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Hydrogen Sensors from Composites of Ultrasmall Bimetallic Nanoparticles and Porous Ion-Exchange Polymers



We have developed the facile and versatile synthesis of ultra-small bimetallic nanoparticles (NPs) using porous ion-exchange polymers. PdPt NPs derived from porous ion-exchange polymers show superior hydrogen (H₂)-sensing performances at room temperature in air, with an ultra-low detection limit (0.4 ppm). The synergistic effect of PdPt NPs on H₂ sensing is demonstrated through experimental results and simulations. In addition, a wireless H₂-sensing system is achieved by combining our synthesis method with radio-frequency communication.



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HIGHLIGHTS

Facile synthesis of bimetallic nanoparticles using porous ionexchange polymers

Ultra-small PdPt nanoparticles show significantly improved H₂sensing properties

Synergies of PdPt nanoparticles on H_2 sensing is demonstrated

Wireless H₂-sensing system using a radio-frequency communication is achieved

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Hydrogen Sensors from Composites of Ultra-small Bimetallic Nanoparticles and Porous Ion-Exchange Polymers

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SUMMARY

Bimetallic nanoparticles (BM-NPs) have attracted much attention in catalysis, sensing, and electronics as a result of their ultra-high activity for surface reactions. For reliable utilization of BM-NPs in various applications, robust synthetic methods for the creation of non-aggregated functional BM-NPs with diameters less than a few nanometers are needed. Herein, we present functional assemblies of ultra-small BM-NPs produced within high-stability porous ion-exchange polymers. Specifically, PdPt NPs can be readily produced with precision dimensional control down to 1 nm. These PdPt NPs with porous polymers display superior hydrogen (H₂)-sensing properties at room temperature in air. We achieve an ultra-low limit of detection (H_2 0.4 ppm), thereby confirming the outstanding sensing performance of the PdPt NPs. We further demonstrate a wireless H₂-sensing system by combining porous polymer-templated PdPt NPs with a radio-frequency identification (RFID) system, which enables the wireless detection of H_2 in a sealed gas head space.

INTRODUCTION

Hydrogen (H_2) is an attractive renewable medium to store energy. It can be produced by electrolysis of water (H₂O) and has high energy density per weight, and water is the exclusive byproduct with the release of stored energy.¹ However, H_2 is a highly flammable gas and can explode in air at concentrations as low as 4%. Considering the fact that H₂ is odorless and colorless, H₂ gas leaks must be detected for safety. To detect H₂, various types of H₂ sensors, such as electrochemical, mechanical, optical, and chemiresistive sensors, have been developed.² For instance, semiconducting metal oxides have been extensively investigated for chemiresistive H₂ sensors.³ In addition, there is a significant advance in optical H₂ sensors through the use of metal-polymer composites that enable ultrafast H₂ detection.⁴ However, their sensing systems are rather complicated, such as the needs of heaters for metal oxides and light sources and detectors for optical sensors, and further enhancement in H₂ sensing performances is required. On the other hand, Pd-based chemiresistors are well known as an efficient H₂ sensor due to their simple sensing system, room temperature (RT) operation, low cost of sensor fabrication, and high H₂ selectivity.⁵ The transduction involves a reaction between H₂ and Pd to produce the more resistive palladium hydride (PdH_x).⁶ Specifically, the resistivity of PdH_{0.7} is 2-fold higher than that of Pd. However, when operated in air, the H₂ reaction on Pd is retarded by adsorbed oxygen,⁷ which deteriorates sensing response, sensing speed, and the detection limits. Existing solutions to address this issue include the minimization of surface-adsorbed oxygen⁸ and the promotion of H₂ reactions by surface

The Bigger Picture

Hydrogen (H₂) is a flammable gas, and even tiny leaks of H₂ must be detected for safety. However, the detection of low levels (below ppm) of H₂ in air still remains an unmet challenge. Herein, we present a facile synthesis of bimetallic nanoparticles (BM-NPs) by using porous ion-exchange polymers in order to develop superior H₂ sensors. The porous ion-exchange polymers enable the versatile fabrication of ultrasmall BM-NPs on various supports. In particular, PdPt NPs derived from our method show excellent H₂-sensing performances at room temperature in air, with an ultralow detection limit (0.4 ppm), as a result of the synergistic effect of PdPt NPs on H₂ sensing. We further developed a wireless H₂sensing system by combining PdPt NPs with radio-frequency communication. Our method can not only pave a new way in the field of H₂ sensors but also be easily extended to the fabrication of various ultra-small BM-NPs for diverse applications needed the superior activity of BM-NPs.

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functionalization⁹ or by alloying Pd with other elements.^{10–12} However, the negative effect of oxygen remains unsolved, and therefore the detection of sub-parts per million (ppm) levels of H_2 in air remains an unmet challenge.

Bimetallic nanoparticles (BM-NPs) are an attractive solution to overcome these challenges because they are known to have superior activity for surface reactions relative to single-element metal NPs.^{13–15} In some cases, synergistic effects are achieved by combinations of elements, which exceed the intrinsic properties of each individual element.¹⁶ Thus, we hypothesized that the combination of Pd with Pt could be complementary for H_2 sensing in air as a result of the fact that Pt is also able to detect H₂ by reactions that remove surface-adsorbed oxygen.¹⁷ In addition, it has been demonstrated that alloying with Pd and Pt into BM-NPs with a diameter of 7.2 nm increases the H₂ storage capacity significantly as compared with pristine Pd NPs.¹⁸ The chemical and physical properties of BM-NPs are strongly correlated with their structure, size, and composition. It is known that BM-NPs have exceptionally high catalytic activity when their size is kept below a few nanometers as a result of unsaturated surface states.^{19,20} These high-energy surfaces produce intrinsic instability and particle fusion is problematic. Hence, producing ultrasmall BM-NPs that are not prone to agglomeration is critical to maintaining this activity. Prior methods of stabilizing or immobilizing PdPt NPs include the impregnation into supports,²¹ chemical reduction,²² polyol method,²³ electrochemical deposition,²⁴ and laser ablation.²⁵ Nevertheless, these methods not only often produce PdPt NPs having a large average size and broad size distributions but also face challenges such as complicated processes, high processing costs, or low yields. In addition, it is difficult to control the optimal loading ratio of respective elements into BM-NPs while maintaining their size to sub-nm scale (the detailed pros and cons are summarized in Table S1). These limitations have hindered the practical usage of BM-NPs in various applications including chemical sensors.

