Surface engineering at the interface of core/shell nanoparticles promotes hydrogen peroxide generation

Yonggang Feng¹, Qi Shao¹, Bolong Huang², Junbo Zhang¹ and Xiaoqing Huang¹,*

ABSTRACT

Hydrogen peroxide (H₂O₂), an environmentally friendly oxidant, has already been widely used in many chemical synthesis and industrials as an alternative to replace traditional oxidants including chlorinated oxidizers and strong acids. However, the conventional synthesis method confronts intense energy cost, tedious separation procedures and high cost, which is not competitive with traditional oxidants. Although direct H₂O₂ synthesis from H₂ and O₂ is a green and atomically economic reaction, satisfactory activity and desirable selectivity still remain formidable challenges. Herein, for the first time, a class of Pd@NiO-x nanoparticles (NPs) (x = 1, 2, 3 and 4) with a unique core@shell interface structure has been created to achieve high activity, selectivity and stability for the direct H₂O₂ synthesis. A precise thermal annealing on Pd@Ni-x NPs revealed that the resulting Pd@NiO-x NPs exhibited the volcano-like activity toward direct H₂O₂ synthesis as a function of annealing temperature and time. By tuning the composition of Pd@NiO-x NPs and the reaction condition, the efficiency of H₂O₂ synthesis could be well optimized with 5 wt% Pd@NiO-3/TiO₂ exhibiting the highest productivity (89 mol/(kg cat h)) and selectivity (91%) to H₂O₂ as well as excellent stability, making it one of the best catalysts for direct H₂O₂ synthesis reported to date.

Keywords: hydrogen peroxide, direct synthesis, Core@shell structure, palladium, nickel oxide

INTRODUCTION

Hydrogen peroxide (H₂O₂) is a versatile chemical in modern industry, widely applied in the bleaching of textiles and pulp, treatment of waste water, removal of organic pollutant and chemical synthesis, etc. [1–5]. To date, H₂O₂ has been industrially manufactured using an indirect process that involves the sequential hydrogenation and oxidation of alkyl anthraquinone, which is, however, a multi-step process with high cost and is energy-intensive [6,7]. In sharp contrast, due to the remarkable advantages of atom economy, low energy consumption and only by-product of H₂O, the direct synthesis of H₂O₂ from H₂ and O₂ is expected to be the most efficient way to produce H₂O₂ [7]. To date, the direct synthetic route has mainly been achieved by supported Pd-based catalysts [8–10]. The major problem associated with that is related to the low selectivity of H₂O₂, since Pd is also very active for side reactions, such as the decomposition and hydrogenation of H₂O₂ as well as the formation of H₂O [9]. Adding a large amount of strong acid or halide promoters to the reaction medium is one solution to achieve high selectivity for H₂O₂ generation via suppressing the side reactions. However, it also leads to metal leaching and requires further purification of H₂O₂ products [10,11]. Recently, Pd–Au nanocatalysts have been demonstrated to have enhanced overall activity mainly due to the alloy effect and the presence of strong acid or halide promoters [8,12,13]. This has accordingly stimulated extensive research to explore the promotional effect by introducing Au, Pt, Ru and Ag into the Pd-based catalysts [14–20]. Without the use of halides, a Pd–Sn catalyst has achieved high H₂O₂ selectivity by creating a tin oxide surface layer onto small Pd-rich particles for preventing the over-hydrogenation and decomposition of H₂O₂ [21]. Despite great efforts being devoted to constructing Pd-based catalysts by introducing second metals, understanding high-performance Pd-based catalysts for direct H₂O₂ generation from either deep characterization or theoretical investigation is still extremely limited.

It is considered that the intrinsic surface property of Pd-based catalysts is essential for the
selectivity and activity of direct H$_2$O$_2$ synthesis. This arises because the barrier for O–O bond scission is sensitive to the Pd surface structure, the key parameter governing H$_2$O$_2$ synthesis and decomposition activity [22]. The oxidized Pd surface (Pd–O) bonding is more selective but less active towards the H$_2$O$_2$ synthesis than the metallic Pd, mostly attributed to the higher propensity of H$_2$O$_2$ to be absorbed on the metallic Pd surface than the Pd–O surface [21–23]. Therefore, it is anticipated that controlling the surface oxidation state of the Pd-based catalysts can be an effective route to regulating their catalytic properties, while precise surface tuning is extremely hard for the Pd-based catalysts due to their obvious tendency for thermal agglomeration or thermal morphology transformation.

