



# A simple fabrication route of porous palladium/palladium oxide/carbon nanostructures using one-step combustion waves for high-performance pH sensors



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## ABSTRACT

Reduction-oxidation controls and synthesis of organic-inorganic hybrid structures are key features associated with their electrochemical properties. However, they involve bulky setup and long-time processes that incur high-cost. Herein, we report one-step combustion waves (CWs) for the fabrication of hybrid-porous palladium/palladium oxides/carbon (Pd/Pd<sub>x</sub>O<sub>y</sub>@C) nanostructures with controllable atomic composition and their application as a high-performance pH sensor. Hybrid composites of Pd/formaldehyde (FA)/nitrocellulose (NC) were prepared as precursors. Self-propagating CWs through the NC networks carried out the transformation from Pd to PdO<sub>2</sub> in the higher oxidation state and the formation of a carbon layer, while the fast release of chemicals in CWs developed the porous nanostructures with large surface areas. The flexible pH sensor using the synthesized Pd/Pd<sub>x</sub>O<sub>y</sub>@C powders exhibited the outstanding specific voltage potential (2.08 V/mg at pH 2.83) and sensitivity (167 mV/mg pH). It showed no hysteresis during cycling of pH values and high stability over 4 h (voltage change < 0.89%). The high oxidation states and conductive carbon layers of Pd/Pd<sub>x</sub>O<sub>y</sub>@C with large surface areas improved the specific potential and the stability in minute changes of pH values and forward-reverse proton exchanges. The physicochemical synthesis using CWs would contribute to developing scalable processing for electrochemical applications, including chemical sensors.

## 1. Introduction

The optimization of electrochemical properties of materials is essential to develop new devices and improve the overall performance of existing platforms, such as energy storage systems [1–3], energy-harvesting systems [4–6], sensors [7–9], and catalysts [10,11], due to high density energy conversion between electrical and chemical potentials without moving mechanical components [12,13]. Control of the active materials, which involves the reduced states of metal oxides, the surface area, and synthesis of organic-inorganic hybrid structures, are key features associated with the performance and stability of electrochemical applications [14–16]. While the chemical composition of metal oxides determines the redox potential and energy barrier, the desirable porous structures expand the surfaces for electrochemical reaction and the organic interfaces improve the conductivity of the active materials [17–19]. For instance, according to the oxidation states in the identical metal core, the binding energy level, physicochemical stability, response time, and reversibility of the active materials appear as different aspects, and the precise manipulation of heterogeneous

composition, morphology, and conductivity is a significant task [20–22].

Palladium is one of the most important hydrogen-specific materials, which allow to develop hydrogen storage or transport, purification treatment with high permeability of hydrogen, hydrogen sensing device, and catalyst accompanying the physicochemical reaction of hydrogen species [23–26]. In particular, mixtures of palladium and palladium(II) oxide have been developed for use in pH sensors, because of the ease of synthesis and stability in sensing operation, as well as the moderate specific potential during chemical reaction with protons [27–29]. However, the improvement of the specific output potential in response to proton concentration changes has been a challenging issue, owing to the relatively low binding energy of palladium(II) oxides, which is theoretically estimated using the Nernst equation [27]. Meanwhile, palladium(IV) oxides which are in higher oxidation states than palladium(II) oxides can produce higher potential voltages due to the strong chemical binding energy when they are used as the active materials of pH sensors. These characteristics can realize the high performances in sensing applications, because only a small amount of

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palladium(IV) oxides enables the high sensitivity in response to the small target-substances that improves the sensing resolution and reduces the measurement errors. Nevertheless, there are critical limitations to the utilization of palladium(IV) oxides as active materials owing to the difficulty of stable transition from precursors to resulting materials in the synthesis, and the irreversibility in the forward and reverse reactions, as well as the inefficiency in cost and time.

Thermal processing such as annealing has been widely explored to manipulate the reduced states of the metal oxides, due to relatively simple handling and post-treatment [30,31]. On the other hand, long-time processing in a bulky chamber with specific ambient gas controls have been required to provide enough thermal energy and induce changes in the thermodynamic threshold for each state. Moreover, the rising and falling temperatures near the optimal processing conditions have inevitably consumed additional resources. In order to overcome these limitations of the thermal treatment, combustion waves lasting a few seconds have been recently used as facile methods to control the reduced states, phase transformation, structural changes, and the direct coatings of the organic materials on metal oxides [32–35]. These studies regarding combustion synthesis have provided the various processing conditions of facile, one-pot control of iron oxides [33], bismuth oxides [36], zinc oxides [37], and manganese oxides [32,38], as well as carbon layers [39]. The interfacial synthesis method between metals and metal oxides has been extended to transition metal oxides [40,41]. However, previous reports have mainly conducted the reduction of targeted metal oxides, induced by the consumption of oxygen in the raw materials comprising solid film layers of metal oxides and chemical fuels, whereas the higher oxidation state of palladium oxides is desirable for the sensing devices to obtain the higher potential voltage.

