NH₃ sensing with self-assembled ZnO-nanowire μHP sensors in isothermal and temperature-pulsed mode


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Abstract

Dielectrophoretic alignment is found to be a simple and efficient method to deposit the solution prepared ZnO nanowires onto micro hot plate substrates. Due to the strong surface effects, positive temperature coefficient for resistance was encountered with ZnO nanowires in the high temperature range (>250°C). The response to ammonia (NH₃) was evaluated in isothermal and temperature-pulsed operation mode; the relative higher response observed in the latter case demonstrates that the use of this methodology is a good strategy to improve the performance of metal oxide sensors based on nanomaterials. Here, we evaluate the response to NH₃ and qualitatively describe the sensing mechanism in temperature-pulsed mode, highlighting the main differences compared to the standard isothermal methodology.

Key words: ZnO; nanowire; micro hot plate; ammonia; gas sensor; temperature-pulsed
1. Introduction

Silicon on insulator (SOI) [1] technology offers the possibility of fabricating mono-crystalline silicon electronics with good thermal isolation. Micro hot plates (μHPs) based on standard complementary metal oxide semiconductor (CMOS) processing technology [2] using tungsten (W) metallization [3] and/or the SOI layer for the micro-heater are an ideal choice of substrates for resistive metal oxides (MOX) gas sensors. In addition to the very low power consumption (tens of mW in DC operation) and fast thermal response (tens of ms) [3], they can be cost effectively manufactured in high volume and integrated with other functional electronics [4, 5].

On top of the μHPs (above the micro-heater), inter digital electrodes (IDEs) are usually patterned to monitor the resistance variation in the sensing layer during the change of gas compositions at the elevated temperature. The size of the whole device is often mm × mm and the dimensions of the IDEs above the heater are of hundreds of micrometers. The miniaturization of the devices creates however a challenge, i.e., the deposition of sensing materials onto the micro-heater membrane in an effective way [6].

Conventional non-localized deposition techniques, e.g., sputtering [7-9], evaporation [10], spray coating [11] or electro-spinning [12] have to be combined with lithography of a deposition window or alignment of shadow masks; whereas localized deposition techniques that utilize the internal micro-heater to activate the growth have to use vapor phase precursors [6]. And if seed layers are required for the localized growth, the non-localized techniques are again needed to first produce them [13-15]. In the case of high precision screen printing [16], the deposition has to be made before the backside etching of the membrane to avoid its damage, making it inconvenient to the user of post CMOS wafer stage. Another set of techniques are those based on the direct deposition of sensing materials presented in liquid form by micro droplet coating [17,
or ink-jet printing [19, 20]. Apart from preparing the stable material suspension and the dedicated apparatuses, these two techniques also lack the capability of manipulating nanomaterials, e.g., the alignment of nanowires.

Dielectrophoretic (DEP) technique has been used to manipulate nanomaterials [21-24], especially metal [25] and semiconductor [23, 26] nanowires. The DEP force arises from the polarization of non-charged elements in a non-uniform electric field and attracts the object to the electrodes. It has been successfully applied to align nanowires [25, 27] or nanorods [28, 29] onto different substrates for later sensing purposes, and it is suggested to be fully compatible with the standard CMOS technology for wafer-scale implementation [30, 31].

MOXs are the most typical compounds studied and used as low cost resistive sensing materials. ZnO nanowires in particular have been identified as potential candidates to fabricate new devices [32]. Although ZnO nanowire-based gas sensors have been intensively studied in the last few years and promising results have been demonstrated [33-35], improvements are still needed to bring them into the commercial stage. On the other hand, μHP gas sensors are often investigated under the so-called temperature-programmed/modulated operation mode [36-40]. In this approach, the sensors are subjected to pulses of different temperatures and duration, instead of keeping the sensors' temperature at constant. Improvement of the sensors' selectivity and even quantification of gases [41, 42] can be achieved by pattern reading and data analysis. A variant to that is the so-called temperature-pulsed operation mode [18, 41, 43, 44], in which the temperature of the sensor is constantly changed between two values (low and high) every few seconds and the resistance variation due to analyte gas at the low or high temperature end define the sensor response. With this approach, the sensitivity enhancement at the low temperature end is usually found.
In this work, the material deposition onto μHPs was further developed by applying the DEP alignment of ZnO nanowires at the post CMOS wafer stage. The gas sensing performance of the devices were tested with NH₃ in both conventional isothermal and temperature-pulsed sensing modes. The mechanism that lies behind the enhanced sensing performance in the temperature-pulsed mode is qualitatively discussed.