Herein, we report a facile synthesis of BM-NPs by using porous ion-exchange polymers to create high-performance H₂ sensors that enable wireless detection. The ability to precisely tune the size and composition of BM-NPs is critically important to the sensory performance. This control is afforded by the use of a porous ion-exchange polymer, which enables homogeneous diffusion and immobilization of ionic metal precursors of complementary charge into the polymer matrix. Chemical reduction to generate NPs within the rigid porous matrix generates a material with high gas permeability and suppresses growth of NPs in size.²⁶ The result is a robust convenient method to create ultra-small (down to 1 nm) well-dispersed BM-NPs in the porous polymer matrix. PdPt NP-based H₂ sensors exhibit improved H₂-sensing properties at RT in air, as a result of the high and unique activity of bimetallic PdPt NPs, which display both H₂ adsorption and oxygen removal reactions. The limit of detection (LOD) for the H₂ sensors is 0.4 ppm, and sensing mechanisms of PdPt NPs are described. Furthermore, the sensor systems can be paired with a radio-frequency identification (RFID) system for the detection of H₂ in a sealed gas head space.

RESULTS AND DISCUSSION

Structural Design and Characterizations

Figure 1 illustrates the polymer synthesis, fabrication of PdPt NPs via ion exchange in a porous ionic polymer, and the application as chemiresistive H₂ sensors. Imidazo-lium-functionalized triptycene polyether sulfone (ITPES) as a porous cationic polymer is synthesized by chloromethylation of TPES and nucleophilic substitution reaction (Figure 1A), as reported previously.^{27,28} The structure of ITPES is confirmed by ¹H-NMR (Figure S1). Drop coating (10 μ L) of ITPES (1 mg mL⁻¹ in methanol)

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Figure 1. BM-NP Porous Ion-Exchange Polymer Composites and Chemiresistive H₂-Sensing System with Wireless Detection

(A) Schematic illustration of the synthesis of ITPES.

(B) Schematic illustration of the preparation of ITPES-PdPt NPs.

(C) Schematic illustration of ITPES-PdPt NPs-based chemiresistors.

(D) Schematic illustration of ITPES-PdPt NPs-based wireless sensors.

produces an ITPES matrix on a substrate with an average thickness of 50 nm (Figure S2). Aqueous $PdCl_4^{2-}$ and $PtCl_4^{2-}$ solutions (3.063 and 2.409 mM, respectively) are deposited on the polymer films, and these ions displace the chloride ions in ITPES. Lastly, PdPt NPs are produced by NaBH₄ reduction (Figure 1B, see details in the Supplemental Information). The free volume imposed by the triptycene creates an ITPES-membrane with highly porous structure,²⁹ and the size of PdPt NPs is restricted by the matrix. Via this method, ITPES-PdPt NPs can be deposited on glass (SiO₂), alumina (Al₂O₃), and polyethylene terephthalate (PET) film for chemiresistive (Figure 1C) and wireless (Figure 1D) sensing.

The size and distribution of PdPt NPs are controlled by the $PdCl_4^{2-}$ and $PtCl_4^{2-}$ loading and the total volume of aqueous solutions used in the ion exchange. As shown in Figure 2A, ultra-small PdPt NPs are formed when 10 µL of metal precursors is spread over an area of ca. 30 mm². The resulting 1.07 \pm 0.56 nm PdPt NPs are isolated from each other in the porous polymer (ITPES) matrix (Figures 2B and S3A). The lattice period (0.230 nm) of the PdPt (111) plane is increased compared with that of Pd (0.225 nm for (111), JCPDS no. 46-1043) and Pt (0.226 nm for (111), JCPDS no. 04-0802) (Figures 2C, S4, and S5). The increased lattice fringe of PdPt NPs was also observed in the previous studies.³⁰ Increased loading amounts of metal anions to 20 µL, produced 1–5 nm PdPt NPs with a percolated network (Figures 2D and S3B). As a result of the free volume constraints of ITPES, the aggregation of PdPt NPs is minimized, and the size of most PdPt NPs is limited in a few nanometers.





Figure 2. TEM Analysis of ITPES-PdPt NPs

(A–F) ITPES-PdPt NPs prepared by the drop coating of Pd and Pt anions with a total volume of (A–C) 10 μ L and (D–F) 20 μ L. Shown are (A and D) TEM images, (B and E) STEM images, and (C and F) high-resolution TEM images.

(G) EDS elemental-mapping analysis corresponding to the region of Figure 2E.

(H) EDS elemental line profiles of the blue line in Figure 2E.

The Cs-corrected scanning transmission electron microscopy (STEM) image of the larger particles also shows the well-dispersed NPs (Figure 2E), and the lattice fringe of (111) plane of PdPt NPs also increased to 0.232 nm (Figure 2F). The energy-dispersive X-ray spectroscopy (EDS) elemental mapping images are consistent with PdPt NPs dispersed in ITPES-matrix. The matrix is uniform as evidenced by the C, N, S, and O maps (Figure 2G). The EDS line profile analysis of the blue line in Figure 2E further confirms that Pd and Pt are homogeneously distributed within PdPt NPs (Figure 2H). However, without the use of ITPES, the same synthetic process produced film-like PdPt structure (PdPt films) as a result of PdPt NP aggregation during the activation process (Figure S6). EDS elemental mapping analysis also reveals a non-homogeneous structure of PdPt films (Figure S6). These results clearly confirm that anion exchange porous polymer-matrix method is a facile and controllable route to ultra-small and well-dispersed BM-NPs on a substrate.