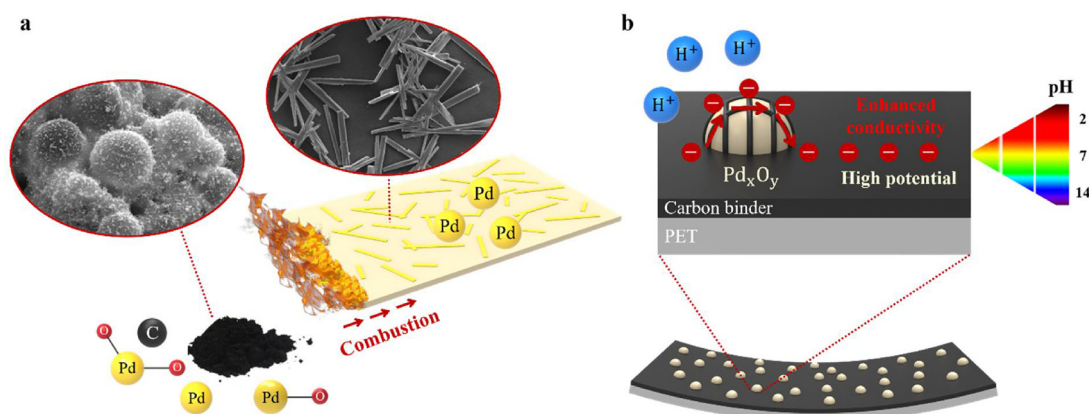
Herein, we report one-step combustion waves (CWs) for the fabrication of hybrid-porous palladium/palladium oxides/carbon (Pd/Pd<sub>x</sub>O<sub>y</sub>@C) nanostructures with controllable atomic composition of Pd<sub>x</sub>O<sub>y</sub> and their application as a high-performance pH sensor (Fig. 1). The precursor solution of palladium acetylacetonate (ACAC), formaldehyde (FA), and nitrocellulose (NC) in acetone was prepared, and the drying process allowed to obtain the hybrid composite of Pd/FA/NC as a free-standing film. One-step CWs through the NC networks induced by laser ignition evolved as a self-propagating thermal-chemical reaction in an open-air environment without any additional chamber or energy inputs (Fig. 1a). The instant thermal energy and excess oxygen from the decomposition of FA directly synthesized Pd/Pd<sub>x</sub>O<sub>y</sub> in the high oxidation states under tens of seconds, while the incomplete fuel combustion caused the deposition of carbon layers among the networks. SEM, EDS mapping, and XPS analysis confirm their physical structures and chemical compositions, which were characterized as hybrid porous nanostructures and mixtures of Pd/Pd<sub>x</sub>O<sub>y</sub>@C. This synthesis condition

was precisely compared with the air-drying and annealing-driven Pd/Pd<sub>x</sub>O<sub>y</sub> materials to elucidate the working mechanism of the one-step CWs with the FA. Based on the quantitative analysis for the maximizing PdO<sub>2</sub> ratio, realized in the optimization of the CWs processing conditions, the synthesized powders were used as the active materials in the flexible pH sensor, comprising of the poly(ethylene terephthalate) (PET) substrate and carbon-binders (Fig. 1b). The flexible pH sensor showed outstanding performances in terms of high specific potential voltage (~2.08 V/mg at pH 2.83) and the sensitivity (167 mV/mg pH) under various pH levels in a Britton-Robinson buffer solution. The percentile error in comparison with other pH meters and the potential drift over 4.5 h were less than 1% and 0.89%, respectively. The higher binding energy of PdO<sub>2</sub> in the higher oxidation states and the enhanced conductivity of the carbon layers significantly improved the sensitivity and stability. One-step CWs in chemicals that can control the physico-chemical environment during synthesis can be developed as a simple route for scalable fabrication of metal oxide micro-nanostructures with controllable oxidation states, as well as hybrid mixtures with carbon species. These precisely controlled metal oxide hybrids could be widely used in various electrochemical applications, including chemical sensors, energy storage materials, and catalytic reactions.

## 2. Materials and methods

### 2.1. Preparation of free-standing Pd/formaldehyde (FA)/nitrocellulose (NC) composites

The precursor solution for Pd/FA/NC hybrid composites was prepared using 1 mg palladium acetylacetonate (ACAC) (Sigma-Aldrich, ≥99%, Mn ~ 304.64, T<sub>m</sub> ≥ 200 ~ < 215 °C), dissolved and saturated in acetone solvent. Formaldehyde (FA) (Daejung, ≥35%, Mn ~ 30.03, Korea) was then added to the solution to supply excess oxygen during the application of one-step combustion waves (CWs). The added amount was controlled to set the weight ratio between palladium ACAC and FA to 1:42, 1:25, 1:10, and 1:1.5. Afterward, collodion (Sigma-Aldrich, diethyl ether ≥50% ~ < 55%, ethanol ≥45% ~ < 50%, cellulose nitrate ≥5% ~ < 10%) was added to the solution of palladium ACAC/FA in 1:1 vol ratio to form a palladium ACAC/FA/collodion precursor solution. Vortex mixing was applied to the solution to maintain homogeneous distribution of precursors. Finally, the precursor solution was dried at room temperature for 12 h to evaporate the solvents, and the remaining material was obtained as a free-standing hybrid composite of Pd/FA/nitrocellulose (NC) with a homogeneous distribution of palladium and FA in the NC-based film. The detailed configuration of the precursor solution is summarized in Table 1.



**Fig. 1.** Schematic of fabrication of Pd/Pd<sub>x</sub>O<sub>y</sub>@C hybrid nanostructures using one-step combustion waves (CW) and application to the active materials for flexible pH sensing devices. (a) One-step CWs for direct conversion from hybrid composites of Pd/formaldehyde (FA)/nitrocellulose (NC) to Pd/Pd<sub>x</sub>O<sub>y</sub>@C hybrid nanostructures under an open-air environment. (b) Direct application of Pd/Pd<sub>x</sub>O<sub>y</sub>@C for high performance pH sensing devices.

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