2. Experimental

2.1 Nanowire preparation

ZnO nanowires were obtained by a hydrothermal process reported earlier [45]. In brief, an 80 nm thick of ZnO seed layer were first sputtered onto indium doped tin oxide (ITO) glass. The ITO glass was then placed in the growth solution that consist of 0.02 M zincnitrate, 0.015 M hexamethylenetetramine (HMTA), 0.004 M polyethyleneimine (end-capped, molecular weight 800g/mol) and 0.024 M ammonium hydroxide. The solution was heated to 88°C, and after 3 h, ZnO nanowires grew to about 6μm in length with diameters ranges between 50 to 300 nm. The resulting ZnO arrays were rinsed with Mili-Q water and dried with nitrogen flow. More characterization results with, e.g., x-ray diffraction (XRD), scanning electron microscopy (SEM) can be found in ref.[45]. The solution of ZnO nanowires was obtained by sonicating the ITO substrate in isopropanol.

2.2 The μHPs

μHPs were obtained from Cambridge CMOS Sensors (www.ccmoss.com) [5]. The μHPs used in this work have IDEs made of gold (Au). Au is inert to oxidation and the rough Au surface provides good attachment to the later deposited nanowires. As shown in Fig.1a, the IDEs span a
circular area of 250 μm in diameter and the gap between the IDE fingers is 10 μm. The heating element made of W is buried under the IDEs within the SiO$_2$ insulation. W is used as an interconnect metal in high temperature CMOS processes and has better stability and lower mechanical stress compared to poly-Si heaters. The circular SiO$_2$ insulating membrane obtained by deep reactive ion etching (DRIE) has a diameter of 640 μm and a thickness of about 5 μm. Several Au bond pads that connect to the heater or IDEs are manufactured on the two sides of the chips for wire bonding. The maximum temperature the μHPs can reach is about 700°C, while the power consumption is only about 55 mW at 450°C.

2.3 DEP assembly of nanowires

The μHP chips were glued onto the transistor outline packages (TO-8) and wire bonded with Au wires (Fig. S1). The devices were then attached to a printed circuit board for ZnO nanowire deposition and later tests. ZnO nanowire solution in isopropanol was briefly sonicated before use. A micropipette was used to apply 2 drops (~2.5μl each) of it onto the μHPs when the AC potential was applied on the IDEs by a function generator (TG2000, TTi). The voltage applied was 15 V$_{p-p}$ in square wave at the frequency of 5 MHz. Once the solvent had evaporated, the AC signal was turned off. The morphology of aligned nanowires on μHPs was examined using a SEM (Auriga, Zeiss). As the annealing/sintering step, the temperature of the μHPs was raised to 400°C in stepwise and dwelled for 2 h.

2.4 Gas sensing tests

Gas sensing tests were performed with a homemade stainless steel chamber. Gas mixtures were introduced with thermal mass flow controllers (Bronkhost) by mixing the synthetic air (SA) with NH$_3$ in SA from the certified gas cylinders (Carburos Metálicos). The total flow rate was always
maintained at 200 ml/min. The micro-heater was powered by a source meter (2400, Keithley). For temperature-pulsed measurement, the pulsed voltage was in square waves and has a period of 10 s, i.e., the temperature of sensor changed between the low and high regime every 5 s. The settle time of both rise and fall of the pulsed input voltage were measured to be within 50 ms. Electrical measurements were made with another source meter (2635A, Keithley).