We proposed that the aforementioned challenges can be overcome by simultaneous surface and interface modulations via constructing a core@shell structure, such as encapsulating Pd nanocrystals (NCs) with a shell [24,25]. To this end, herein we report the design of a class of Pd core–porous NiO shell catalysts in which the porous NiO shell is beneficial in protecting Pd NCs from aggregation during the reaction process as well as providing pore paths to allow the reactant gases to reach the Pd core and to further explore the correlations between the catalytic efficiency and the surface features. As a consequence, the supported Pd@NiO-x core–shell NCs were found to be a class of highly active, selective and stable catalysts towards direct H$_2$O$_2$ synthesis from H$_2$ and O$_2$. These Pd@NiO-x NCs with unique core–shell interface structure were created by direct thermal annealing of Pd@Ni-x NCs with precise annealing temperature and time. By optimizing the Pd:Ni ratio as well as reaction conditions, 5 wt% Pd@NiO-3/TiO$_2$ performed the highest selectivity to H$_2$O$_2$ of 91%, the highest activity of 89 mol/(kg cat h), as well as excellent stability. The X-ray photoelectron spectroscopy (XPS) results demonstrated that the surface of the Pd core was partially oxidized, revealing that the active metallic Pd core is co-modified by Pd$_{\text{II}}$ and NiO, which is effective to abate side reactions. Moreover, the first-principles simulations further interpreted the mechanism from both electronic and energetic views, which confirmed that the presence of a unique interface structure with cavities in Pd@NiO NCs guarantees the high selectivity of direct H$_2$O$_2$ synthesis.

**RESULTS AND DISCUSSION**

The Pd@Ni-x NCs (x = 1, 2, 3 and 4) with tunable compositions were first prepared through a facile solvothermal approach. They are highly monodisperse and employ the obvious core/shell structure (Supplementary Fig. 1, available as Supplementary Data at NSR online). The obtained Pd/Ni-x NCs were further loaded onto commercial TiO$_2$ (P25) to make Pd@Ni-x/TiO$_2$ catalysts with a total Pd content of 5 wt%, as determined by inductively coupled plasma mass spectroscopy (ICP-MS). The Pd@Ni-3/TiO$_2$ catalysts were further characterized by transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), STEM-energy dispersive X-ray spectroscopy (EDS) elemental mapping and EDS line-scan analysis. TEM imaging reveals that Pd@Ni-3 NC supported on TiO$_2$ has a diameter of ~22 nm (Fig. 1a and b). The STEM-EDS elemental mappings reveal that Ni presents as a thick shell (~5 nm) coated on a Pd core (~17 nm) (Fig. 1c and d), consistently with the powder X-ray diffraction (PXRD) results that both the face-centered cubic (fcc) Pd (JCPDS no. 87–0638) and fcc Ni (JCPDS no. 89–7128) observed in the Pd@Ni-x NCs/TiO$_2$ (Fig. 2a and b). In the very first attempt, we directly applied the Pd@Ni-x/TiO$_2$ catalysts for direct H$_2$O$_2$ synthesis. As shown in Supplementary Table 1, available as Supplementary Data at NSR online, the H$_2$O$_2$ productivity of these 5 wt% Pd@Ni-x/TiO$_2$ (x = 1, 2, 3 and 4) catalysts are calculated to be only 1.4, 1.0, 1.0 and 0.8 mol/(kg cat h), respectively. Since Pd is considered to be the active element for direct H$_2$O$_2$ synthesis, we ascribe the low activity of these Pd/Ni core/shell catalysts toward H$_2$O$_2$ synthesis to the thick NiO shell, by which the activity of Pd is heavily blocked.

To this end, to enhance the H$_2$O$_2$ productivity of these Pd@Ni-x/TiO$_2$ catalysts, exposing the active Pd sites in the Pd core to effectively access H$_2$ and O$_2$ is highly desirable. Since NiO has the nature of a porous structure, which can be made through a simple oxidation treatment [26–29], we calcined the 5 wt% Pd@Ni-3/TiO$_2$ catalyst in air. After thermal treatment, we measured the activities of these catalysts toward direct H$_2$O$_2$ synthesis. As shown in Supplementary Table 2, available as Supplementary Data at NSR online, after being calcined at 250°C for 1 h, 5 wt% Pd@Ni-3/TiO$_2$ exhibits H$_2$O$_2$ productivity of 14 mol/(kg cat h). Once the calcined temperature was raised to 300°C, the H$_2$O$_2$ productivity increased to 46 mol/(kg cat h). We also tested the H$_2$O$_2$ productivity by prolonging the reaction time to 1 h for annihilating the negative influence on the diffusion rates of O$_2$ and H$_2$ due to the thick NiO shell newly formed. As expected, the H$_2$O$_2$ productivity of the 5 wt% Pd@Ni-3/TiO$_2$ calcined at 250°C for 1 h increased sharply to 89 mol/(kg cat h). Nevertheless, the 5 wt%
Figure 1. Structural and compositional characterizations of Pd@Ni-3/TiO₂ and Pd@NiO-3/TiO₂. (a) and (e) Low-magnification HAADF-STEM images; (b) and (f) high-magnification TEM images; (c) and (g) HAADF-STEM images and corresponding elemental mappings of (a), (b) and (c) 5 wt% Pd@Ni-3/TiO₂, and (e), (f), (g) and (h) 5 wt% Pd@NiO-3/TiO₂, respectively. EDS line-scan analysis of (d) 5 wt% Pd@Ni-3/TiO₂ and (h) 5 wt% Pd@NiO-3/TiO₂ across the blue arrow in the insets of (c) and (g), respectively. The red dotted line in (f) indicates the interface structure between the Pd core and the NiO shell.
The optimization of catalysts and reaction conditions. The optimization of catalysts for achieving high H$_2$O$_2$ productivity. The effects of (a) thermal treatment with different temperature and calcined time, (b) the reaction time, (c) the Pd loadings and (d) the support materials for the direct H$_2$O$_2$ synthesis.

