

## Bifunctional Catalysts | Hot Paper |

# Metal–Organic Framework (MOF)-Derived Electron-Transfer Enhanced Homogeneous PdO-Rich $\text{Co}_3\text{O}_4$ as a Highly Efficient Bifunctional Catalyst for Sodium Borohydride Hydrolysis and 4-Nitrophenol Reduction

Shasha Dou<sup>+, [a]</sup>, Shuqing Zhou<sup>+, [a]</sup>, Hexiu Huang<sup>, [a]</sup>, Puxuan Yan<sup>, [a]</sup>, Elvis Shoko<sup>, [b]</sup>,  
Tayirjan Taylor Isimjan<sup>,\* [c]</sup> and Xiulin Yang<sup>,\* [a]</sup>

**Abstract:** Developing a bifunctional catalyst with low cost and high catalytic performance in  $\text{NaBH}_4$  hydrolysis for  $\text{H}_2$  generation and selective reduction of nitroaromatics will make a significant impact in the field of sustainable energy and water purification. Herein, a low-loading homogeneously dispersed Pd oxide-rich  $\text{Co}_3\text{O}_4$  polyhedral catalyst (PdO- $\text{Co}_3\text{O}_4$ ) with concave structure is reported by using a metal–organic framework (MOF)-templated synthesis method. The results show that the PdO- $\text{Co}_3\text{O}_4$  catalyst has an exceptional turnover frequency ( $3325.6 \text{ mol}_{\text{H}_2} \text{ min}^{-1} \text{ mol}_{\text{Pd}}^{-1}$ ), low activation energy ( $43.2 \text{ kJ mol}^{-1}$ ), and reasonable reusability in cat-

alytic  $\text{H}_2$  generation from  $\text{NaBH}_4$  hydrolysis. Moreover, the optimized catalyst also shows excellent catalytic performance in the  $\text{NaBH}_4$  selective reduction of 4-nitrophenol to 4-aminophenol with a high first-order reaction rate of approximately  $1.31 \text{ min}^{-1}$ . These excellent catalytic properties are mainly ascribed to the porous concave structure, mono-dispersed Pd oxide, as well as the unique synergy between PdO and  $\text{Co}_3\text{O}_4$  species, which result in a large specific surface area, high conductivity, and fast solute transport and gas emissions.

## Introduction

Metal–organic frameworks (MOFs) are attracting significant attention in the field of material science because of their high surface area, tunable porosities, and specific coordinated metal centers.<sup>[1]</sup> Additionally, these unique features also lead to the potential application of MOFs as pyrolysis precursors for various heterogeneous catalysts.<sup>[2]</sup> Depending upon the pyrolysis and post-treatment conditions, MOF precursors could result in bulk or supported composites bearing extraordinary catalytic performances.<sup>[3]</sup> This type of MOF-templated synthesis (MOFTS), generally performed either under air or inert atmosphere, leads to highly dispersed metal species encapsulated by

a porous carbon matrix thereby minimizing catalyst sintering. Notably, the MOF carbonization under an inert environment at high temperatures often results in highly porous carbon cages that are capable of hosting well-dispersed metal species.<sup>[4]</sup> As a result, not only is the electrical conductivity of these materials improved compared with similar composites prepared under air, but also the electrical interaction between various components is enhanced. Therefore, the main current applications of MOFTS catalysts are mostly focused on electrochemical research, including electrochemical water splitting, energy storage, and energy conversion, where the enhanced electrical properties play an important role.<sup>[5]</sup> Moreover, recent progress on the MOFTS technique has been extended to the field of heterogeneous composite catalysis because of the excellent compatibility of MOFs with both organic and inorganic materials. This work has led to the synthesis of a wide range of nanocomposites achieving diverse spatial morphologies and catalytic activities.<sup>[6]</sup> Nevertheless, most of the works are focused on a single functional catalyst. Multifunctional catalysts prepared through MOFTS methods have not yet been widely studied. However, progress in this direction is now emerging in bifunctional catalysts. For example, Zhang et al. synthesized a unique 3D hierarchical rod-like structure by using a MOF template that exhibited better electrocatalytic activities for oxygen reduction and oxygen evolution reactions (ORR and OER, respectively) than that of commercial Pt/C and  $\text{RuO}_2$ , respectively. Additionally, the rechargeable Zn-air batteries based on their catalyst showed initial charge and discharged potentials at 1.81 and

[a] S. Dou,<sup>+</sup> S. Zhou,<sup>+</sup> H. Huang, P. Yan, Prof. Dr. X. Yang  
Guangxi Key Laboratory of Low Carbon Energy Materials  
School of Chemistry and Pharmaceutical Sciences  
Guangxi Normal University, Guilin 541004 (China)  
E-mail: xlyang@gxnu.edu.cn

[b] Dr. E. Shoko  
Department of Chemistry, University of Liverpool, Liverpool L69 3BX (UK)

[c] Dr. T. T. Isimjan  
Saudi Arabia Basic Industries Corporation (SABIC) at  
King Abdullah University of Science and Technology (KAUST)  
Thuwal 23955-6900 (Saudi Arabia)  
E-mail: isimjant@sabic.com

[\*] These authors contributed equally to this work.

 Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:  
<https://doi.org/10.1002/chem.202003793>.

1.28 V (2 mA cm<sup>-2</sup>), along with excellent cycling stability.<sup>[5]</sup> As usual, the focus is still on the electrochemistry.

The MOFTS catalysts also show remarkable performance for hydrogen production from NaBH<sub>4</sub> hydrolysis. Although hydrogen is considered the most promising clean energy source of the 21st century, there are still major barriers to its large-scale adoption related to its safe transportation and storage.<sup>[7]</sup> NaBH<sub>4</sub> has been extensively investigated as a hydrogen storage material because of its low molecular weight, high hydrogen content (10.57 wt%), and high stability in solution.<sup>[8]</sup> Meanwhile, there are reports showing that the MOFTS catalysts can also catalyze nitrophenols (NPs) to aminophenols (APs).<sup>[9]</sup> As carcinogenic pollutants, NPs are extremely toxic to the environment, and they have a devastating effect on the kidney, liver, and the central nervous system of both animals and humans.<sup>[10]</sup> Conversion of NPs to some other useful intermediate chemicals such as APs is always highly desired. The most effective approach to reducing NPs is to use catalytic NaBH<sub>4</sub> reduction.<sup>[11]</sup> There are mainly three types of nano-catalysts used in this process, including noble metals,<sup>[12]</sup> non-noble metals,<sup>[13]</sup> and carbon materials.<sup>[14]</sup> To the best of our knowledge, there is no report on the bifunctional feature of MOFTS catalysts, where it can be used both in NaBH<sub>4</sub> hydrolysis and NPs reduction.