3. Results and discussion

3.1 The assembled device

From the microscope images (Fig. 1b&c), we see that most of the nanowires were attached to the IDEs after the DEP process. The rest of the membrane surface was clean, and the small amount of nanowires left on the membrane presumably does not affect the overall performance of the device. As it is shown in Fig. 1c and Fig. S2, both the finger tips and the outmost of the IDEs had attracted the nanowires more efficiently compared to the center area. This result might arise from the interference presented at the center area when multiple IDEs fingers with an opposite potential were located very close to each other. The potential interference from nearby IDEs fingers can offset the polarization and attraction effects on the nanowires, leaving the center with fewer nanowires. SEM image in Fig. 2 shows that nanowires were aligned into bundles and interconnected to each other. Since their lengths are shorter than the gap between the IDEs, multiple nanowires are required to bridge the gap. Comparing to the nanowries that grow vertically on the membrane [13-15] and only having their bottom parts in contact with the membrane, the direct lying of nanowires on the μHP membrane offers better heat transfer property between the membrane and nanowires. This assures the annealing/sintering step can be
used to strengthen the connections between the nanowires or nanowire-electrodes. The finally obtained structures were proved to be stable, since no direct evidence of degradation or change of their properties was found after regularly testing and handling. This suggests that the bond strength among nanowires and nanowire-electrodes are strong enough to fabricate functional devices following our approach.

3.2 Electrical properties

The contact between semiconductor and metal can be either ohmic or rectifying depending on whether a Schottky barrier is present. Ideally, ohmic contact is obtained with n-type semiconductor if the work function of the metal is close or smaller than the electron affinity of the semiconductor [46]. In our case, Au has a work function of 5.1±0.1eV [47] which is larger than the theoretical electron affinity of ZnO (∼4.2eV) [46]. The room temperature (RT) I-V curves (inset in Fig. 3a) of the annealed/sintered devices were found non-linear, indicating thus the formation of Schottky barrier at the Au-ZnO interface. The Schottky barrier however could be overcome by increasing the temperature [48]. The I-V curves became linear at 200°C and above, so the contact resistance contribution can be neglected in the later gas sensing measurements at high temperature.

The current values in I-V tests were found to increase with temperature until 300°C and then slightly declined at higher temperatures (Fig. 3a). These two opposite trends correspond to the negative (NTC) and positive temperature coefficients (PTC) of resistance, respectively. The negative one at low T results from the thermal generation of charge carriers and the overcoming of the Schottky and nanowire-nanowire junction barriers by electrons. On the other hand, the PTC after 300°C resembles the results reported for ZnO thin films by Min et al. [9, 49] and
shows the same tendency as those reported for ZnO nanorods [50] and nanofibers [51] in a slightly varied temperature range. The resistance was further measured with increasing the temperature in steps (Fig. 3b). The resistance was found to decrease along with the temperature rise until 250°C and only small drifts were observed during the dwell period. When the μHP temperature were raised to higher values, immediate drop of resistance were followed by drastic increase in the dwell period. The final resistance at 300°C has surpassed 250°C and even higher resistances were reached above this threshold. Such gradual increase of resistance also indicates that the I-V measurements are dependent on both the temperature and the dwell time at that temperature. As the I-V results in Fig. 3a were obtained about 1-2 minutes after the temperature adjustment, it follows the order of $R(250^\circ C) > R(400^\circ C) > R(350^\circ C) > R(300^\circ C)$, which is consistent with Fig. 3b only in the non-stabilized region right after the temperature change (marked with circles in Fig. 3b). Moreover, the more stabilized region in Fig. 3b with $R(400^\circ C) > R(350^\circ C) > R(300^\circ C) > R(250^\circ C)$ is consistent with Fig. 4 in the next section.

Regarding the origin of the PTC phenomenon, we first exclude the possibility of bulk chemical structure or composition change as the nanowires were pre-annealed and had experienced long hours of repeated gas sensing tests at high temperatures, in which we have seen a stabilized resistance base line. Furthermore, the nanowire-electrode contacts were shown to be ohmic at the elevated temperatures, making no contribution to the measured resistance. ZnO nanowires studied here also do not satisfy the two well-known PTC effects caused by interfaces: the PTC effect in ferroelectric ceramic materials [52] and the PTC effect in composite oxides materials [53]. On the other hand, due to the strong surface dependence of nanomaterials, the cause of the PTC in MOX nanomaterials has been ascribed to the complex dynamics of thermal desorption of water and related hydroxyl group (-OH) or generation of charged atomic O species ($O^-/O^{2-}$) on
the surface [9, 49-51, 54, 55]. For oxygen, the adsorbed molecular $O_2^-$ dissociate into $O^-$ and $O^2-$ at high temperatures, which apparently withdraw the electron more efficiently. And for the chemisorbed $H_2O$ and its by-product -$OH$, they act as the electron donor to the oxides, lowering the resistance at low temperature and increasing the resistance when removed by high temperature. Considering the high defect density of the solution prepared ZnO nanowires, the defects may have strong influence on their properties and have deeply involved in the aforementioned surface chemistries. Nevertheless, as will be shown next, despite the presence of the PTC, it doesn't undermine the capability of ZnO nanowires for gas sensing.