Figure 2. The optimization of catalysts and reaction conditions. The optimization of catalysts for achieving high H$_2$O$_2$ productivity. The effects of (a) thermal treatment with different temperature and calcined time, (b) the reaction time, (c) the Pd loadings and (d) the support materials for the direct H$_2$O$_2$ synthesis.

Figure 3. The productivity of sequential H$_2$O$_2$ synthesis and TEM image after sequential H$_2$O$_2$ synthesis. (a) Sequential H$_2$O$_2$ synthesis reactions over 5 wt% Pd@NiO-$2$/TiO$_2$, 5 wt% Pd@NiO-$3$/TiO$_2$ and 5 wt% Pd/TiO$_2$. (b) TEM image of 5 wt% Pd@NiO-$3$/TiO$_2$ after sequential H$_2$O$_2$ synthesis.

Pd@Ni-$3$/TiO$_2$ that calcined at 300°C for 1 h reduced dramatically to 4 mol/(kg$_{cat}$ h). In order to figure out the interesting observations, detailed characterizations of the 5 wt% Pd@Ni-$3$/TiO$_2$ calcined at 250 and 300°C were carried out.

The reason for the significantly different catalytic activity of 5 wt% Pd@Ni-$3$/TiO$_2$ catalysts calcined at 250 and 300°C was first characterized by TEM. Supplementary Fig. 3a, available as Supplementary Data at NSR online, clearly shows that the intermediate void was formed when the 5 wt% Pd@Ni-$3$/TiO$_2$ was calcined at 300°C for 1 h. The formation of a NiO shell was confirmed by STEM-EDS elemental mappings (Fig. 3b). When it was calcined at 250°C for 1 h, the distinct interface structure between the Pd core and the porous NiO shell was clearly observed (Fig. 1e and f). The element distribution was also investigated by STEM-EDS elemental mappings and EDS line-scan analysis, where the Pd core was encapsulated by the NiO shell (Fig. 1c, d, g and h). Therefore, these two different catalysts were denoted as 5 wt% Pd@void@NiO-$3$/TiO$_2$ and 5 wt% Pd@NiO-$3$/TiO$_2$, respectively. In the thermal treatment, the pristine Ni shell was exposed to oxygen so that the porous NiO shell was formed as a priority. When outward diffusion of the Ni is faster than the inward diffusion of the Ni at the elevated temperature, the void appears at the inside of the core/shell interface and then grows up until the hollow interior structure forms due to the Kirkendall effect [30–33].

The creation of a porous NiO shell is beneficial for exposing Pd active sites and thus enhancing the productivity of H$_2$O$_2$ as the reaction time is prolonging to 1 h (Supplementary Table 1, entry 3 and Supplementary Table 2, entry 2, available as Supplementary Data at NSR online). Noticeably, the H$_2$O$_2$ hydrogenation activity of 5 wt% Pd@NiO-$3$/TiO$_2$ was much lower than that of 5 wt% Pd@void@NiO-$3$/TiO$_2$ (Supplementary Table 2, entries 2 and 4, available as Supplementary Data at NSR online). Compared with 5 wt% Pd@NiO-$3$/TiO$_2$, the void space in 5 wt% Pd@void@NiO-$3$/TiO$_2$ is beneficial to expose more of the Pd core surface, but hardly any contact interface between the Pd core and the NiO shell, which can be highly active for H$_2$O$_2$ synthesis and but also highly active for its subsequent hydrogenation and decomposition. Therefore, 5 wt% Pd@void@NiO-$3$/TiO$_2$ exhibits high activity for H$_2$O$_2$ degradation as well as favoring a short reaction time for higher H$_2$O$_2$ productivity (Supplementary Table 2, entries 3 and 4, available as Supplementary Data at NSR online). From the significantly different performances between 5 wt% Pd@NiO-$3$/TiO$_2$ and 5 wt% Pd@void@NiO-$3$/TiO$_2$, it is apparent that the created interface structure between the Pd core and the NiO shell is essential to promote productivity and low hydrogenation activity.