Setting this goal in our mind, we developed a concave structure of Pd oxide-decorated Co<sub>3</sub>O<sub>4</sub> polyhedra (PdO-Co<sub>3</sub>O<sub>4</sub>) with low Pd loading (0.9 wt% Pd) by using a MOFTS method. This was followed by a controllable two-step calcination treatment. The crystal structure, microscopic morphology, and chemical state of the composites were analyzed in detail, among which scanning electron microscopy (SEM) showed the concave structure, transmission electron microscopy (TEM) mapping confirmed the uniform distribution of elements, and X-ray photoelectron spectroscopy (XPS) proved the strong interaction between PdO and Co<sub>3</sub>O<sub>4</sub> species. The catalytic performance indicates that the designed PdO-Co<sub>3</sub>O<sub>4</sub> catalyst has a high specific H<sub>2</sub> generation rate (6300.5 mL<sub>H<sub>2</sub></sub> min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>), turnover frequency (3325.6 mol<sub>H<sub>2</sub></sub> min<sup>-1</sup> mol<sub>Pd</sub><sup>-1</sup>), and good reusability. In addition, the catalyst also exhibits an excellent reduction performance of 4-NPs to 4-APs with a first-order kinetic rate of 1.31 min<sup>-1</sup>, which is more than 7-fold and 17-fold faster than conventional Pd/C (0.172 min<sup>-1</sup>) and Pt/C (0.077 min<sup>-1</sup>) catalysts, respectively.

## Experimental Section

### Synthesis of Pd-Co-MOF

All chemicals were analytical grade and used without further purification. In a typical synthesis, a mixture of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.62 g) and Pd(acac)<sub>2</sub> (0.08 g) was dissolved in methanol (80 mL) and then added to methanol (80 mL) containing 2-methylimidazole (2-MI, 3.70 g). The resulting purple solution was aged at room temperature for 24 h. After that, the purple powder was collected by centrifugation, washed with methanol several times, and finally dried at 70 °C overnight to obtain the Pd-Co-MOF crystals.

### Synthesis of Pd-Co-NC and PdO-Co<sub>3</sub>O<sub>4</sub>

The as-prepared Pd-Co-MOF crystals (100 mg) were placed in a tube furnace, heated to 435 °C with a heating rate of 2 °C min<sup>-1</sup> and kept for another 8 h under Ar atmosphere. After cooling to room temperature, the black powder was collected and named as Pd-Co-NC. The obtained Pd-Co-NC powder was then continuously calcined at 300 °C with a heating rate of 2 °C min<sup>-1</sup> in air for 2 h to prepare the PdO-Co<sub>3</sub>O<sub>4</sub> composite (two-step calcination).

As a control, the Co<sub>3</sub>O<sub>4</sub> and PdO-Co<sub>3</sub>O<sub>4</sub> (air) powders were also synthesized, in which the Co<sub>3</sub>O<sub>4</sub> powder was prepared by calcining the Co-ZIF precursor in the two-step process as mentioned above. In contrast, the PdO-Co<sub>3</sub>O<sub>4</sub> (air) was prepared by directly calcining the Pd-Co-ZIF at 300 °C in air for 2 h (one-step calcination).

### Synthesis of Pd-Zn-MOF and PdO<sub>x</sub>-ZnO

Typically, a mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.62 g) and Pd(acac)<sub>2</sub> (0.08 g) was dissolved in methanol (80 mL) and then added to methanol (80 mL) containing 2-MI (3.70 g). After vigorous magnetic stirring for 24 h, the obtained precipitate was centrifuged, washed with methanol, and vacuum-dried at 70 °C to prepare the Co-Zn-ZIF powder. Then, we adopted the two-step calcination method as mentioned above to prepare the control PdO<sub>x</sub>-ZnO powder.

### Catalytic hydrolysis of hydrogen generation

The catalytic activity, cycle stability, and activation energy of the catalytic materials were obtained by the following methods. First, 150 mm NaBH<sub>4</sub> (50 mL, containing 0.4 wt% NaOH) was added to a three-necked round-bottom flask (100 mL) and continuously stirred in a water bath at 25 °C for 0.5 h until the connected electronic balance stabilized to zero. Then, the catalyst (10 mg) was added to the above solution at 25 °C under continuous stirring. The generated H<sub>2</sub> was evaluated by the drainage method, where the overflow water was collected during the catalytic H<sub>2</sub> production process, and the quantity of the water was recorded in real-time by a computer-connected electronic balance. The hydrogen generation rate (HGR) can be obtained by converting the quantity of the drainage water over time. To test the recyclability of the catalyst, we continued to use the fresh NaBH<sub>4</sub> solution instead of the fully decomposed NaBH<sub>4</sub> solution for five consecutive cycles at 25 °C. After each stability test, we centrifuged the catalytic material, dried it under vacuum at room temperature, and weighed the catalytic material. All experiments were repeated three times to ensure reliable results. The activation energy of the designed catalyst was evaluated in the same device in the temperature range of 298 to 318 K.

The specific hydrogen generation rate (HGR) and turnover frequency (TOF) values are calculated as follows [Equations (1, 2)]:<sup>[15]</sup>

$$\text{HGR} = \frac{V_{\text{H}_2\text{O}} (\text{mL})}{t (\text{min}) \times m (\text{g})} \quad (1)$$

$$\text{TOF} = \frac{n_{\text{H}_2} (\text{mol})}{t (\text{min}) \times n_{\text{Pd}} (\text{mol})} \quad (2)$$

where  $V_{\text{H}_2\text{O}}$  is the volume of the drained water,  $m$  is the total mass of the catalyst,  $n_{\text{H}_2}$  are moles of generated H<sub>2</sub>,  $n_{\text{Pd}}$  are moles of Pd in the catalyst, and  $t$  is the total reaction time in minutes.

