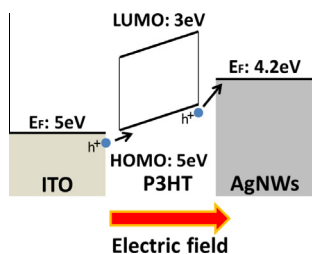
**Fig. 2.** The energy band diagram of the proposed sensor.

diode with different scaling orders are shown in Fig. 3(b) and (c). The intertwined silver nanowires cover P3HT well by drop-casting method and successfully form numerous meshes structure. These meshes play an important role to enable ammonia molecules pass through the AgNW electrode and interact with P3HT sensing layer. In recent years, silver nanowires have been widely used in solar cells and light-emitting diodes. The solution dispersed silver nanowires is a cost effective approach to form a conductive, transparent and flexible electrodes [16–19]. It was also reported that AgNWs can act as ammonia sensor when ammonia concentration is larger than 3% [20]. Here, in our work, AgNWs act as a gas permeable electrode. Also, a mesh-like vertical diode can be formed by contacting AgNWs with the underlying organic sensing layer. The concept is shown by the 2-dimensional simulated current density distribution in Fig. 4(a) [21]. Due to the large resistivity of P3HT, carriers are mostly confined within the regions covered by the top electrode. Mesh-like top electrode hence creates mesh-like vertical diode as shown in Fig. 4(a).

The mesh-like vertical diode acts like numerous connected nanometer organic diodes to react with ambient gas and thus exhibits high sensitivity. In this work, the sensor ability is demonstrated by using P3HT sensing layer to react with ammonia. According to previous reports, ammonia molecules act like acceptors to dedope P3HT material and to increase the effective resistivity of P3HT. Fig. 4(b) shows the real-time current sensing behavior of the proposed AgNW-covered P3HT diode. The current is plotted as a function of time. Blue region represents the injection of ammonia into the microfluid system with different ammonia concentrations. White regions indicate that the injected gas turns to be pure nitrogen (the background of the testing). It is clearly observed that the current density immediately drops as ammonia molecules are injected to dedope the P3HT film. When ammonia injection is interrupted, with a constant pumping flow (flow rate as 3 SLM.), the remaining ammonia concentration in the microfluid chamber decreases with time and the current density gradually recovers. To clearly observe the sensing response to ammonia with different concentrations, the current variation ratios (i.e. the ratio between the current difference, $\Delta I$, and the initial current, $I_0$) are plotted as a function of time in Fig. 4(c) when ammonia concentrations are 30 ppb, 100 ppb, and 500 ppb. The x-axis includes 300-s sensing period and 300-s recovering period. When 500 ppb ammonia is injected into the sensing system, during the first 20 s, the current variation ratio increases quickly with a steep slope. Then, from 20 s to 300 s, the increase of current variation ratio becomes slower. We can define that, as indicated in Fig. 4(b), the current exhibits two-region response after ammonia injection. The initial 20 s is the region-1 response and the duration from 100 s to 300 s is the region-2 response. To investigate the sensitivity of different sensing parameters, the region-1 slope, the region-2 slope, and the current variation ratio with a fixed 200-s sensing period are plotted as a function of ammonia concentration in Fig. 4(d). It is clearly observe that the region-1 slope and the 200-s current variation ratio are both sensitive sensing parameters. The region-2 slope, however, is insensitive to the change of ammonia concentration from 30 ppb to 500 ppb.