3.3 NH$_3$ sensing

NH$_3$ sensing tests were first performed at temperatures between 200°C and 400°C in the isothermal mode. As shown in Fig. 4, the response baseline in SA was fixed after the complete stabilization of the electrical resistance following a change in $T$. For this reason and in agreement with the abovementioned positive temperature coefficient of the devices, the initial resistance was found to slightly increase from 300°C and above. In all cases, nanowires responded to NH$_3$ by decreasing the resistance and the change was reversible when NH$_3$ was purged from the chamber. The decrease of the resistance upon exposure to NH$_3$ was expected as ZnO is an n-type semiconductor and NH$_3$ is a reducing gas. Here we define the isothermal mode response $S_{iso}$ to be $R_{SA}/R_{gas}$, where $R_{SA}$ and $R_{gas}$ are the resistance values in SA and in gas mixture, respectively. Response and recovery time ($t_{res}$ and $t_{rev}$) were counted as the time it took to complete 90% of the total resistance change. The optimal working temperature for NH$_3$ ($S_{iso} = 4.2$ for 200 ppm; 2.3 for 50 ppm and 1.5 for 10 ppm) was found to be 350°C (Fig. 5). At this temperature, $t_{res}$ were 7.4, 6.4 and 3.8 min for 10, 50 and 200 ppm of NH$_3$, and the corresponding $t_{rev}$ were 18.4, 19.9 and
21.5 min, respectively. All these values are however convoluted with the dynamics of the chamber.

A survey of literature reported resistive nano-sensors is given in table S1 of the supplementary material. The $S_{iso}$ value here obtained is found comparable to other studies of similar materials [56-58]. Indeed, the dependence of the gas response with the nanowires diameter is a well-known effect [35]; the response clearly benefits from the smaller diameters. This is more significant with thickness approaching to the Debye length. Herein, ZnO nanowires with diameters between 50 and 300 nm were tested and the thicker nanowires are believed to be the major current pathway. So the nanowires diameter is not favored by the high response and improvement can be simply made by making more uniform and thinner nanowires.

The NH$_3$ response of ZnO nanowires can be explained using the classic model [59] of MOX gas sensors: the surface oxygen species (molecular O$_2^-$ and atomic O$^-$, O$_2^-$) withdraw electrons from the ZnO, creating a depletion region that acts as a non-conductive region at the surface and charge transfer barrier between the nanowire junctions (as shown in Fig. 6). When the NH$_3$ is present, surface reaction occurs between the surface oxygen species and the adsorbed NH$_3$ molecule. These complex surface reactions can be simply described by the following equation [60]:

$$O_2^-/O^-/O_2^- + NH_3 (ad) \leftrightarrow N \text{ species} + H_2O + e^-$$

With N$_2$ as the main reaction product, electrons are released by the surface reactions and the resistance of ZnO decreases. In more specific, ohmic contacts formation was previously confirmed between nanowires and electrodes at the elevated temperatures. So the measured resistance is composed of the resistance of nanowire themselves ($R_{\text{nanowire}}$) and the resistance at
nanowire-nanowire junctions ($R_{\text{junction}}$). As illustrated in Fig. 6, the surface reactions release the electrons back into the nanowires, causing the reduction of depletion region width and lowering of junction potential barriers. The two contributors of the total resistance, $R_{\text{nanowire}}$ and $R_{\text{junction}}$ are therefore both lowered and finally lead to the reduction of the measured resistance.