Ex situ ultraviolet-visible (UV-vis) spectra confirm the conversion $PdCl_4^{2-}$ and $PtCl_4^{2-}$ to NPs in the porous polymers after NaBH₄ reduction (Figure S7). Prior to reduction, broad absorbance spectra at 325 and 230 nm are indicative of $PdCl_4^{2-}$ and $PtCl_4^{2-}$ in



Figure 3. High-Resolution XPS and EXAFS Spectra of the Samples (A) XPS spectra of Pd films, PdPt films, ITPES-Pd NPs, and ITPES-PdPt NPs in the vicinity of Pd 3d. (B) XPS spectra of Pt films, PdPt films, ITPES-Pt NPs, and ITPES-PdPt NPs in the vicinity of Pt 4f. (C) The fitted EXAFS spectra of Pd foil and ITPES-PdPt NPs at the Pd *K*-edge. (D) The fitted EXAFS spectra of Pt foil and ITPES-PdPt NPs at the Pt *L*₃-edge.

the ITPES-matrix.^{31,32} The PdCl₄²⁻ absorbance spectra are absent after NaBH₄ reduction, and a new metal NP resonance is present at the location of the $PtCl_4^{2-}$ peak. The attenuated total reflection-Fourier-transform infrared (ATR-FTIR) spectra of ITPES-PdPt NPs match with pristine ITPES (Figure S8A), confirming that the chemical integrity of the polymer is maintained. X-ray diffraction (XRD) analysis of ITPES-PdPt NPs displays the weak peaks at 40° (Figure S8B), whose position is similar to the XRD PdPt film patterns (Figure S9). To further support the formation of bimetallic PdPt NPs in ITPES, we conducted X-ray photoelectron spectroscopy (XPS) analysis of ITPES-PdPt NPs relative to monometallic control samples ITPES-Pd NPs and ITPES-Pt NPs, as well as films of Pd, Pt, and PdPt synthesized by the same conditions without ITPES. In the PdPt NPs, the Pd 3d and Pt 4f peaks are shifted to low binding energy as compared with the control samples (Figures 3A and 3B). The Pd and Pt phases separate in PdPt films, and the peaks in the PdPt NPs are shifted from those observed in the films (from 335.3 eV for Pd $3d_{5/2}^{33}$ to 334.9 eV and from 71.0 eV for Pt 4f_{7/2}³⁴ to 70.7 eV). These peak shifts demonstrate the formation of BM-NPs and are consistent with reported previously results.^{35,36} In addition, the high-resolution XPS spectra of C 1s, N 1s, and S 2p confirm C-C, C-O, and C-N bonds,³⁷ imidazolium,³⁸ and sulfone groups³⁹ (Figures S10–S12), demonstrating the existence of intact ITPES in each of the ITPES-PdPt NP, ITPES-Pd NP, and ITPES-Pt NPs compositions.

The formation of bimetallic PdPt NPs is further supported by X-ray absorption spectroscopy (XAS) analysis. The X-ray absorption near edge structure (XANES) spectra of ITPES-PdPt NPs indicate the metallic state of Pd and Pt (Figure S13). The slight shifts of the white line peaks in both the Pd K-edge and Pt L₃-edge XANES spectra result from the surface-adsorbed oxygen on Pd and Pt elements.⁴⁰ We also fitted the Fourier transforms of extended X-ray absorption fine structure (EXAFS) spectra of

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the samples to investigate atomic bonding states in the ITPES-PtPd NPs (Figures S14 and S15). Both Pd K-edge and Pt L_3 -edge EXAFS spectra show the new peak at 1.0–2.0 Å and Pd–M (M = Pd or Pt) and Pt–M bonding at 2.0–3.0 Å compared with those of references (Figures 3C and 3D). These new peaks are related to surface oxygen bonding or metal–metal bonding having a low coordination number (CN).⁴¹ In addition, the EXAFS fit parameters confirm the presence of Pt–Pd and Pd–Pt bonding and the decreased total CN of ITPES-PdPt NPs (9.9 for Pd and 8.8 for Pt and 12 for reference foils) (Table S2). These results clearly demonstrate the formation of ultra-small bimetallic PdPt NPs, which are consistent with TEM and XPS analysis.

Sensing Characteristics of ITPES-PdPt NPs

To probe the activity of ITPES-PdPt NP to detect H₂, we fabricated chemiresistors (see the Supplemental Information for details). Unfortunately, 1-nm-sized ITPES-PdPt NPs did not display sufficient electrical conductivity; however, with increased metal precursor loading, ITPES-PdPt NPs exhibited a percolated network and electrical conductivity.⁴² To optimize the system, we varied the molar ratio of Pd to Pt in PdPt NPs to Pd_{0.75}Pt_{0.25}, Pd_{0.67}Pt_{0.33}, Pd_{0.5}Pt_{0.5}, and Pd_{0.33}Pt_{0.67} through the loading of the Pd and Pt precursors (Figure S16). The sensing tests were conducted at RT in air, and Pd_{0.5}Pt_{0.5} NPs exhibited the best sensing properties. In these investigations, we investigated the H₂-sensing properties of different ITPES-PdPt NPs as well as the control samples: ITPES-Pd NPs, ITPES-Pt NPs, and PdPt films. ITPES-PdPt NPs exhibit significant resistive responses for exposures of 1%-4% of H₂ (Figure 4A), and a normalized response ($|\Delta R/R_a|$) to 4% H₂ is 16.0%. In contrast, the PdPt films show lower resistance changes and a response ($|\Delta R/R_a|$) of 0.53% to H₂ (4%). The reasons for the baseline drift after H₂ exposures are not clear; however, similar drifts were observed in previous studies.^{8,10} ITPES-Pd NPs and ITPES-Pt NPs also display increased H₂ responses relative to the PdPt films, with H₂ (4%) responses ($|\Delta R/R_a|$) of 6.78% and 5.09% for ITPES-Pd NPs and ITPES-Pt NPs, respectively, confirming the fact that NPs increase activity. ITPES-PdPt NPs, ITPES-Pd NPs, and ITPES-Pt NPs are all capable of detecting 0.01%-0.8% of H₂; however, the PdPt films will not function at these low concentrations (Figure S17). The triplicate response traces of ITPES-PdPt NPs-based sensors display stable resistance changes to repeated 0.8% H₂ exposures of 10 h (Figure S18A), demonstrating high reproducibility and stability. In addition, the ITPES-PdPt NPs show stable response traces after storage in ambient air for 1–3 months, although the 4% H₂ $|\Delta R/R_a|$ decrease to 6.95% after 1 month, 4.67% after 2 months, and 4.50% after 3 months (Figures S18B and S18C).