To further evaluate the correlation between the NiO shell and its catalytic performance, other Pd@NiO-$x$/TiO$_2$ ($x = 1$, 2 and 4) were also prepared by the same thermal treatment as executed on the 5 wt% Pd@Ni-$3$/TiO$_2$. The STEM-EDS elemental mappings and EDS line-scan analysis show that the thickness of the NiO shell increased from ~2 to ~7 nm as the Ni content increased (Supplementary Figs 4–6, available as Supplementary Data at NSR online). In addition, 5 wt% Pd/TiO$_2$ without the NiO shell was also prepared for H$_2$O$_2$ synthesis through acid etching of 5 wt% Pd@Ni-$3$/TiO$_2$ (details in Supporting Information). The TEM image shows that the size of the NPs decreases to...
around 15 nm due to the removal of the NiO shell (Supplementary Fig. 7a, available as Supplementary Data at NSR online). The STEM-EDS elemental mappings and EDS line-scan analysis show a very strong Pd signal but negligible Ni signal, confirming that the Ni shell was removed by the acid (Supplementary Fig. 7c, d available as Supplementary Data at NSR online). As shown in Table 1, 5 wt% Pd/TiO2 exhibits rather low productivity (12 mol/(kgcat h)) and selectivity (41%) relative to Pd@NiO-x/TiO2 catalysts, indicating that the NiO shell plays a significant role in promoting the catalytic performance of H2O2 synthesis. Moreover, among the 5 wt% Pd@NiO-x/TiO2 catalysts, 5 wt% Pd@NiO-3/TiO2 exhibits improved H2O2 productivity and the best selectivity over 5 wt% Pd@NiO-1/TiO2 and 5 wt% Pd@NiO-2/TiO2. Unexpectedly, the catalytic performance was not improved as the NiO shell thickness further increased. The 5 wt% Pd@NiO-4/TiO2 displays relatively lower H2O2 productivity and selectivity than the 5 wt% Pd@NiO-3/TiO2 even if it has the thickest NiO shell. Furthermore, these catalysts were also tested for H2O2 hydrogenation with varying concentrations of H2O2. As shown in Supplementary Table 3, available as Supplementary Data at NSR online, 5 wt% Pd/TiO2 shows much higher H2O2 hydrogenation activity than 5 wt% Pd@NiO-x/TiO2 catalysts due to the loss of the NiO shell. Noticeably, 5 wt% Pd@NiO-3/TiO2 shows no hydrogenation activity in a low concentration of H2O2 (2 wt%), whereas 5 wt% Pd@NiO-1/TiO2 and 5 wt% Pd@NiO-2/TiO2 show substantially higher H2O2 degradation activity at all concentrations studied. Especially, the H2O2 hydrogenation of 5 wt% Pd@NiO-4/TiO2 is relatively higher than that of 5 wt% Pd@NiO-3/TiO2. From the above results, we can conclude that the catalytic performance of 5 wt% Pd@NiO-x/TiO2 is not proportional to the NiO thickness. Because metallic Pd is more effective for H2O2 synthesis and hydrogenation than oxidized Pd, the surface feature of the catalyst, in particular the oxidation state of the active core, plays a crucial role in obtaining high selectivity as well as activity. Therefore, it is reasonable to speculate that, in addition to the thickness effect of the NiO shell, there should be subtle differences on the Pd core surface of different 5 wt% Pd@NiO-x/TiO2 (x = 1, 2, 3 and 4).

Hence, the surface structures of all these catalysts were further analysed by XPS (Supplementary Table 4, available as Supplementary Data at NSR online). XPS spectra of the pristine 5 wt% Pd@Ni-x/TiO2 reveal that the Ni content on the surface is very high, with only metallic Pd observed (Supplementary Table 4, entries 1–4, available as Supplementary Data at NSR online). After thermal treatment, Ni is still the dominating species in 5 wt% Pd@NiO-x/TiO2 but the Pd/Ni ratio decreases obviously in 5 wt% Pd@NiO-3/TiO2 and 5 wt% Pd@NiO-4/TiO2, due to the formation of a thicker NiO shell. In addition, Pd2+ is observed in all the Pd@NiO-x/TiO2, although Pd3+ is still the major form after thermal treatment (Supplementary Table 4, entries 5–8, available as Supplementary Data at NSR online). It is worth noting that the Pd3+/Pd2+ ratio of 5 wt% Pd@NiO-x/TiO2 (x = 1, 2 and 3) is about 3 (Supplementary Table 4, entries 5–7, available as Supplementary Data at NSR online). However, it is close to 9 in 5 wt% Pd@NiO-4/TiO2 (Supplementary Table 4, entry 8, available as Supplementary Data at NSR online), ascribed to the thick NiO shell that hinders the oxidation of the Pd core during thermal treatment. In addition, Pd2+ is regarded as more selective but less active towards H2O2 synthesis than that of the metallic Pd due to the low propensity of H2O2 on Pd2+. From the above evidence, the reduced percentage of Pd2+ on the surface of the Pd core can be responsible for the lowest catalytic performance of 5 wt% Pd@NiO-4/TiO2 among the different 5 wt% Pd@NiO-x/TiO2 catalysts. Therefore, in the Pd@NiO-x/TiO2 system, the unique interface structure with the appropriate Pd3+/Pd2+ ratio and the desirable NiO shell, which make the active metallic Pd core co-modified by Pd2+ and NiO, is essential to improve catalytic performance for the direct synthesis of H2O2 (Scheme 1).