In Fig. 4, it can be noted that the resistance indeed showed upward shifting after a prior drop at the 10 ppm response of 400°C. And the recovered resistance after 10, 50 ppm exposure exceeded the base value. Such character could be ascribed to the generation of NO$_2$ in addition to N$_2$ by the surface reactions; as NO$_2$ is considered to get adsorbed on the surface and withdraws electron [40, 61, 62]. The reason it appeared only at the low NH$_3$ level and highest temperature might be the request on high energy and selectively producing of NO$_2$ [57]. Moreover, the counter-balancing effect of NH$_3$ might also cause it to be more visible at the low NH$_3$. All in all, the ammonia response follows a typical bell-shaped curve (Fig.5), which reveal that ammonia sensing is (i) a thermally activated process but also that (ii) the response (reaction rate) is given by the ammonia adsorption-reaction probabilities at the surface, following a non-linear dependence of the sensor output with increasing concentration. Actually, this behavior was explained by Ahlers et al. [63] in terms of competing phenomena described by two energetic parameters: the strength of Langmuir adsorption $E_{\text{ads}}$ of NH$_3$ molecules at the surface, and the activation energy for the combustion reaction $E_{\text{RES}}$. These two factors are thus the decisive parameters to explain the high-temperature drop-off of the sensitivity $S$. It must be pointed out that between 350°C and 400°C the response starts to decrease.

In the temperature-pulsed mode, the sensor temperature was continuously changed between a low (200°C or 250°C) and a higher value for every 5 s. The resistance of the nanowires was simultaneously recorded when the gas flow was switched from pure SA to 200 ppm NH$_3$ in SA
and then purged back to SA. The resistance in the low temperature end was used to calculate the corresponding response $S_{\text{pulsed,low}}$. As shown in the Fig. 7, when the sensors were operated in the temperature-pulsed mode, the low or high end resistance no more equals to that in the isothermal mode of same temperature. And only the negative temperature coefficient was observed when changing the temperature in short pulses. A significant enhancement of response $S_{\text{pulsed,low}}$ compared to the isothermal mode of same temperature was observed. For 200°C or 250°C as the low end temperature, the response $S_{\text{pulsed,low}}$ increased with the high end temperature following a linear dependence (Fig. 8a). And the response $S_{\text{pulsed,low}}$ of a particular high end temperature were highly approximate to each other. This indicates that in this mode, $S_{\text{pulsed,low}}$ is determined by the high end temperature. The relative response compared to that of the isothermal mode was calculated as $\Delta S = (S_{\text{pulsed,low}} - S_{\text{iso,low}})/S_{\text{iso,low}} \times 100\%$ and given in Fig. 8b. Here, $S_{\text{iso,low}}$ is the isothermal response in the corresponding temperature. From the tests, $\Delta S$ with 200°C as the low end temperature were found to be always higher than that of 250°C, indicating that $\Delta S$ also increases with the difference between the high and the low end temperatures. Although strongly affected by the chamber volume and the gas flow rate, the response and recovery of the resistance also became faster in the pulsed mode (see Fig. S3). Overall, the low temperature end $t_{\text{res}}$ at the pulsed mode decreased with increasing high end temperature and the values are about on a par with that of the isothermal mode in the temperature same to the high end. An equivalent correlation was found for the recovery. Due to the fact that resistance did not recover completely within the given time (10 min), the recovery ratio ($R_{\text{end}}/R_{\text{SA}} \times 100\%$, where $R_{\text{end}}$ is the resistance when ending the SA refill) is defined. With pulsed temperature (especially at 300°C and 350°C high end $T$), the recovery ratio of the pulsed mode increased to higher values.
Similar response enhancement effects in the temperature-pulsed mode operation of μHP gas sensors have been previously reported in several works [18, 41, 43, 44]. As the surface oxygen species play a key role in the sensing mechanisms of reducing gases, A. Heilig et al. [41], proposed that the enhancement is mainly caused by the presence of high temperature surface oxygen species, i.e., O⁻/O₂⁻ [59] in the low temperature period, which would be less or not existed in the equivalent isothermal mode. O⁻/O₂⁻ are produced after the dissociation [64] of surface adsorbed molecular oxygen at high temperatures and remains there in the low temperature period due to the fast thermal transition of this mode. They strongly regulate the electron concentration near the surface and when surface reaction with reducing gas occurs, electrons will be released back to the surface to cause the resistance change. Furthermore, the higher reactivity of atomic O⁻/O₂⁻ with NH₃ will also lead to the faster response and recovery processes.