The resistance for the ITPES-PdPt NPs sensors decreased when exposed to H₂ concentrations over 100 ppm (Figures 4B and S17) and then switches to an increase in resistance with H_2 exposures below 16 ppm (Figures 4B and S19). This switchover is the result of reactions at high H₂ concentrations to liberate surface oxygen species that are generating interparticle resistance. The ITPES-PdPt NPs enable trace H₂ detection to 0.4 ppm (Figure 4C), which is superior to the limits of detection of 100 ppm for ITPES-Pd NPs and ITPES-Pt NPs, and 0.1% for PdPt films (Figures S17 and S20). The sensor responses H₂ concentrations are summarized in Figures 4D and 4E. ITPES-PdPt NPs show the highest response to 1% H₂ of 7.56%, and the other responses are 2.50% for ITPES-Pd NPs, 4.15% for ITPES-Pt NPs, and 0.13% for PdPt films. In addition, the time to obtain a 90% response (t_{90}) is accelerated from 386 s for PdPt films to 92 s at ITPES-PdPt NPs for the detection of H_2 1%, and the recovery time to 10% of the total response (t_{10}) also reduced from 476 to 304 s (Figure S21). The ITPES-PdPt NPs are selective for H_2 with minimal cross-response to interfering gases such a NO₂, NO, CO, NH₃, HCHO, and C₂H₅OH (Figure S22). Furthermore, the ITPES-PdPt NP sensor response of 11.0% to H₂ (2%) in 50% relative humidity







Figure 4. Sensing Characteristics of the Samples

Sensing characteristics of ITPES-Pd NPs, ITPES-Pt NPs, ITPES-PdPt NPs, and PdPt films at RT in air.

(A–C) Response traces of the sensors: (A) in the range of 1%–4% of H₂, (B) to 5 and 16 ppm and 0.05%, 0.01%, 0.25%, 1%, and 4% of H₂, and (C) in the range of 0.1–1 ppm of H₂. The shaded area shows the standard deviation.

(D and E) Normalized responses of the sensors to (D) high levels of H_2 and (E) low levels of H_2 .

(F) Comparison of H₂ detection limits of Pd-based H₂ sensors.

air is very similar to 11.2% measured in dry air (Figure S23). These results confirm the feasibility of ITPES-PdPt NPs as a selective and stable H₂ sensor. Figure 4F shows the comparative LOD of our system with other Pd-based H₂ sensors operated at RT in air, as reported in recent literature (see the summary in Table S3).^{4,8–10,43–51} As shown, although the response times are not fast, the ITPES-PdPt NPs sensors show a superior H₂ LOD as compared with previous Pd-based H₂ sensors.

H₂-Sensing Mechanisms of ITPES-PdPt NPs

We carried out *ex situ* XPS analysis to elucidate the H₂-sensing mechanism of ITPES-PdPt NPs detailing (1) H₂ adsorption at low [H₂] and (2) the removal of surface-adsorbed oxygen at high [H₂]. The ITPES-PdPt NPs-based sensors were exposed to 5 ppm and 1% of H₂ for 10 min before XPS measurements (Figures 5A and 5B). The ratio of Pd²⁺ to Pd decreases after H₂ exposures, while the ratio of Pt²⁺/Pt is unchanged. These ratio changes suggest that the oxygen adsorbed on PdPt NPs is removed by H₂ and that the reaction dominantly occurs at Pd sites. The oxygen reduction that occurs on Pd sites is consistent with the catalytic water formation on the Pd surfaces.⁹ Thus, the *ex situ* XPS results support (1) the atomically distributed PdPt NPs and (2) that reductive release of surface oxygen at higher concentrations of H₂ leads to a decrease in the resistance of PdPt NPs. The sensing tests in oxygen-free atmospheres (N₂ balance) further support our hypothesis (Figure S24). ITPES-Pd NPs and ITPES-PdPt NPs sensors show increase of resistances for exposures of 0.1 ppm to 4% of H₂ with the ITPES-Pd NPs devices having much larger responses. In contrast, the ITPES-Pt NPs-based sensors that lack Pd did not display





Figure 5. Investigation of Sensing Mechanisms of ITPES-PdPt NPs

Sensing mechanisms of ITPES-PdPt NPs at RT in air.

(A and B) $\mathit{Ex\,situ}\,XPS$ spectra after exposures of 5 ppm and 1% of H_2 in the vicinity of (A) Pd 3d and (B) Pt 4f.

(C and E) DFT calculations. (C) Top views of the optimized structures of an adsorbed H₂ (red circles) on the (111) surface of Pt, Pd, and PdPt NPs. (E) Calculated binding energies for the adsorption of H₂ and H on the surface of Pt, Pd, and PdPt NPs.

(D) Same as (C) but with an adsorbed H (red circles) on the (111) surfaces of NPs.

(F) Schematic illustration of the H₂ sensing mechanisms of ITPES-PdPt NPs.

noticeable responses. Thus, we confirm that the nanoscopic Pd or PdPt dramatically promote H₂ reactions due to their nanosize effect. However, compared with the H₂-sensing properties in air, the LOD of ITPES-Pd NPs are severely degraded from 0.1 ppm for N₂ atmospheres to 100 ppm for air because adsorbed oxygen on Pd retards H₂ reactions with Pd.⁷ On the other hand, ITPES-PdPt NPs (1) induce more increased H₂ adsorption in air because of the bimetallic synergies of PdPt¹⁰ and (2) translate oxygen reactions with H₂ on PdPt NPs into signals of chemiresistors. Therefore, their excellent sensing properties remain even in air operation (H₂ LOD: 0.1 ppm for N₂ and 0.4 ppm for air).

To further demonstrate the bimetallic synergies of PdPt NPs on H_2 sensing, we conducted density functional theory (DFT) calculations. We calculated (1) molecular H_2 adsorption and (2) dissociative H_2 adsorption (H adsorption) energies on the dominant surface plane of Pd, Pt, and PdPt NPs. Figures 5C and 5D show the optimum structures for the



adsorption of H₂ and H (red circles in Figures 5C and 5D) on (111) facet of Pt, Pd, and PdPt. The calculated binding energies for H₂ adsorption are -5.02 kJ mol⁻¹ on Pt, -9.31 kJ mol⁻¹ on Pd, and -15.12 kJ mol⁻¹ on PdPt, and the H adsorption energies are -83.95 kJ mol⁻¹ on Pt, -108.22 kJ mol⁻¹ on Pd, and -125.48 kJ mol⁻¹ on PdPt (Figure 5E). These binding energies indicate that the adsorption of H₂ and H has a stronger preference for the PdPt surfaces as opposed to pure ones. These results are well matched with previous studies on H₂ adsorption on Pd–Pt alloy.^{10,52–54} The hybridization of d-orbitals of Pd and Pt atoms in vacuum or in ambient air induces a shift in the d-band to deeper levels (lower energy), lowering the adsorption energy of H₂ on Pd/Pt interfaces. Thus, PdPt NPs lead to synergetic H₂ adsorption properties, which is in good agreement with our sensing results.