To this end, we further optimized the conditions for direct H2O2 synthesis by tuning the different parameters, such as thermal treatment, reaction time, mass loading, as well as support. As shown in Fig. 2, when the calcined temperature decreased to 200°C for 1 h, 5 wt% Pd@NiO-3/TiO2 exhibits lower productivity (7 mol/(kgcat h)) than that at 250°C for 1 h (89 mol/(kgcat h)). The productivity of H2O2 was not improved by changing the calcined temperature to

### Table 1. Direct H2O2 synthesis and selectivity results of 5 wt% Pd@NiO-x/TiO2.

| Entry | Catalyst | H2O2 productivity (mol/(kgcat h)) | H2O2 selectivity (%) |
|-------|----------|---------------------------------|----------------------|
| 1     | 5 wt% Pd@NiO-1/TiO2 | 28 | 62 |
| 2     | 5 wt% Pd@NiO-2/TiO2 | 68 | 82 |
| 3     | 5 wt% Pd@NiO-3/TiO2 | 89 | 91 |
| 4     | 5 wt% Pd@NiO-4/TiO2 | 44 | 75 |
| 5     | 5 wt% Pd/TiO2 | 12 | 41 |

All catalysts were calcined in air at 250°C for 1 h before catalytic investigations. H2O2 productivity was determined under the following reaction conditions: 5% H2/N2 (3.6 MPa) and 99% O2 (0.4 MPa), 8.5 g solvent (2.9 g HPLC water, 5.6 g MeOH), 0.0025 g catalyst, 2°C, 1200 rpm and 1 h.

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Scheme 1. Schematic illustration showing the activity and selectivity toward H₂O₂ synthesis of 5 wt% Pd@Ni-3/TiO₂, 5 wt% Pd@NiO-x/TiO₂ (x = 1, 2, 3 and 4), 5 wt% Pd@void@Ni-3/TiO₂ and 5 wt% Pd/TiO₂.

0.5 h (29 mol/(kg cat h)) and 2 h (25 mol/(kg cat h)) (Fig. 2a). The reaction time of the direct H₂O₂ synthesis is another critical factor. When the reaction time changes from 0.5 to 2 h, the productivity of H₂O₂ exhibits a volcano shape. When the reaction time reaches 1 h, the 5 wt% Pd@NiO-3/TiO₂ exhibits the best productivity of H₂O₂ (Fig. 2b). Moreover, Pd loading was also taken into consideration, which shows that the 5 wt% Pd loading is better than that of the 1 (5 mol/(kg cat h)), 3 (32 mol/(kg cat h)) and 7 wt% (22 mol/(kg cat h)) (Fig. 2c). In direct H₂O₂ synthesis, the support is another key factor that affects the catalytic performance. Therefore, we also prepared different 5 wt% Pd@NiO-3/supports for direct H₂O₂ synthesis (Supplementary Fig. 8, available as Supplementary Data at NSR online). We can see that, besides TiO₂, CeO₂ (49 mol/(kg cat h)) also exhibits relatively high activity for H₂O₂ direct synthesis, while the other supports, such as Al₂O₃ (6.2 mol/(kg cat h)), ZrO₂ (4.8 mol/(kg cat h)), ZnO (4.1 mol/(kg cat h)) and C (5.4 mol/(kg cat h)) (Fig. 2d), are not suitable for this Pd-NiO system toward direct H₂O₂ synthesis.

The catalytic durability of 5 wt% Pd@NiO-x/TiO₂ (x = 2 and 3) and 5 wt% Pd/TiO₂ was also evaluated. After running the reaction for six cycles, we found that 5 wt% Pd@NiO-x/TiO₂ can retain high productivity for direct H₂O₂ synthesis, while the 5 wt% Pd/TiO₂ lost most of its H₂O₂ productivity after four cycles (Fig. 3a). The excellent recyclability of 5 wt% Pd@NiO-x/TiO₂ can be by virtue of the encapsulation of the Pd core by the NiO shell, which immobilizes the Pd core. In contrast, the low stability of 5 wt% Pd/TiO₂ is probably due to the lack of a unique interface structure between the Pd core and the NiO shell, which inevitably results in leaching and/or aggregation of Pd NPs during the reaction cycles. To verify this assumption, ICP-MS was carried out to determine the Pd content variation of 5 wt% Pd@NiO-3/TiO₂ and 5 wt% Pd/TiO₂ after cycles. The results show negligible loss of Pd (4 ppb) of 5 wt% Pd@NiO-3/TiO₂ after six cycles, implying nearly no variation in the composition of 5 wt% Pd@NiO-3/TiO₂, while a high amount of Pd leaching (2 ppm) occurred on 5 wt% Pd/TiO₂. This observation was also confirmed by the TEM images and EDS of these catalysts after reaction cycles, where the morphology and compositions of 5 wt% Pd@NiO-2/TiO₂ and 5 wt% Pd@NiO-3/TiO₂ were largely maintained while the aggregated feature was observed for 5 wt% Pd/TiO₂ (Fig. 3b and Supplementary Fig. 9, available as Supplementary Data at NSR online).