### Catalytic reduction of 4-nitrophenol

PdO-Co<sub>3</sub>O<sub>4</sub> catalyst (15 mg), water (9.5 mL), ethanol (8 mL), and 4-nitrophenol (70 mg) were mixed in one pot, a 50 mL beaker, to form a homogeneous solution by magnetic stirring (600 rpm). The reaction started immediately after 4.0 M NaBH<sub>4</sub> solution (0.5 mL) was added into the beaker at 298 K. The progress of the reaction was monitored by taking 1 mL samples from the reaction mixture at various time intervals. For each sample, CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and ethanol (2 mL) were immediately added, followed by dilution of the solution with water 20 times before testing by UV/Visible spectroscopy.

The first-order reaction rate ( $k$ ) was calculated as follows [Eq. (3)]:<sup>[16]</sup>

$$k = -\ln\left(\frac{c_t}{c_0}\right)/t \quad (3)$$

in which  $c_t/c_0$  is the ratio of the concentration after  $t$  time to the initial concentration, replaced by the intensity ratio of the ultraviolet absorption spectrum, and  $t$  is the time.

## Results and Discussion

### Synthetic strategy and crystallinity analysis

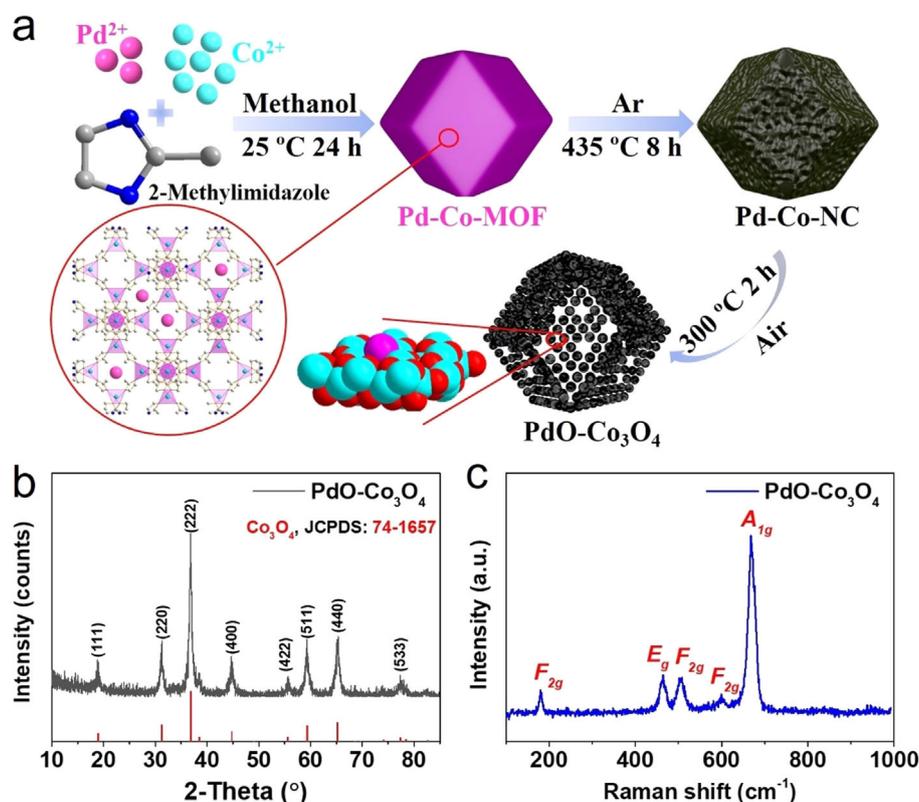
A schematic diagram of the preparation of the concavely structured porous PdO-Co<sub>3</sub>O<sub>4</sub> polyhedron is shown in Figure 1a. The Pd-Co-MOF composite is obtained by simple solvothermal aging of the cobalt nitrate, palladium acetylacetonate, and 2-MI

precursors in methanol, where the Pd species are evenly distributed throughout the frameworks. Through a controlled heating rate and an optimized calcination temperature, during the pyrolysis of the MOF in an inert atmosphere, Pd and Co species undergo partial reduction, thereby obtaining the Pd-Co-CN composite. After further air oxidation treatment, the nitrogen-carbon species were removed, and the Pd-Co species were oxidized to construct the targeted porous PdO-Co<sub>3</sub>O<sub>4</sub> polyhedron with abundant oxygen defects.

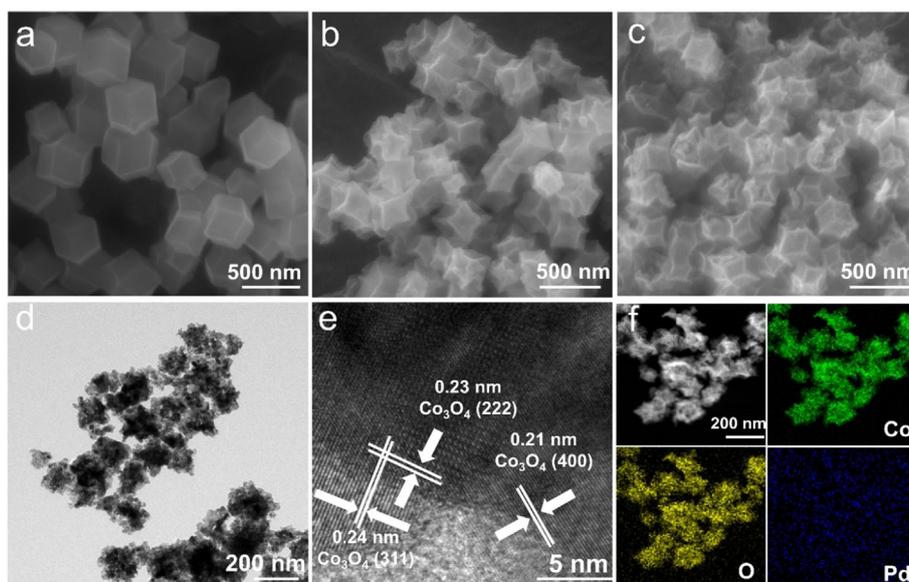
X-ray diffraction (XRD) patterns are used to explore the crystal structure of the materials. As shown in Figure 1b, the diffraction peaks indicated by the PdO-Co<sub>3</sub>O<sub>4</sub> composite are consistent with the cubic structure of Co<sub>3</sub>O<sub>4</sub> (JCPDS: 74-1657).<sup>[17]</sup> Still, the presence of PdO species is not detected owing to the low content of PdO. Raman spectroscopy was then used to further explore the microstructure of the PdO-Co<sub>3</sub>O<sub>4</sub> composite. Figure 1c shows five Raman active modes at 179, 463, 507, 598, and 668 cm<sup>-1</sup>, which are lower than the reported pure spinel structure of Co<sub>3</sub>O<sub>4</sub> materials at about 15–25 cm<sup>-1</sup>.<sup>[18]</sup> This phenomenon may be a reflection of the strong interaction between Co and Pd species in the composite, which is also detected by X-ray photoelectron spectroscopy (XPS).