From these results, we conclude the H_2 -sensing mechanisms of ITPES-PdPt NPs as follows (Figure 5F). When PdPt NPs are exposed to H_2 , two reactions occur: (1) the removal of surface-adsorbed oxygen gives a decrease in resistance, and (2) H_2 adsorption results in an increase in resistance. Both reactions occur simultaneously, but the former dominants the resistance at high levels of $[H_2]$ and the latter at low levels of $[H_2]$. Therefore, the detection limits and responses of the sensors are increased in air, but response times are not accelerated.

Wireless H₂-Sensing System

To take advantage of our method that can easily apply to various substrates, we further developed wireless H₂-sensing systems by combining ITPES-PdPt NPs with an RFID system. The ITPES-PdPt NPs were directly deposited on a conventional RFID tag with the same synthetic process used in the chemiresistor fabrication. To translate the chemiresistive sensing behaviors of PdPt NPs to signals in radio-frequency (RF) communications, the ITPES-PdPt NPs bridged the disconnected ends of the RF resonant circuit. The ITPES-PdPt NPs-RFID tag was placed in the sealed chamber (Figures 6A and 6B), and the RFID antenna was positioned 4 cm above the tag in the chamber (Figure 6C). Figure 6D shows the traces of received signal strength (S_{11}) changes (Δ Gain) of the ITPES-PdPt NPs-based wireless H_2 sensor. Because S_{11} is inversely proportional to circuit resistance, $^{55}\Delta$ Gain has a positive value as a result of the resistance decrease observed from the ITPES-PdPt NPs with exposure to 1%-4% of H₂. The wireless H₂ sensor showed sensitive responses to H_2 with $\Delta Gain = 1 \text{ dB}$ at 4% H_2 . The phase changes also indicate that ITPES-PdPt NPs wirelessly detected H₂ in real time (Figure 6E). Although the LOD (1%) of the wireless H₂-sensing system is lower than that (0.4 ppm) of the ITPES-PdPt NPs-based chemiresistors due to the noise signals in air and interferences with surrounding,⁵⁶ the chemiresistive behaviors of ITPES-PdPt NPs are successfully translated into RF communication signals. On the other hand, controls using the pristine RFID tag did not show any noticeable signals toward H_2 exposure (Figure S25). These results clearly demonstrate the realization of wireless H₂ sensing by hybridizing the ITPES-PdPt NPs sensing layer and RFID tag. Note that, because the wireless sensing system using our method is a proof-of-concept demonstration of the future sensing systems, we did not further optimize the wireless sensing performances. With the rational design of RF communication systems, the wireless H_2 -sensing system is applicable to various fields, such as leakage detection in a sealed space, environmental monitoring, and drone sensors.

In conclusion, we developed the facile synthesis method to create conductive networks of ultra-small BM-NPs by using anion exchange in the porous cationic polymers and subsequent reductive activation. The porous ion-exchange polymers allow the facile diffusion of heterogeneous ionic metal precursors in the polymer matrix and also limit the growth of NPs, enabling the reproducible formation of highly active 1 nm scale BM-NPs. The porous polymer matrix also allows for gas accessibility to the BM-NPs.





Figure 6. Photographs of the Experimental Setup for Wireless Sensing Tests and Wireless Sensing Characteristics

(A) Photograph of the RFID tag-embedded gas chamber. The RFID tag was attached to a holder.
(B) Photograph of the ITPES-PdPt NPs-deposited RFID tag. ITPES-PdPt NPs were deposited in the region of the blue box in Figure 5B.

(C) Photograph of a RFID antenna placed on the gas chamber. The distance between the RFID tag and RFID antenna was 4 cm.

(D) Dynamic changes of received signal strengths (S $_{11}).$

(E) Phase changes of ITPES-PdPt NPs-based wireless H_2 sensors to exposures of 1%–4% of H_2 .

As a result of the superior activity of PdPt NPs, the ITPES-PdPt NPs-based sensor exhibited high stability and excellent H₂-sensing properties with a 15.7% response to 4% H₂ and a LOD of 0.4 ppm. The H₂-sensing mechanism of PdPt NPs in air was verified to be related to the two reactions: (1) the removal of surface-adsorbed oxygen (decreased resistance) at Pd sites at the interfaces of Pd/Pt atoms and (2) H₂ adsorption (increased resistance) within the PdPt NPs. Based on outstanding H₂-sensing performance, we further demonstrated the wireless sensing system, for detection of H₂ in a sealed head space, by combining RFID tag with ITPES-PdPt NPs. Our approach can be extended to (1) diverse BM-NPs deposited onto various supports and (2) applications that require the superior activity of BM-NPs.

EXPERIMENTAL PROCEDURES

Resource Availability

Lead Contact

Further information and requests for resources should be directed to and will be fulfilled by the Lead Contact, Il-Doo Kim (idkim@kaist.ac.kr).

Materials Availability

ITPES can be produced according to the procedures outlined below from standard reagents and procedures.





Data and Code Availability

This study did not generate any datasets.

Materials

Triptycene-1,4-hydroquinone was purchased from Triton Systems, Inc and recrystallized from acetone before use. Dimethylacetamide (DMAc), chloromethyl methyl ether, 1-methylimidazole, anhydrous toluene, N-methyl-2-pyrrolidone, potassium tetrachloropalladate(II) (K₂PdCl₄), potassium tetrachloroplatinate(II) (K₂PtCl₄), and sodium borohydride (NaBH₄) were obtained from Sigma-Aldrich and used as received. Bis(4-chlorophenyl) sulfone, potassium carbonate (K₂CO₃), and zinc chloride (ZnCl₂) were purchased from Sigma-Aldrich and dried in vacuum oven at 60°C overnight before use.