According to previous reports, there are many possible mechanisms to explain the interactions between gas molecules and conducting polymer materials [22]. Carrier transport in conducting polymer is due to (1) the polaron hopping inside the conjugated polymer and (2) the conduction between polymer molecules. The crystalline order, the nanostructure boundaries, the planarity of the conjugate polymer, the polymer molecule spacing, and the oxidation/reduction condition strongly influence the conductivity. When gas molecules diffuse into conducting polymer thin film, several mechanisms may occur simultaneously to affect the polymer conductivity. When detecting gas analytes, the decrease in conductivity for P3HT
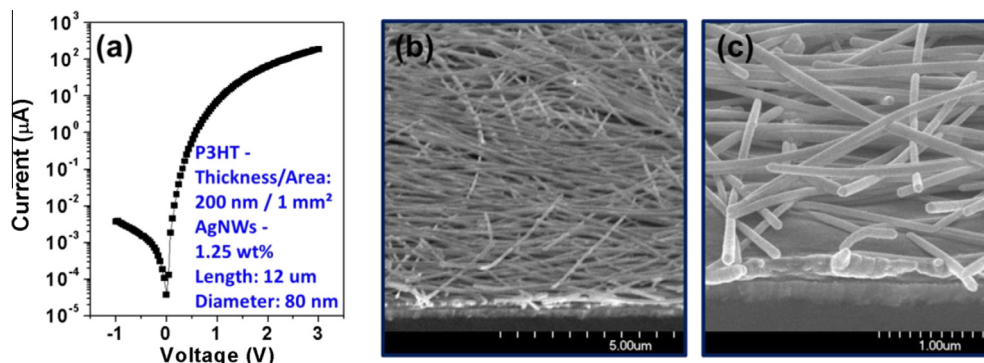


**Fig. 3.** (a) *I–V* curve of P3HT diode with Ag nanowires as a gas permeable top electrode. (b) and (c) SEM images of AgNW-covered P3HT diode with different scaling orders.
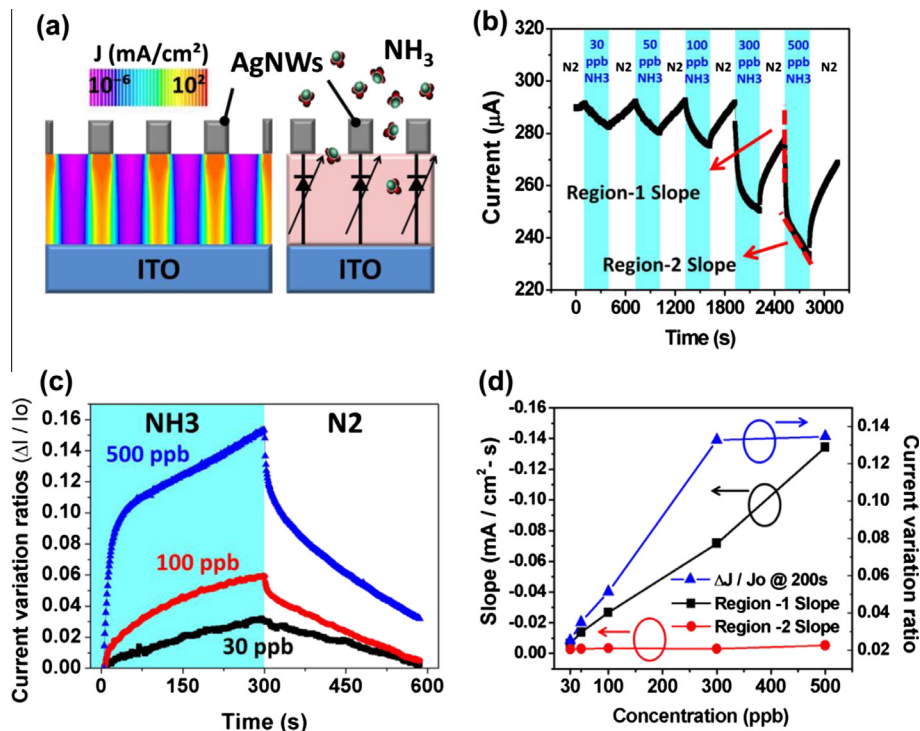
**Fig. 4.** (a) The 2-dimensional simulated current density distribution. (b) The real-time current sensing of the proposed AgNW-covered P3HT diode. Both reaction and recover periods are 300 s. (c) The current variation ratios as a function of time with 30 ppb, 100 ppb, 500 ppb ammonia. (d) The region-1 slope, the region-2 slope, and the current variation ratio with a fixed 200-s sensing period are plotted as a function of ammonia concentration.