### Microstructure and porosity analysis

Scanning electron microscopy (SEM) images were used to investigate the changes in the morphology of materials at differ-



**Figure 1.** (a) Schematic diagram of the synthesis of concavely structured PdO-Co<sub>3</sub>O<sub>4</sub> polyhedra. (b) XRD patterns and (c) Raman spectrum of PdO-Co<sub>3</sub>O<sub>4</sub>.



**Figure 2.** SEM images of (a) Pd-Co-MOF, (b) Pd-Co-NC, and (c) PdO-Co<sub>3</sub>O<sub>4</sub>. (d) TEM and (e) high-resolution TEM images of PdO-Co<sub>3</sub>O<sub>4</sub>. (f) HAADF-STEM image of PdO-Co<sub>3</sub>O<sub>4</sub> and corresponding element mappings of Co, O, Pd.

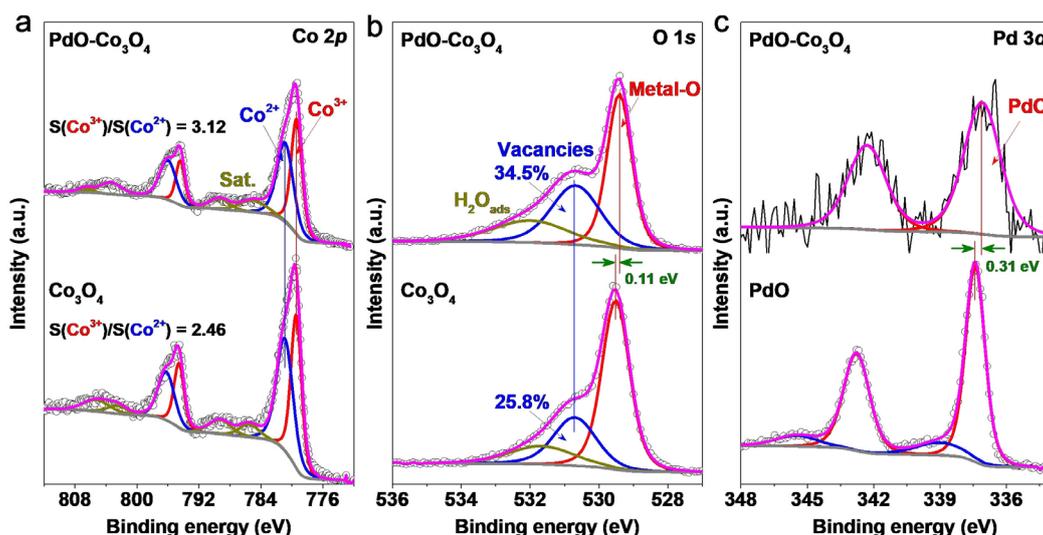
ent stages of transformation. As shown in Figure 2a, the synthesized Pd-Co-MOF has a rhombic dodecahedron structure with an average size of about 420 nm (Figure S1 in the Supporting Information), and its crystal structure is consistent with ZIF-67 (Figure S2 in the Supporting Information).<sup>[19]</sup> After carbonization at 435 °C in Ar atmosphere, the surface of the regular dodecahedron of the MOF collapsed and the volume decreased to an average size of approximately 320 nm (Figure 2b). At the same time, the Co species was reduced to metallic Co clusters (Figure S3 in the Supporting Information)<sup>[20]</sup> as the Pd-Co-NC phase formed. Thermogravimetric analysis (TGA) was used to track the pyrolysis process of Pd-Co-MOF in Ar gas (Figure S4 in the Supporting Information). Significant weight loss for the MOF occurred above 435 °C; this may be undesirable as excessive weight loss is reported to lead to metal agglomeration.<sup>[21]</sup> Accordingly, we performed all the calcinations under Ar atmosphere at 435 °C to reduce the risk of metal agglomeration. Subsequent calcination in air revealed that the carbon species could be rapidly removed by burning at temperatures higher than 229 °C (Figure S5 in the Supporting Information). Therefore, to ensure complete elimination of the carbon species, we performed all calcinations in air at 300 °C. The corresponding PdO-Co<sub>3</sub>O<sub>4</sub> powders maintained a similar pre-calcined morphology, but the average particle size further decreased to about 290 nm (Figure 2c).

Transmission electron microscopy (TEM) was used to further observe the microstructure of PdO-Co<sub>3</sub>O<sub>4</sub> powders (Figure 2d). The high-resolution TEM image of the PdO-Co<sub>3</sub>O<sub>4</sub> nanocrystals shown in Figure 1e shows two distinct crossed lattice fringes with a plane spacing of 0.23 nm and 0.24 nm, which are attributed to the (222) and (311) planes of Co<sub>3</sub>O<sub>4</sub>, respectively.<sup>[22]</sup> The lattice spacing of 0.21 nm corresponds to the (400) crystal plane of Co<sub>3</sub>O<sub>4</sub>.<sup>[23]</sup> As shown in Figure S6 (in the Supporting Information), the energy-dispersive X-ray (EDX) spectrum of PdO-

Co<sub>3</sub>O<sub>4</sub> confirms the existence of Pd, Co, and O elements. The high angle annular dark field (HAADF)-STEM and the elemental mappings show that Pd, Co, and O elements are evenly distributed in the framework structure of the PdO-Co<sub>3</sub>O<sub>4</sub> composite (Figure 2f). We further investigated the textural features of the PdO-Co<sub>3</sub>O<sub>4</sub> powders by N<sub>2</sub> adsorption/desorption isotherms and observed a type III isotherm (Figure S7 in the Supporting Information). The Brunauer–Emmett–Teller (BET) surface area of the PdO-Co<sub>3</sub>O<sub>4</sub> powders was 67.3 m<sup>2</sup>g<sup>-1</sup>, and the pore size distribution was about 38 nm. The porous structure helps to expose more active sites and to enhance the mass transfer, that is, solute transport and product release from the surface.