Synthesis of ITEPS

ITPES as a porous ion-exchange polymer was synthesized according to the procedures reported in our previous paper.^{27,28} First, TPES copolymers were prepared using aromatic nucleophilic substitution (SNAr) reaction of triptycene hydroquinone (10.0 mmol) and bis(4-fluorophenyl) sulfone (10.0 mmol) in DMAc (30 mL) and anhydrous toluene (5 mL) under N₂ atmosphere.²⁷ K_2CO_3 (11.5 mmol), as a base catalyst, was added, and the solution was heated to 140°C to remove water via azeotropic distillation. After the removal of water, the solution was stirred at 165°C (reflux) for 18 h. Then, the reaction was precipitated in boiling water, and the obtained polymer was purified by dissolving in DMAc and precipitating twice in boiling water and in methanol. The polymer powder was dried in the vacuum oven at 75°C overnight. Chloromethylation of TPES was conducted using chloromethyl methyl ether with ZnCl₂.²⁸ TPES was dissolved in tetrachloroethane (3 w/v %), and chloromethyl methyl ether was added to the solution. After mixing the solution homogeneously, ZnCl₂ was added and the mixture was stirred at 60°C for 3 h. Then, chloromethylated-TPES (CI-TPES) was obtained by the precipitation in methanol and dried in the vacuum oven at 60°C overnight. Lastly, ITPES was produced by nucleophilic substitution of benzyl chloride groups in CI-TPES with 1-methylimidazole. CI-TPES was dissolved in N-methyl-2-pyrrolidone (10 w/v %) and 1-methylimidazole was added in excess (10 equiv). The solution was stirred at RT for 10 h. Then, the reaction was precipitated in acetone and washed by acetone. ITPES was dried in a vacuum oven at 60°C overnight.

Synthesis of ITEPS-PdPt NPs

ITPES-PdPt NPs were synthesized by drop coating and a subsequent reduction process. First, ITPES was drop coated on a substrate, such as glass (amorphous SiO₂), alumina (Al₂O₃), and polyethylene terephthalate (PET) film. 10.0 μ L of ITPES dispersed in methanol (1 mg/1 mL) was dropped on the substrate and dried on a hot plate at 65°C for 5 min. To utilize anion exchange through a porous cationic polymer (ITPES), a total of 10 μ L of K₂PdCl₄ (3.063 mmol) and K₂PtCl₄ aqueous solutions (2.409 mmol) were drop coated on the substrate. The molar ratio of Pd to Pt in PdPt NPs was controlled by changing the relative ratio of K₂PdCl₄ and K₂PtCl₄ aqueous solutions. For the ion exchange of PdCl₄²⁻ and PtCl₄²⁻ ions, the substrate was placed on a hot plate at 65°C for 30 min. Lastly, PdPt NPs were activated by NaBH₄ solution (1 mg/1 mL). After 30 min, the substrate was washed with deionized water and dried at 60°C overnight.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr. 2020.07.015.



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AUTHOR CONTRIBUTIONS

W.-T.K. conceived the concept and designed experiments. Y.K. synthesized porous ion-exchange polymers. W.-T.K. prepared the materials and conducted structural characterization and sensing measurements. W.-T.K. and S.K. performed wireless sensing measurements. S.S. assisted sensing measurements. S.-J.L. supported wireless sensing tests. B.L.S. and J.K. conducted DFT calculations. All authors contributed to the writing of the manuscript. All authors discussed the results and the manuscript. I.-D.K. and T.M.S. were responsible for managing all aspects of this project.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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REFERENCES

- Jacobson, M.Z., Colella, W.G., and Golden, D.M. (2005). Cleaning the air and improving health with hydrogen fuel-cell vehicles. Science 308, 1901–1905.
- 2. Hübert, T., Boon-Brett, L., Black, G., and Banach, U. (2011). Hydrogen sensors – a review. Sens. Actuators B 157, 329–352.
- Sharma, B., Sharma, A., and Kim, J.-S. (2018). Recent advances on H₂ sensor technologies based on MOX and FET devices: a review. Sens. Actuators B 262, 758–770.
- Nugroho, F.A.A., Darmadi, I., Cusinato, L., Susarrey-Arce, A., Schreuders, H., Bannenberg, L.J., da Silva Fanta, A.B.d.S., Kadkhodazadeh, S., Wagner, J.B., Antosiewicz, T.J., et al. (2019). Metal–polymer hybrid nanomaterials for plasmonic ultrafast hydrogen detection. Nat. Mater. 18, 489–495.
- Favier, F., Walter, E.C., Zach, M.P., Benter, T., and Penner, R.M. (2001). Hydrogen sensors and switches from electrodeposited palladium mesowire arrays. Science 293, 2227–2231.
- 6. Lewis, F.A. (1967). The Palladium Hydrogen System (Academic Press).
- Yang, F., Kung, S.C., Cheng, M., Hemminger, J.C., and Penner, R.M. (2010). Smaller is faster and more sensitive: the effect of wire size on the detection of hydrogen by single palladium nanowires. ACS Nano 4, 5233–5244.

- Koo, W.T., Qiao, S., Ogata, A.F., Jha, G., Jang, J.S., Chen, V.T., Kim, I.D., and Penner, R.M. (2017). Accelerating palladium nanowire H₂ sensors using engineered nanofiltration. ACS Nano 11, 9276–9285.
- Li, X., Liu, Y., Hemminger, J.C., and Penner, R.M. (2015). Catalytically activated palladium@platinum nanowires for accelerated hydrogen gas detection. ACS Nano 9, 3215–3225.
- Jung, W.B., Cho, S.Y., Suh, B.L., Yoo, H.-W., Jeon, H.J., Kim, J., and Jung, H.-T. (2019). Polyelemental nanolithography via plasma ion bombardment: From fabrication to superior H₂ sensing application. Adv. Mater. *31*, e1805343.
- Hughes, R.C., and Schubert, W.K. (1992). Thin films of Pd/Ni alloys for detection of high hydrogen concentrations. J. Appl. Phys. 71, 542–544.
- Hassan, K., Iftekhar Uddin, A.S.M., and Chung, G.-S. (2016). Fast-response hydrogen sensors based on discrete Pt/Pd bimetallic ultra-thin films. Sens. Actuators B 234, 435–445.
- Lim, B., Jiang, M., Camargo, P.H.C., Cho, E.C., Tao, J., Lu, X., Zhu, Y., and Xia, Y. (2009). Pd-Pt bimetallic nanodendrites with high activity for oxygen reduction. Science 324, 1302–1305.
- 14. Wang, D., and Li, Y. (2011). Bimetallic nanocrystals: liquid-phase synthesis and

catalytic applications. Adv. Mater. 23, 1044–1060.