As mentioned in ref. [18] and [39], the surface cleaning effect during the high temperature period could also be the reason behind the response enhancement. Here, for the NH₃ sensing with ZnO nanowires, we propose two potential adsorbates that can deteriorate the performance of the sensor in isothermal mode and can be removed at high temperatures. The first is H₂O and its by product, hydroxyl group (-OH). H₂O is a well-known substance that interferes the output of MOX gas sensors [65, 66]. H₂O and its byproduct -OH has been appointed as one of the causes of positive temperature coefficient in the previous section. There are three sources of H₂O that can be adsorbed onto ZnO surface: i) when the sensor is exposed to ambient air at RT; ii) the trace level of H₂O presented in the SA; iii) the residual H₂O in the test chamber. The second adsorbate is NO₂, which was considered to be a secondary product of oxygen-NH₃ reaction at the surface and has a counter effect on NH₃ sensing [40, 61, 62]. When operated in the temperature-
pulsed mode, the amount of H$_2$O/-OH and NO$_2$ can be diminished during the high temperature period. Exposing the free surface active sites to O$_2$ and NH$_3$ at low temperature period will enable a higher response and faster surface sensing mechanisms. Fig. S4 shows, in a shorter time scale, the resistance of the device working in temperature-pulsed mode between 200 and 350°C in constant SA flow. As expected, the resistance was found to drift continuously in both high and low temperature period after a sudden large change due to the fast temperature switch. This indicates the material was in a meta-stable state, which is evidence to the as proposed sensing mechanism and the response enhancement.

4. Conclusions

ZnO nanowires were successfully deposited onto CMOS SOI μHP substrates for gas sensing applications. By DEP, nanowires prepared from a wide range of methods can be readily integrated onto μHPs. When working in the pulsed mode, a significant enhancement in the NH$_3$ sensing performance was observed at the low temperature end. It is proposed that this phenomenon is not only related to the high temperature surface oxygen species but also to the modulation of H$_2$O (-OH) and N$_2$O on the surface. The combination of the highly advanced CMOS SOI μHPs with this operation mode provides a new option to obtain reliable low cost gas sensors with even lower power consumption and high response.

Acknowledgement

The research was supported by the Framework 7 program under the project SOI-HIT (FP7-ICT-2011-7) and European Regional Development Funds (ERDF). Authors from IREC
acknowledge the financial support given by the XaRMAE Network of Excellence on Materials for Energy of the “Generalitat de Catalunya”. F.H.-R. also acknowledges the support of the DAAD (D/11/43761). J. Fan also thanks for the support of the Secretary for Universities and Research of the Ministry of Economy and Knowledge of the Government of Catalonia.
References


Figure captions

Fig. 1. (a) Layout of the CMOS SOI μHP substrate with gold IDEs. (b) The μHP substrate after wire bonding and nanowire deposition (ZnO nanowires appear in white under optical microscope). (c) Digital microscope image of the membrane after nanowire deposition (nanowires and IDEs both appear in deep colour).

Fig. 2. SEM image showing nanowires assembled between the IDEs (The right half is the magnified image of the area in the small box on the left side).

Fig. 3. (a) I-V curves of the annealed device at different temperatures, (inset) room temperature (RT) I-V curve. Note the measurements were made about 1-2 minutes after the temperature adjustment, the resistance order of $R(250^\circ C)>R(400^\circ C)>R(350^\circ C)>R(300^\circ C)$ can be retrieved. (b) Resistance variation with temperature increasing in steps (measured with probing current of 100 nA); ○: non-stabilized region, □: stabilized region.

Fig. 4. NH$_3$ sensing of the ZnO nanowire device in isothermal mode.

Fig. 5. Response vs. $T$ of ZnO nanowires to different concentration of NH$_3$ in isothermal mode ($S_{iso} = \frac{R_{S}}{R_{gas}}$).

Fig. 6. Schematic illustrating the mechanism of NH$_3$ sensing.

Fig. 7. Temperature-pulsed and isothermal sensing of 200 ppm NH$_3$.

Fig. 8. (a) Response $S_{pulsed,low}$ for low end temperature of 200 and 250°C. (b) Relative response increase $\Delta S$. The error bars represent the sample standard deviation of 3 measurements.
Figure (3b)

The graph shows the variation of resistance and temperature over time. The lines indicate the changes in resistance and temperature with time, with specific events at 250°C, 300°C, 350°C, and 400°C.
$O_2^- / O^- / O^{2-} + NH_3 (ad) \leftrightarrow N \text{ species} + H_2O + e^-$
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Vitae

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