### Chemical state analysis

XPS was used to analyze the surface chemical state and composition of the PdO-Co<sub>3</sub>O<sub>4</sub> powder. Figure S8a (in the Supporting Information) shows that the PdO-Co<sub>3</sub>O<sub>4</sub> polyhedron is mainly composed of Co, O, and C elements, where the Pd signal intensity is weak owing to the low content. The high-resolution XPS spectra of the C 1s regions (Figure S8b in the Supporting Information) are deconvoluted into C=C (284.0 eV), C–C (284.8 eV), and C–O (286.0 eV) and used as a calibration standard.<sup>[24]</sup> Figure 3a is the high-resolution Co 2p spectra of PdO-Co<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub>. The Co 2p<sub>3/2</sub> region of the PdO-Co<sub>3</sub>O<sub>4</sub> polyhedron is deconvoluted into four peaks at 779.4, 780.9, 785.0, and 789.4 eV, corresponding to the Co<sup>3+</sup>, Co<sup>2+</sup>, and two satellite peaks, respectively.<sup>[23,25]</sup> It can be seen that a small number of coexisting Pd species makes the area ratio of Co<sup>3+</sup>/Co<sup>2+</sup> markedly increase from 2.46 to 3.12. The high-resolution O 1s spectra of the two samples were further analyzed in Figure 3b, in which three signals generated at 529.4, 530.7, and 532.0 eV are attributed to metal oxides, oxygen vacancies, and adsorbed H<sub>2</sub>O, respectively.<sup>[26]</sup> It is worth mentioning that the



**Figure 3.** High-resolution XPS spectra of (a) Co 2p and (b) O 1s regions of PdO-Co<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub>, (c) Pd 3d regions of PdO-Co<sub>3</sub>O<sub>4</sub> and commercial PdO powders.

oxygen vacancies increased rapidly from 25.8% to 34.5% after the introduction of Pd species. Studies indicate that a higher proportion of oxygen vacancies corresponds to faster electron transfer, stronger adsorption properties, and more active sites.<sup>[27]</sup>

The high-resolution Pd 3d spectrum was analyzed by fitting two asymmetric peaks (Figure 3c). The fitted Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> peaks located at 337.1 eV and 342.3 eV are attributed to PdO.<sup>[28]</sup> Compared with commercial PdO, it can be found that the Pd 3d<sub>5/2</sub> peak in PdO-Co<sub>3</sub>O<sub>4</sub> moved by −0.31 eV owing to the electron transfer from Co species to Pd species, resulting in higher electron density on PdO species.<sup>[29,31]</sup> As the content of Co<sub>3</sub>O<sub>4</sub> in PdO-Co<sub>3</sub>O<sub>4</sub> is much higher than that of PdO, almost no change in Co 2p is observed. The strong electronic interaction between different species will affect the adsorption, transformation, and desorption capabilities of active sites, thereby synergistically improving the catalytic activity. Notably, this strong interaction may be unique to the PdO-Co<sub>3</sub>O<sub>4</sub> composite as no such shift was observed when we used a similar method to replace Co with Zn to construct PdO<sub>x</sub>-ZnO (Figure S9 in the Supporting Information).

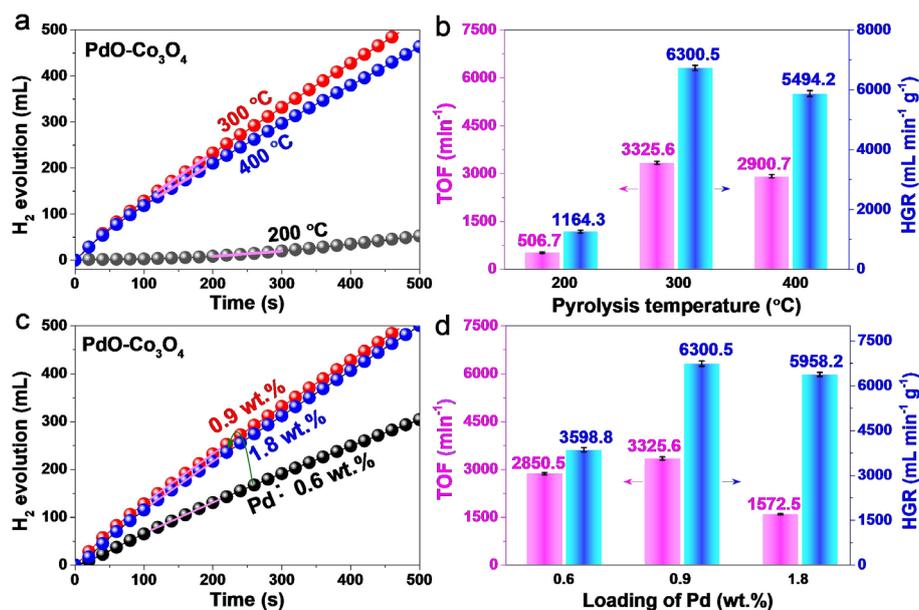
### Catalytic NaBH<sub>4</sub> hydrolysis analysis

The catalytic H<sub>2</sub> production from the hydrolysis of NaBH<sub>4</sub> in alkaline solution was performed at 25 °C by employing an experimental setup schematically illustrated in Figure S10 (in the Supporting Information). The amount of H<sub>2</sub> produced was calculated based on the volume of water discharged by H<sub>2</sub>. Figure 4a–b shows the comparison of the catalytic hydrolysis of NaBH<sub>4</sub> by PdO-Co<sub>3</sub>O<sub>4</sub> materials prepared from the calcination of Pd-Co-NC at different temperatures in air. We can observe that, of the three samples, the PdO-Co<sub>3</sub>O<sub>4</sub> catalyst prepared by calcination at 300 °C yields both the highest HGR (6300.5 mL<sub>H2</sub> min<sup>−1</sup> g<sub>cat</sub><sup>−1</sup>) and TOF (3325.6 mol<sub>H2</sub> min<sup>−1</sup> mol<sub>Pd</sub><sup>−1</sup>). We emphasize that this TOF value is the largest ever reported to the best of our knowledge. Among the highest TOF values