To simulate the proposed catalytic reaction of H₂O₂ synthesis, we built the local interface (IF) structure of the Pd/NiO (core/shell) system with bonding along the (100) surface for a simplified straightforward illustration (Fig. 4a). The fcc-Pd and rocksalt NiO (simple cubic) have the least lattice mismatch on the (100) surface of each other. The Pd sites at the interface are bonded with O epitaxially expanded from the NiO shell layer. The interface without a cavity is an anisotropic metallic system exhibiting anti-bonding orbitals while the NiO and Pd layers present bonding orbitals, respectively (Fig. 4b). The Pd-4d orbital levels are predominantly covering the highest occupied bands near the Fermi level (E_F, 0 eV), implying a high tendency to be electron-rich and more active in transfer. Moreover, the difference of d-orbital levels has indeed reflected the differentiation of electronic activity (Fig. 4c) between Pd and Ni sites from the bulk and interface (IF), respectively, which means the interfacial homogenization of the d-electron distribution has been inhibited. The peak of the Pd-4d orbital at the IF is obviously lower than those in the bulk, indicating that the activity of the Pd-4d-electrons at the interface has been suppressed by the presence of the O-sites via interfacing over-coordinated Pd–O bonding. In line with experimental observation, the choice of porous NiO is understandable, as NiO with a cavity or wall in the local morphology can exhibit more selectivity to form intermediate Ni–(O–O)* (∗ denotes the absorbing state) bonding without O–O cleavage, and is more energetically favorable to the Pd–(O–O)*. Therefore, it is necessary to further investigate the IF with a NiO cavity.
Figure 4. Interface structures and the electronic properties. (a) The local atomic structure and charge densities of bonding and anti-bonding $d$-orbitals of the interface (IF) region, based on cavity-free NiO and Pd (100) fully oxidized. (b) The electronic band structure and total density of states (TDOSs) of the IF model without NiO cavity. (c) The partial density of states (PDOSs) of Pd-$4d$ and Ni-$3d$ orbital levels from the bulk and IF regions according to the IF model without NiO cavity. (d) The local atomic structure of the IF model with NiO cavity with coexistence of lower-coordinated Pd and Ni sites within the cavity wall. (e) The charge densities of bonding and anti-bonding $d$-orbitals of the cavity region near the IF. (f) The PDOSs of Pd-$4d$ and Ni-$3d$ orbital levels from different sites in the bulk and those within the cavity region. (Bonding orbital = blue surface, anti-bonding orbital = green surface, Pd = dark green, Ni = light blue, O = red and H = white).

(Fig. 4d). The charge densities of the bonding and anti-bonding orbitals show that the NiO cavity at the IF gives more contrast and directional distribution than the bulk NiO (Fig. 4e). We further investigated the partial density of states (PDOSs) of Ni-$3d$ and Pd-$4d$ orbital levels (Fig. 4f). The Ni-$3d$-state within the cavity stays at higher levels next to the $E_F$ and possesses the largest weight in the PDOS compared to the Ni-$3d$ at the IF bonded with O or Pd sites, and those in the bulk. Accordingly, the Ni sites within the cavity show relatively higher electronic activity than those from the other regions. Similarly, we also found that the 4d orbital level of the Pd site exposed to the cavity vacuum has the highest peak and weight in the PDOSs. Thus, the Pd exposed to the cavity vacuum and lower-coordinated Ni sites on the cavity wall synchronously match the criteria of the highly selective and direction $H_2O_2$ synthesis, and can actively adsorb the $H_2$ and $O_2$, respectively, without interferences with each other based on the differentiated energy barrier of $d$-electron transfers at the interface.

To understand the related mechanism, we present the evolutions of the transition energy
profile regarding the aforementioned reaction. The route-map of the synthesis is illustrated in terms of the reaction free energy diagram ($\Delta G$), formation energy and the chemisorption energy, as shown in Fig. 5a and b, respectively. Within this cavity region (Fig. 5c), the most stable configuration for the O$_2$ location on the cavity wall of the NiO is the bridge-bonding between two adjacent Ni sites, with the O–O bond along the diagonal line of the Ni-O local square motif in the NiO lattice, while this configuration is rather unstable for H$_2$ as contrasted in the formation energies (Fig. 5b). The H$_2$ prefers to be adsorbed on the Pd surface that is exposed to the cavity vacuum. In addition, high 4d orbital electronic activity of the lower coordinate Pd site will further induce the bond cleavage of H–H and individually forms of Pd–H–Pd bonding at the bridge site within the Pd square lattice. However, the most stable location for the H is the hollow site on the Pd (100) surface. Spontaneous
The evolution of absorption sites of H takes place from the bridge site to the hollow site driven by the energetic downhill process, after the H–H cleavage. The charge transfers for both H and O2 with the cavity region at the interface are more energetically favorable. With the Coulombic attractive potential, the 2H+ will have a fast recombination with O2− and react into the H2O2 finally. Generally, the energetic interval between the reacting state and the thermoneutral line (∆G = 0 eV) moderately determines the absorption and desorption abilities of species molecules—the deeper the stronger absorption, but rather weaker in desorption, and vice versa. The direction synthesis of H2O2 near the cavity wall within the NiO layer (∆G = −0.048 eV) shows uniquely high performance to continuously yield H2O2 compared with the other alloy systems such as Pd (∆G = −3.30 eV) or PdAg (∆G = −0.068 eV). This arises because of the energetic contrast in the formation of energy between the surface and the H2O2 molecule. Therefore, the calculations show that the Pd@porous NiO system has rather high performance for the direct synthesis of H2O2 with high selectivity via morphology control on the interface together with an efficient desorption. The superiority in selectivity is achieved by a spontaneous bond scission of H–H and charge transfer from O2 to O2− within the cavity of the NiO interfacing with the Pd surface.