- Cortie, M.B., and McDonagh, A.M. (2011). Synthesis and optical properties of hybrid and alloy plasmonic nanoparticles. Chem. Rev. 111, 3713–3735.
- Ferrando, R., Jellinek, J., and Johnston, R.L. (2008). Nanoalloys: from theory to applications of alloy clusters and nanoparticles. Chem. Rev. 108, 845–910.
- Yang, F., Donavan, K.C., Kung, S.C., and Penner, R.M. (2012). The surface scatteringbased detection of hydrogen in air using a platinum nanowire. Nano Lett. 12, 2924–2930.
- Kobayashi, H., Yamauchi, M., Kitagawa, H., Kubota, Y., Kato, K., and Takata, M. (2010). Atomic-level Pd-Pt alloying and largely enhanced hydrogen-storage capacity in bimetallic nanoparticles reconstructed from core/shell structure by a process of hydrogen absorption/desorption. J. Am. Chem. Soc. 132, 5576–5577.
- Burda, C., Chen, X., Narayanan, R., and El-Sayed, M.A. (2005). Chemistry and properties of nanocrystals of different shapes. Chem. Rev. 105, 1025–1102.
- Xia, Y., Xiong, Y., Lim, B., and Skrabalak, S.E. (2009). Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics? Angew. Chem. Int. Ed. 48, 60–103.

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- Ying, J., Yang, X.-Y., Hu, Z.-Y., Mu, S.-C., Janiak, C., Geng, W., Pan, M., Ke, X., Van Tendeloo, G.V., and Su, B.-L. (2014). One particle@one cell: highly monodispersed PtPd bimetallic nanoparticles for enhanced oxygen reduction reaction. Nano Energy 8, 214–222.
- Esparza, R., Santoveña, A., Ruíz-Baltazar, A., Angeles-Pascual, A., Bahena, D., Maya-Cornejo, J., Ledesma-García, J., and Pérez, R. (2017). Study of PtPd bimetallic nanoparticles for fuel cell applications. Mat. Res. 20, 1193– 1200.
- Liu, J., Yin, J., Feng, B., Li, F., and Wang, F. (2019). One-pot synthesis of unprotected PtPd nanoclusters with enhanced catalytic activity, durability, and methanol-tolerance for oxygen reduction reaction. Appl. Surf. Sci. 473, 318–325.
- Yang, X., Yang, Q., Xu, J., and Lee, C.-S. (2012). Bimetallic PtPd nanoparticles on nafion– graphene film as catalyst for ethanol electrooxidation. J. Mater. Chem. 22, 8057–8062.
- Censabella, M., Torrisi, V., Boninelli, S., Bongiorno, C., Grimaldi, M.G., and Ruffino, F. (2019). Laser ablation synthesis of mono- and bimetallic Pt and Pd nanoparticles and fabrication of Pt-Pd/graphene nanocomposites. Appl. Surf. Sci. 475, 494–503.
- Rifai, S., Breen, C.A., Solis, D.J., and Swager, T.M. (2006). Facile in situ silver nanoparticle formation in insulating porous polymer matrices. Chem. Mater. 18, 21–25.
- Kim, Y., Moh, L.C.H., and Swager, T.M. (2017). Anion exchange membranes: enhancement by addition of unfunctionalized triptycene poly(ether sulfone)s. ACS Appl. Mater. Interfaces 9, 42409–42414.
- Koo, W.-T., Kim, Y., Savagatrup, S., Yoon, B., Jeon, I., Choi, S.-J., Kim, I.-D., and Swager, T.M. (2019). Porous ion exchange polymer matrix for ultrasmall Au nanoparticle-decorated carbon nanotube chemiresistors. Chem. Mater. 31, 5413–5420.
- Tsui, N.T., Paraskos, A.J., Torun, L., Swager, T.M., and Thomas, E.L. (2006). Minimization of internal molecular free volume: a mechanism for the simultaneous enhancement of polymer stiffness, strength, and ductility. Macromolecules 39, 3350–3358.
- Zhou, L.N., Zhang, X.T., Wang, Z.H., Guo, S., and Li, Y.J. (2016). Cubic superstructures composed of PtPd alloy nanocubes and their enhanced electrocatalysis for methanol oxidation. Chem. Commun. 52, 12737–12740.
- Schiavo, L., Aversa, L., Tatti, R., Verucchi, R., and Carotenuto, G. (2016). Structural characterizations of palladium clusters prepared by polyol reduction of [PdCl₄]²⁻⁻ ions. J. Anal. Methods Chem. 2016, 9073594.
- 32. van Wyk, P.H., Gerber, W.J., and Koch, K.R. (2011). A robust method for speciation, separation and photometric characterization of all [PtCl_{6-n}Br_n]²⁻ (n = 0-6) and [PtCl_{4-n}Br_n]²⁻ (n = 0-4) complex anions by means of ionpairing RP-HPLC coupled to ICP-MS/OES,

validated by high resolution ¹⁹⁵Pt NMR spectroscopy. Anal. Chim. Acta *704*, 154–161.