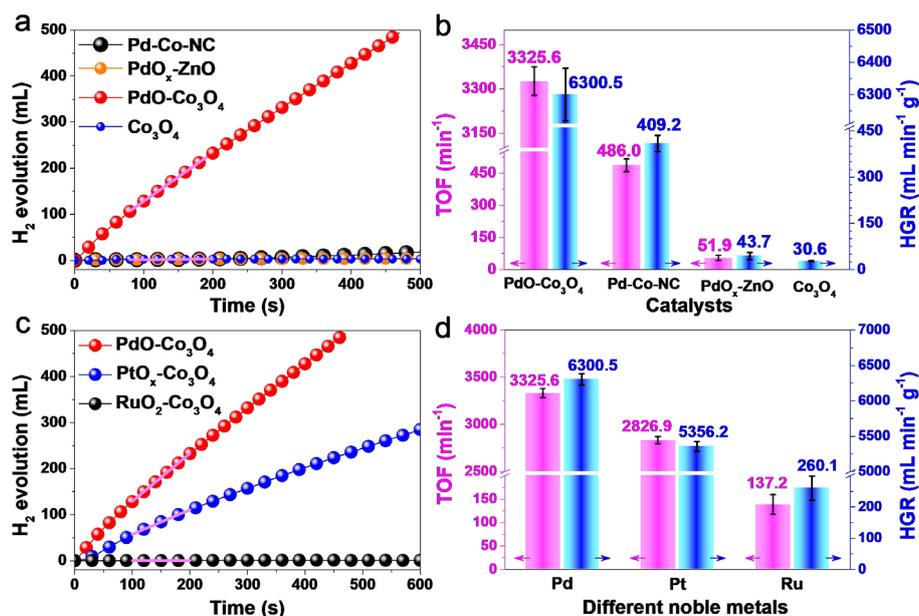
we found in the literature are included Ni<sub>2</sub>Pt@ZIF-8,<sup>[30]</sup> Co-Ru-P@NF,<sup>[31]</sup> and Ni<sub>0.9</sub>Pt<sub>0.1</sub>/Ce<sub>2</sub>O<sub>3</sub>.<sup>[32]</sup> In Figure 4c, we explore the effect of Pd loading on the rate of hydrogen evolution. It can be seen that the highest HGR and TOF values are obtained at 0.9 wt% Pd loading (Figure 4d and Table S1 in the Supporting Information). The somewhat counterintuitive poor catalytic performance at higher Pd loading probably results from increased particle agglomeration, which in turn reduces the overall surface area. As the best catalytic performance was obtained for the PdO-Co<sub>3</sub>O<sub>4</sub> calcined in air at 300 °C with 0.9 wt% Pd loading, unless stated otherwise, our discussion of PdO-Co<sub>3</sub>O<sub>4</sub> will focus on this sample henceforth.

To investigate the effects of the different components of the PdO-Co<sub>3</sub>O<sub>4</sub> catalyst on H<sub>2</sub> generation by NaBH<sub>4</sub> hydrolysis, we explored PdO-Co<sub>3</sub>O<sub>4</sub> alongside Pd-Co-NC, PdO<sub>x</sub>-ZnO, and Co<sub>3</sub>O<sub>4</sub> control catalysts (Figure 5a). The results show that none of the individual components of the PdO-Co<sub>3</sub>O<sub>4</sub> catalyst system exhibit any meaningful catalytic activity, clearly demonstrating that the observed outstanding catalytic activity of PdO-Co<sub>3</sub>O<sub>4</sub> must at least be grounded in the synergy between its PdO and Co<sub>3</sub>O<sub>4</sub> components (Figure 5b). To further explore the influence of different precious metals, we used similar methods to prepare two other catalysts, PtO<sub>x</sub> and RuO<sub>2</sub> decorated Co<sub>3</sub>O<sub>4</sub> catalysts (Figure 5c). It can be seen that the catalytic activity of PdO-Co<sub>3</sub>O<sub>4</sub> is significantly higher than those of the two control catalysts and most previously reported catalysts (Figure 5d and Table S2 in the Supporting Information). These variations in catalytic performance could be related to differences in the chemical interactions among the constituents of the different catalysts. We also explored the impact of both the concentration of NaBH<sub>4</sub> and the percentage of NaOH on the H<sub>2</sub> generation by the NaBH<sub>4</sub> hydrolysis reaction. In line with previous studies,<sup>[15a]</sup> we find no important role for these variables on the HGR (Figure S11 in the Supporting Information).

The temperature dependence of the catalytic activities was investigated in the range 298–318 K. We can clearly observe a gradual increase of the H<sub>2</sub> generation rate of the PdO-Co<sub>3</sub>O<sub>4</sub>



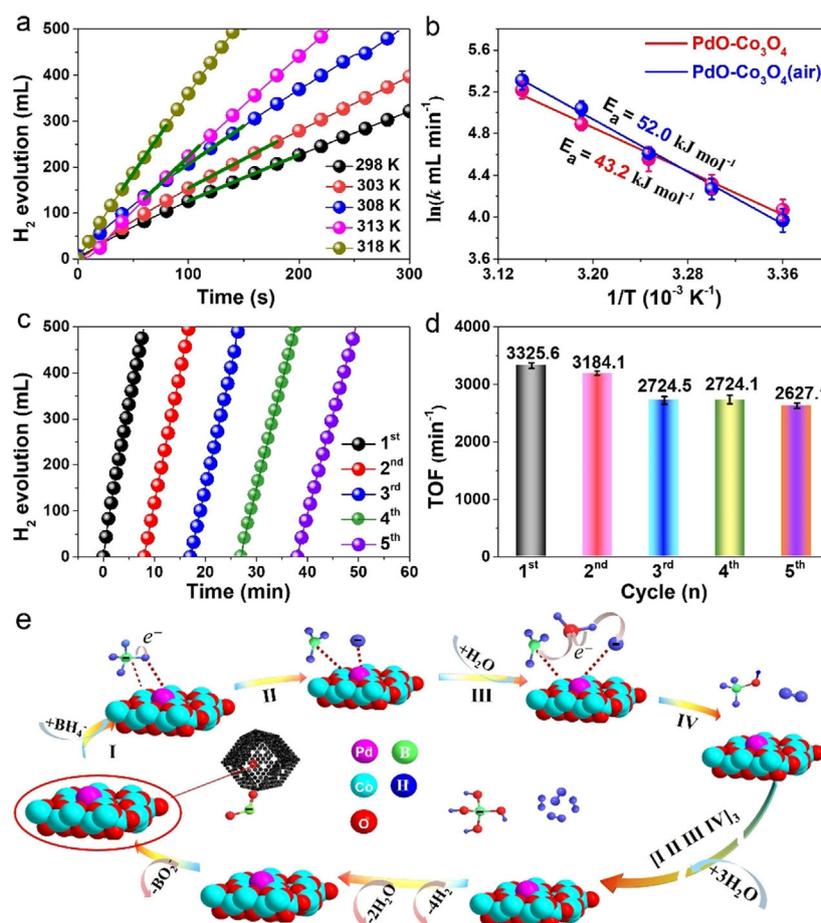
**Figure 4.** (a) Stoichiometric H<sub>2</sub> evolution and (b) the summarized TOF and HGR values by PdO-Co<sub>3</sub>O<sub>4</sub> catalysts with different pyrolysis temperatures. (c) Relationship between H<sub>2</sub> evolution and loadings of Pd species in PdO-Co<sub>3</sub>O<sub>4</sub> catalysts, and (d) Summarized TOF values and HGR. All the experiments were conducted in 150 mM NaBH<sub>4</sub>+0.4 wt% NaOH solution at 25 °C.