CONCLUSIONS

In summary, a unique class of supported Pd@NiO-x core–shell catalysts have been successfully constructed as highly efficient catalysts toward direct H2O2 generation. By tuning the catalyst composition and the reaction conditions, the optimized 5 wt% Pd@NiO-3/TiO2 exhibited high activity, superior selectivity, low degradation activity and excellent stability toward direct H2O2 generation. The presence of partially oxidized Pd on the surface of the Pd core as well as the unique NiO shell makes the active Pd core co-modified by oxidized Pd and NiO, which is effective to prevent H2O formation and guarantees the high selectivity of direct H2O2 synthesis. The theoretical investigation revealed that the enhanced performance is due to the cavity-contained unique interface structure between the Pd core and the porous NiO shell, which suppresses the overbinding between the Pd core and (O−O)∗ via modifications of the Pd core surface electronic properties. The present work reported here highlights the importance of surface and interface engineering of Pd-based catalysts for direct H2O2 synthesis with largely enhanced activity and selectivity.

METHODS

Preparation of Pd@Ni-x core–shell nanoparticles (NPs)

In a typical synthesis of Pd@Ni-3 core–shell NPs, 3.5 mg Pd(acac)2, 7.5 mg Ni(HCO2)2·2H2O, 36 mg AA, 2.5 mL OAm and 2.5 mL ODE were added into a vial (volume: 30 mL). After the vial had been capped, the mixture was ultrasonicated for around 30 min. The resulting homogeneous mixture was heated from room temperature to 160°C for around 0.5 h and kept at 160°C for 5 h in an oil bath. After cooling to room temperature, the colloidal products were collected by centrifugation and washed three times using cyclohexane/ethanol (v:v = 1:9) mixture. For the synthesis of Pd@Ni-1, Pd@Ni-2 and Pd@Ni-4 core–shell NPs, all the conditions are similar to those of the Pd@Ni-3 core–shell NPs except by changing the dosage of Ni(HCO2)2·2H2O to 5, 10 and 12 mg, respectively.

Preparation of 5 wt% Pd@Ni-x/TiO2 and 5 wt% Pd@NiO-x/TiO2

In a typical preparation of 5 wt% Pd@Ni-x/TiO2, the as-prepared Pd@Ni-x core–shell NPs were dispersed in 15 mL chloroform. TiO2 was then added to the solution with stirring. After stirring for 3 h, the products were collected by centrifugation and dried in 60°C for 5 h. All the catalysts had the Pd loading of 5 wt% unless otherwise stated. The obtained 5 wt% Pd@Ni-x/TiO2 were then calcined in static air at different temperatures with a ramp rate of 10°C min−1 for a desirable time to generate the 5 wt% Pd@NiO-x/TiO2.

Preparation of 5 wt% Pd/TiO2

In a typical preparation of 5 wt% Pd/TiO2, 5 wt% Pd@Ni-3/TiO2 was dispersed in the diluted HCl solution (20 wt%) and sonicated for 30 min. The products were collected by centrifugation and then washed five times using H2O.

Catalytic measurements

H2O2 synthesis and degradation were performed using a Parr Instruments stainless steel autoclave with a nominal volume of 50 mL and a maximum working pressure of 14 MPa. For the standard H2O2 synthesis, the autoclave was charged with the catalyst (0.0025 g unless otherwise stated), solvent (5.6 g MeOH and 2.9 g H2O, both high performance liquid chromatography (HPLC) grade). The charged autoclave was then purged three times with
O$_2$ (0.2 MPa) before filling with O$_2$ to a pressure of 0.4 MPa at room temperature, and then filled with 5% H$_2$/N$_2$ (3.6 MPa) at a total pressure of 4.0 MPa. All experiments were carried out at the desired temperature of 2°C and under stirring (1200 rpm) for 30 min unless otherwise stated. The H$_2$O$_2$ productivity was determined by titrating aliquots of the final solution with acidified Ce(SO$_4$)$_2$ (0.01 M) in the presence of two drops of ferroin indicator. The Ce(SO$_4$)$_2$ solutions were standardized against (NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O using ferroin as indicator. Gas analysis was performed by gas chromatography (Shiweipx GC-7806) equipped with a GDX-502 column connected to a thermal conductivity detector. Conversion of H$_2$ was calculated by gas analysis before and after reaction.

H$_2$O$_2$ hydrogenation was carried out in a similar manner to the H$_2$O$_2$ synthesis, but in the absence of O$_2$ in the gas stream and with the presence of varying concentrations of H$_2$O$_2$ (2, 4 and 8 wt%) in the solvent (2 wt%: 0.56 g 30 wt% H$_2$O$_2$; 2.34 g HPLC water, 5.6 g CH$_3$OH; 4 wt%: 1.13 g 30 wt% H$_2$O$_2$, 1.77 g HPLC water, 5.6 g CH$_3$OH; 8 wt%: 2.27 g 30 wt% H$_2$O$_2$, 0.63 g HPLC water, 5.6 g CH$_3$OH). The decrease in H$_2$O$_2$ concentration (as determined from measurements taken before and after the reaction) is attributed to a combination of H$_2$O$_2$ hydrogenation and decomposition. H$_2$O$_2$ selectivity was calculated according to the following equation:

\[
\text{Selectivity} = \frac{\text{moles of H}_2\text{O}_2 \text{formed}}{\text{moles of H}_2 \text{reacted}} \times 100\%
\]

### Calculations on the Pd-4d orbital feature and electronic structures

We used the CASTEP code to perform our DFT+U calculations [34]. In this framework, we used the rotationally invariant (Anisimov-type) DFT+U functional [35] and the Hubbard U parameter self-consistently determined for the psuedized Pd-4d and Ni-3d orbital by our newly devised two-way crossover linear response method [36,37], which has been already successfully reflecting that the electron–electron Coulomb potential for semi-core orbitals should be considered when using DFT+U [36,37]. The geometry optimization used the Broyden-Fletcher-Goldfarb-Shannon (BFGS) algorithm throughout all calculations.