- Gigola, C.E., Moreno, M.S., Costilla, I., and Sánchez, M.D. (2007). Characterization of Pd– CeO_x interaction on α-Al₂O₃ support. Appl. Surf. Sci. 254, 325–329.
- Jerdev, D.I., and Koel, B.E. (2002). Fe deposition on Pt (111): a route to Fe-containing Pt–Fe alloy surfaces. Surf. Sci. 513, L391–L396.
- 35. Zhang, G., Huang, C., Qin, R., Shao, Z., An, D., Zhang, W., and Wang, Y. (2015). Uniform Pd–Pt alloy nanoparticles supported on graphite nanoplatelets with high electrocatalytic activity towards methanol oxidation. J. Mater. Chem. A 3, 5204–5211.
- Chang, J., Feng, L., Liu, C., Xing, W., and Hu, X. (2014). Ni₂P enhances the activity and durability of the Pt anode catalyst in direct methanol fuel cells. Energy Environ. Sci. 7, 1628–1632.
- 37. Koo, W.-T., Cha, J.-H., Jung, J.-W., Choi, S.-J., Jang, J.-S., Kim, D.-H., and Kim, I.-D. (2018). Few-layered WS₂ nanoplates confined in Co, N-doped hollow carbon nanocages: abundant WS₂ edges for highly sensitive gas sensors. Adv. Funct. Mater. 28, 1802575.
- 38. Thomason, M.J., Seabourne, C.R., Sattelle, B.M., Hembury, G.A., Stevens, J.S., Scott, A.J., Aziz, E.F., and Schroeder, S.L.M. (2015). Selfassociation of organic solutes in solution: a NEXAFS study of aqueous imidazole. Faraday Discuss. 179, 269–289.
- 39. Joo, S.H., Pak, C., Kim, E.A., Lee, Y.H., Chang, H., Seung, D., Choi, Y.S., Park, J.-B., and Kim, T.K. (2008). Functionalized carbon nanotubepoly(arylene sulfone) composite membranes for direct methanol fuel cells with enhanced performance. J. Power Sources 180, 63–70.
- Guilera, G., Newton, M.A., Polli, C., Pascarelli, S., Guinó, M., and Hii, K.K. (2006). In situ investigation of the oxidative addition in homogeneous Pd catalysts by synchronised time resolved UV-vis/EXAFS. Chem. Commun. 41, 4306–4308.
- Knecht, M.R., Weir, M.G., Myers, V.S., Pyrz, W.D., Ye, H., Petkov, V., Buttrey, D.J., Frenkel, A.I., and Crooks, R.M. (2008). Synthesis and characterization of Pt dendrimer-encapsulated nanoparticles: effect of the template on nanoparticle formation. Chem. Mater. 20, 5218–5228.
- Kim, Y., Zhu, J., Yeom, B., Di Prima, M.D., Su, X., Kim, J.G., Yoo, S.J., Uher, C., and Kotov, N.A. (2013). Stretchable nanoparticle conductors with self-organized conductive pathways. Nature 500, 59–63.
- Kim, D.H., Kim, S.J., Shin, H., Koo, W.T., Jang, J.S., Kang, J.Y., Jeong, Y.J., and Kim, I.D. (2019). High-resolution, fast, and shapeconformable hydrogen sensor platform: polymer nanofiber yarn coupled with nanograined Pd@Pt. ACS Nano 13, 6071–6082.
- Yoo, H.W., Cho, S.Y., Jeon, H.J., and Jung, H.T. (2015). Well-defined and high resolution Pt nanowire arrays for a high performance

hydrogen sensor by a surface scattering phenomenon. Anal. Chem. *87*, 1480–1484.

Chem Article

- Cho, S.Y., Ahn, H., Park, K., Choi, J., Kang, H., and Jung, H.T. (2018). Ultrasmall grained Pd nanopattern H₂ sensor. ACS Sens. 3, 1876– 1883.
- 46. Shim, Y.-S., Jang, B., Suh, J.M., Noh, M.S., Kim, S., Han, S.D., Song, Y.G., Kim, D.H., Kang, C.-Y., Jang, H.W., et al. (2018). Nanogap-controlled Pd coating for hydrogen sensitive switches and hydrogen sensors. Sens. Actuators B 255, 1841–1848.
- 47. Jang, J.S., Qiao, S., Choi, S.J., Jha, G., Ogata, A.F., Koo, W.T., Kim, D.H., Kim, I.D., and Penner, R.M. (2017). Hollow Pd–Ag composite nanowires for fast responding and transparent hydrogen sensors. ACS Appl. Mater. Interfaces 9, 39464–39474.
- 48. Lim, M.A., Kim, D.H., Park, C.O., Lee, Y.W., Han, S.W., Li, Z., Williams, R.S., and Park, I. (2012). A new route toward ultrasensitive, flexible chemical sensors: metal nanotubes by wet-chemical synthesis along sacrificial nanowire templates. ACS Nano 6, 598–608.
- Hassan, K., and Chung, G.-S. (2017). Fast and reversible hydrogen sensing properties of Pdcapped Mg ultra-thin films modified by hydrophobic alumina substrates. Sens. Actuators B 242, 450–460.
- Fahad, H.M., Shiraki, H., Amani, M., Zhang, C., Hebbar, V.S., Gao, W., Ota, H., Hettick, M., Kiriya, D., Chen, Y.-Z., et al. (2017). Room temperature multiplexed gas sensing using chemical-sensitive 3.5-nm-thin silicon transistors. Sci. Adv. 3, e1602557.
- Ndaya, C.C., Javahiraly, N., and Brioude, A. (2019). Recent advances in palladium nanoparticles-based hydrogen sensors for leak detection. Sensors 19, 4478.
- Yoo, S.J., Park, H.Y., Jeon, T.Y., Park, I.S., Cho, Y.H., and Sung, Y.E. (2008). Promotional effect of palladium on the hydrogen oxidation reaction at a PtPd alloy electrode. Angew. Chem. Int. Ed. 47, 9307–9310.
- Weng, Y.-C., and Hsieh, C.-T. (2011). Scanning electrochemical microscopy characterization of bimetallic Pt–M (M=Pd, Ru, Ir) catalysts for hydrogen oxidation. Electrochim. Acta 56, 1932–1940.
- Kodchakorn, K., Lee, V.S., Yana, J., and Nimmanpipug, P. (2016). Density functional theory calculations of hydrogen dissociative adsorption on platinum-involved alloy surfaces. Surf. Coat. Technol. 306, 35–40.
- Zhu, R., Desroches, M., Yoon, B., and Swager, T.M. (2017). Wireless oxygen sensors enabled by Fe(II)-polymer wrapped carbon nanotubes. ACS Sens. 2, 1044–1050.
- Ruiz-Garcia, L., Lunadei, L., Barreiro, P., and Robla, J.I. (2009). A review of wireless sensor technologies and applications in agriculture and food industry: state of the art and current trends. Sensors 9, 4728–4750.