**Figure 5.** (a) Stoichiometric H<sub>2</sub> evolution and (b) the summarized TOF and HGR values of different catalysts. (c) Relationship between H<sub>2</sub> generation and different noble metal catalyst decorated Co<sub>3</sub>O<sub>4</sub> and (d) summarized TOF values and HGR. All the experiments are conducted in 150 mM NaBH<sub>4</sub>+0.4 wt% NaOH solution at 25 °C.

catalyst with increasing reaction temperature (Figure 6a). From the Arrhenius plots in Figure 6b, the activation energies of the PdO-Co<sub>3</sub>O<sub>4</sub> and PdO-Co<sub>3</sub>O<sub>4</sub> (air) catalysts are calculated to be 43.2 and 52.0 kJ mol<sup>-1</sup>, respectively. Here, the PdO-Co<sub>3</sub>O<sub>4</sub> (air) refers to Figure S12 (in the Supporting Information). The significantly lower activation energy obtained for the PdO-Co<sub>3</sub>O<sub>4</sub> catalyst indicates an enhanced catalytic activity.<sup>[33]</sup> The recycling test was used to evaluate the catalyst reusability. After the

complete consumption of NaBH<sub>4</sub>, a fresh NaBH<sub>4</sub> powder sample was then added to the reactor for the next cycle (Figure 6c). The horizontal axis in Figure 6c is the running time for the experiment showing the instances at which each cycle was initiated. The results show that the H<sub>2</sub> production starts immediately and maintains high activity without a significant induction period. This test cycle was repeated five times, and around 80% of the initial activity was retained after five cycles



**Figure 6.** (a) Stoichiometric H<sub>2</sub> evolution of PdO-Co<sub>3</sub>O<sub>4</sub> and PdO-Co<sub>3</sub>O<sub>4</sub> (air) in 150 mM NaBH<sub>4</sub>+0.4 wt% NaOH solution at different reaction temperatures and (b) the summarized Arrhenius plots from (a). (c) Recycling stability test of PdO-Co<sub>3</sub>O<sub>4</sub> catalyst and (d) the corresponding TOF values from (c). (e) Proposed catalytic mechanism of PdO-Co<sub>3</sub>O<sub>4</sub> catalyst for H<sub>2</sub> generation.

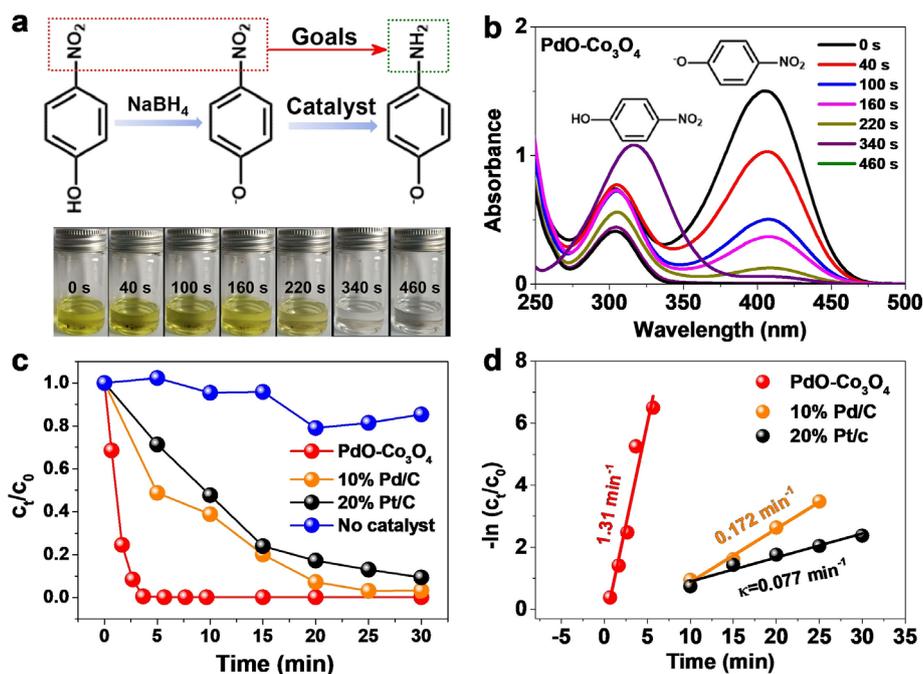
(Figure 6d). The slight decrease in catalytic activity may be mainly due to the structural damage (Figure S13 in the Supporting Information), Pd clusters exfoliation (Table S1 in the Supporting Information), surface chemical state changes (Figure S14 in the Supporting Information), and BO<sub>2</sub><sup>-</sup> poisoning.<sup>[29a,34]</sup>