The PBE functional was chosen for PBE+U calculations with a kinetic cutoff energy of 750 eV, with the valence electron states expressed in a plane-wave basis set. The ensemble DFT (EDFT) method of Marzari et al. [38] was used for convergence. The supercell of the fcc-Pd (100) surface model was chosen as 3 × 3 × 1 with sizes of 108 atoms (i.e. Pd$_{108}$) and is established at six layers thick. The vacuum thickness is set to 15 Å. We only allowed the top two layers to be varied freely. The reciprocal space integration was performed using the mesh of 2 × 2 × 1 with a Gamma-center-off, which was self-consistently selected for total energy minimization [39]. With these special k-points, the total energy was converged to less than 5.0 × 10$^{-7}$ eV per atom. The Hellmann-Feynman forces on the atom are converged to less than 0.001 eV/Å. Since the rocksalt NiO (100) has a relatively small lattice mismatch to the Pd (100), we built the NiO shell layer by choosing the same lattice parameters. To model the cavity area of the as-synthesized porous NiO shell layer, we create a vacant area with a volume of 8.62 × 6.04 × 8.62 Å$^3$. This porous NiO shell layer was set to four layers thick. Since the interface model has two faces in bonding, we set the one face of the Pd (100) facing the cavity of the NiO as partially and moderately bonded by O-sites, and the other face as fully oxidized by the O-sites from the NiO shell layer, respectively.

As for the norm-conserving pseudopotentials, these can reflect electron behavior for outer shell valence electrons for S-matrix $= 1$ and provide a better response in DFT+U calculations, especially for the calculations of defects [40–42]. In addition, the almost identical values of the U parameters for both norm-conserving and ultra soft pseudopotentials obtained in our method indicate that the obtained value has an intrinsic physical meaning for the studied objects. Meanwhile, this will help us to reflect the all-electron behavior of the valence electrons especially for the subtle effect of the 4$d$ electrons and outer 5$s$ electrons. The Pd and Ni norm-conserving pseudopotentials were generated using the OPIUM code in the Kleinman-Bylander projector form [43] and the non-linear partial core correction [44] and a scalar relativistic averaging scheme [45] were used to treat the spin-orbital coupling effect. For this treatment, we similarly choose the non-linear core correction technique for correcting the valence-core charge density overlapping in such heavy fermions elements. In particular, the (4$d$, 5$s$, 5$p$) states were treated as the valence states of both Pd and the (3$d$, 4$s$, 4$p$) for Ni atoms. The pseudopotentials were optimized by the RRKJ method [46].

Prior to ab-initio predictions of the Hubbard U on orbitals, the PBE functional calculations were used to optimize the geometries and lattice parameters of all Pd and NiO structural models. We used this well-developed pseudopotential technique before Hubbard U determination due to the reliability of DFT for the structural optimization of...
compound solids even with 4f or 5f orbitals [37] and ultrasoft pseudopotentials [36,42]. More importantly, as shown by the little difference in the DFT and DFT+U calculated lattice parameters, the electrons on semi-core orbitals can be treated as valence electrons, but the U parameter must be determined more carefully [36,37,42].

With the above preliminary structure determination, the corresponding electronic structure was further estimated using the anisimov-type rotational invariant DFT+U method with the CASTEP code [35]. We previously devised a method to ab-initi ally determine the semi-core d/f orbital energy in order to further self-consistently correct the electronic structures from routine first-principles calculations [36,37]. Our work shows that the method is particularly valid for those materials synthesized via extremely physical or chemical conditions [36,37]. The Hubbard U parameter has been self-consistently determined based on our previously developed method [36,37]. For all of the electronic structure calculations in the Pd@NiO models, we used self-consistent determination for the U correction on the localized 4d orbitals to correct the on-site Coulomb energy of the electron spurious self-energy. By that method, the Hubbard U parameters on the completely filled shell of 4d\(^ {10}\) orbitals of the Pd was self-consistently determined to be U\(_d\) = 10.13 eV and U\(_f\) = 5.58 eV for Ni-3d\(_8\). Meanwhile, to stabilize the hole states induced by the O-2p orbitals, we self-consistently chose U\(_p\) = 4.23 eV for O-2p\(_{4s}\) orbitals in the anti-ferromagnetic NiO lattice, based on our devised linear response method [36,37]. With our self-consistent determination process, the on-site Hubbard U potential parameters for the Pd-4d, Ni-3d and O-2p orbitals have been determined in Supplementary Fig. 10, available as Supplementary Data at NSR online.

**SUPPLEMENTARY DATA**

Supplementary data are available at NSR online.

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