may be due to two possible mechanisms. (1) The dissolved gas molecules enlarge the spacing between polymer molecules and hence reduce conductivity. (2) The formation of polaron between gas analyte and the oxidized P3HT molecules leads to reduction reaction in P3HT and hence reduce conductivity [23]. The first mechanism is a kind of physical absorption and is usually less of selectivity. In our prior work on VNJ P3HT diode, we found that the sensor exhibited large response (i.e. a large current drop) to ammonia and little response to acetone and ethanol [10]. Moreover, when detecting strong oxidation gas like nitric oxide, the VNJ P3HT diode shows an obvious current increase, indicating that the response mechanism is dominated by reduction–oxidation (redox) reaction. Here in this work, the reaction between AgNW-covered P3HT diode to ammonia is also explained by the redox reaction. The long pairs in ammonia molecules cause the redox reaction with the bipolarons in P3HT to gradually increase the channel resistivity [23]. Though detail mechanism requires further investigation, it is possible that the redox reaction between ammonia and P3HT is a two-steps reaction [23]. In the first step, a fast response exhibits a reaction rate proportional to the ammonia concentration. Hence, in region 1, the slope is highly dependent on ammonia concentration. The second step then occurs in region 2. The reaction rate drops to be a very low reaction rate and is almost independent of ammonia concentration. The region-1 slope is concluded as a good sensing parameter to exhibit a short response time (<20 s) and a very high sensitivity to ammonia concentration ranged from 30 ppb to 500 ppb.

In addition to the redox reaction between ammonia and P3HT, the sensing mechanism may also be related to the change of conductivity in AgNW [20], the change of contact between AgNW/P3HT [15], and the change of P3HT morphology [24–26]. We discuss these possible mechanisms as follows. The conductivities of AgNW network before and after ammonia sensing are compared in Fig. S1. No significant variation can be observed. Though AgNW network was reported to detect 3% ammonia [20], in this work, AgNW electrode does not response to ammonia in ppb regime. The change of contact properties between AgNW/P3HT may also be ignored because in the proposed sensor, carriers (holes) are injected from ITO into P3HT and collected by AgNW electrode. As shown in Fig. 2, holes arrive AgNW without surmounting potential barrier. Hence, we expect that the channel current is not significantly dependent on the contact properties between AgNW and P3HT. Finally, the morphologies of P3HT before and after ammonia sensing are compared by the AFM images as shown in Fig. S2. No obvious morphology change can be observed. We then propose that the primary sensing mechanism is the redox reaction between ammonia and P3HT.

The very high sensitivity in our work is due to the gas permeable property in top electrode, the AgNW electrode. To further demonstrate the advantage of metallic nanowire electrode, we discuss the difference between AgNW electrode and graphene electrode in gas sensing applications. It is known that, in addition to metallic nanowires, graphene is also considered as a promising electrode to exhibit high conductivity and high transparency. Recently, Yi
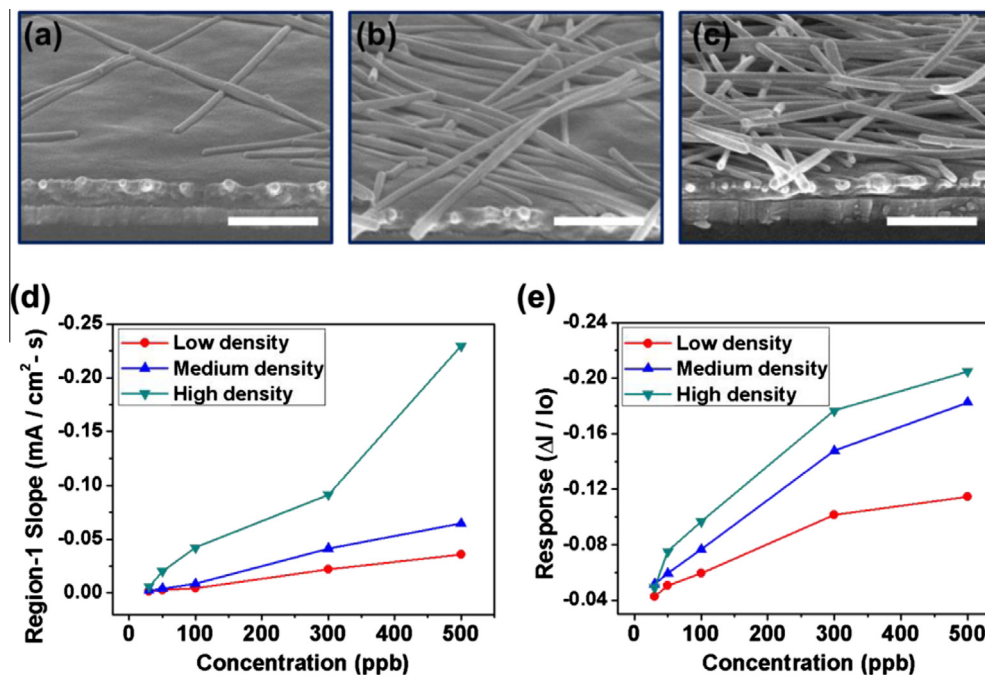
**Fig. 5.** (a)–(c) The SEM images of the proposed AgNW-covered P3HT diodes with low-density, medium-density, and high-density AgNWs, respectively. Scale bar represents 1 μm. (d) The region-1 slope as a function of ammonia concentration. (e) The 200-s current variation ratio as a function of ammonia concentration.

et al. used transfer process to coat graphene on vertically aligned ZnO nanorods to detect ethanol at 300 °C [27]. The detection limit is in parts-per-million (ppm) regime. Though the graphene sheet acts as the top electrode, it is not gas permeable. Ahn et al. verify that graphene exhibits gas barrier property. Reduced graphene oxide (rGO) can even be used to cover silver nanowire to prevent the thermal oxidation of nanowires [28]. Here in our work, the AgNW-covered P3HT diode exhibits a detection limit down to ppb regime. It is believed that, among various kinds of vertical gas sensors, the key to obtain very high sensitivity is the gas permeable property in the top electrode.

We then verified the robustness of the proposed sensor. As shown in Fig. S3, the sensor delivers similar and reversible sensing response to 5-times sensing periods with fixed ammonia concentration (500 ppb). For applications such as breath analyzing, the proposed sensor is expected to be used as a disposable sensor. Hence, the reliable response in 5-times sensing period is acceptable. In future, we can further improve the sensor air-stability by introducing air-stable organic active layer [29].

Finally, the influence of silver nanowires density is investigated. The SEM images of the proposed AgNW-covered P3HT diodes with low-density, medium-density, and high-density AgNWs as top electrodes are shown in Fig. 5(a)–(c), respectively. With electrode formed by three different AgNW densities, the proposed P3HT diodes turn on within 1 V and the electric characteristics are good enough for gas sensing. The sensing responses are compared by plotting the region-1 slope and the 200-s current variation ratio as a function of ammonia concentration in Fig. 5(d) and (e), respectively. We clearly observe that, in both Fig. 5(d) and (e), nanowire density is proportional to the sensitivity. These results reveal that increasing nanowire density can improve the surface coverage ratio to create more mesh-like diodes. As a result, within the 1 mm² active area, the increased mesh-like diodes react with gas molecules to deliver an enhanced sensitivity. Such a nanowire-density-enhanced reaction can be further explained by an increase of surface-to-volume ratio. As shown by the simulated current density distribution in Fig. 4(a), due to the low conductivity of P3HT, high current density (marked by red[1] color) is observed only in the regions covered by the top electrode. Since the response of the sensor is related to the current variation, the most sensitive sensing regions are the high-current–density regions (marked by red in Fig. 4(a)). If one considers these high-current–density regions as "sensing surfaces", increasing nanowire density leads to an increase of "surface to volume" ratio as well as the sensing response.

## 4. Conclusion

In this work, we successfully demonstrate a very sensitive gas sensor by using silver nanowires (AgNW) as a gas permeable top electrode. With a simple one-step drop-casting process, AgNW covers P3HT to form a vertical polymer diode. The mesh-like structure in AgNW enables gas molecules to diffuse into the underlying P3HT sensing

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[1] For interpretation of color in Fig. 4, the reader is referred to the web version of this article.

layer. When detecting ammonia, a fast current drop in the proposed diode is observed and is due to the redox reaction between ammonia and P3HT. The mesh-like top electrode induces mesh-like vertical current paths to react with ammonia and hence delivers a detection limit lower than 30 ppb. Increasing the AgNW density improves the sensing response. Such a very sensitive ammonia sensor can be used to detect breath ammonia for point-of-care application. The very simple structure with low-cost solution process facilitates future development of a diode array with different sensing materials as a portable breath analyzer.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2014.08.012.

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