As discussed above, the PdO-Co<sub>3</sub>O<sub>4</sub> catalyst has the largest HGR and TOF values compare with other catalysts. The outstanding performance is mainly attributed to a large specific surface area, high conductivity, and synergy between PdO and Co<sub>3</sub>O<sub>4</sub> species. According to the XPS study, the negative shift of the Pd3d binding energy in PdO-Co<sub>3</sub>O<sub>4</sub> caused by the partial electron transfer from Co species to Pd species indicates a higher electron density on Co species compared with that of Pd species. Accordingly, the partially negatively charged hydrogen atoms preferred to attach to the Pd atoms. As a result, the BH<sub>4</sub><sup>-</sup> dissociates at the Co and Pd metal sites, hydrogen atoms are adsorbed on Pd, and BH<sub>3</sub> is attached to Co species. After the B–H bond is broken, the negatively charged B species immediately transfers the negative charge to the adsorbed H atoms through the conductive bulk. Finally, the negatively charged H atom on the Pd surface extracts hydrogen from water to release an H<sub>2</sub> molecule, whereas the OH<sup>-</sup> ion attacks

the BH<sub>3</sub> to form a BH<sub>3</sub>OH molecule, followed by transfer of one hydrogen atom of the BH<sub>3</sub>OH to a free Pd site. After the first cycle, the surface of the catalyst releases a hydrogen molecule and a BH<sub>3</sub>OH species. As the reaction proceeds, all of the H atoms in the borohydride are replaced by OH<sup>-</sup> ions (Figure 6e), ultimately releasing the B(OH)<sub>4</sub><sup>-</sup> species.<sup>[35]</sup>

### Catalytic reduction of 4-nitrophenol

Since Pal et al. first reported the reduction of 4-NPs to 4-APs by using a Ag catalyst in 2002, the reaction has become a well-controlled model reaction that does not produce byproducts.<sup>[11]</sup> Thus, we selected this model reduction reaction in an aqueous system with NaBH<sub>4</sub> as the hydrogen source to study the catalytic efficiency of the PdO-Co<sub>3</sub>O<sub>4</sub> polyhedron (Figure 7a). The reaction was monitored at the specific UV wavelength.<sup>[36]</sup> After adding NaBH<sub>4</sub> to 4-NP, the solution was observed to turn bright yellow with the absorption peak shifting to about 405 nm; however, we noticed no further changes in color after 1 h, indicating that the 4-nitrophenol ion was formed.<sup>[16b,37]</sup> After further addition of the PdO-Co<sub>3</sub>O<sub>4</sub> catalyst, the UV/Vis absorption peak decreased rapidly, demonstrating that 4-nitrophenol ions were reduced to 4-aminophenol ions (Fig-



**Figure 7.** (a) Schematic diagram of the conversion of 4-NP to 4-AP and photos taken at different conversion times using the PdO-Co<sub>3</sub>O<sub>4</sub> catalyst. (b) UV/Vis spectra of successive reduction of 4-NP to 4-AP over PdO-Co<sub>3</sub>O<sub>4</sub> in the presence of NaBH<sub>4</sub>. (c) Summarized conversion effects of different catalysts over time from the UV/Vis spectra. (d) Corresponding pseudo-first-order plots of 4-NPs reduction from (c).

ure 7b and Figure S15 in the Supporting Information). As shown in Figure 7c, we observed that the PdO-Co<sub>3</sub>O<sub>4</sub> (0.9 wt% Pd) catalyst needs only about 220 s to complete the full conversion of 4-NP to 4-AP. This is a much faster rate compared with commercial 10 wt% Pd/C or 20 wt% Pt/C catalysts for the same initial 4-NP concentration. Furthermore, the kinetic constants of PdO-Co<sub>3</sub>O<sub>4</sub> catalysts were calculated according to the slope of  $\ln(c_t/c_0) = -kt$  in the linear range. As shown in Figure 7d, the  $k$  value of PdO-Co<sub>3</sub>O<sub>4</sub> is 1.31 min<sup>-1</sup>, which is significantly higher than that of the control catalysts and most previously reported catalysts (Table S3 in the Supporting Information), implying that the catalyst has faster catalytic kinetics and has good application potential.<sup>[30,38]</sup>

The catalytic conversion mechanism of 4-NP to 4-AP has been extensively studied, and a possible catalytic mechanism is proposed by the Langmuir–Hinshelwood model.<sup>[16b,39]</sup> As shown in Figure S16 (in the Supporting Information), the catalytic process proceeds through the following four steps. Step 1: the borohydride anion (BH<sub>4</sub><sup>-</sup>) dissociates on the surface of the PdO-Co<sub>3</sub>O<sub>4</sub> catalyst, thereby forming Pd-H<sub>ads</sub> at the PdO active site. Step 2: the 4-NP is adsorbed on PdO clusters, and interacts with nearby Pd-H<sub>ads</sub> species through their -NO<sub>2</sub>. Step 3: the -NO<sub>2</sub> in the adsorbed 4-NP reacts quickly with the adsorbed H through electron transfer and atomic exchange.<sup>[16a]</sup> Step 4: the formed 4-AP is desorbed from the catalyst surface to provide free active sites for the next catalytic cycle.

## Conclusion

We have prepared a PdO-Co<sub>3</sub>O<sub>4</sub> composite with a concave structure by a MOFTS method. The resulting catalysts show

outstanding bifunctional performance in both NaBH<sub>4</sub> hydrolysis and 4-NPs reduction. The two main parameters, namely, the calcination temperature and Pd loading, were optimized. The optimal catalyst that was achieved at 350 °C calcination temperature and 0.9 wt% Pd loading has the highest HGR and TOF values, small activation energy, and excellent reusability. Meanwhile, the optimized catalyst also shows a much higher 4-NPs reduction rate compare with that of Pd/C. In addition, the corresponding possible catalytic mechanism was further proposed according to the experimental results, which can provide a new insight into designing and preparing a highly active multifunctional catalyst for various applications, including chemical/electrochemical catalysis, nitrophenols reduction, fuel cells, supercapacitors, and so on.

## Acknowledgments

This work has been supported by the National Natural Science Foundation of China (no. 21965005), Natural Science Foundation of Guangxi Province (2018GXNSFAA294077, 2018GXNSFAA281220), Project of High-Level Talents of Guangxi (F-KA18015, 2018ZD004), and Guangxi Technology Base and Talent Subject (GUIKE AD18126001).

## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** electron transfer · NaBH<sub>4</sub> hydrolysis · nitrophenol reduction · PdO-Co<sub>3</sub>O<sub>4</sub> · synergistic effect

- [1] H. Park, S. Oh, S. Lee, S. Choi, M. Oh, *Appl. Catal. B* **2019**, *246*, 322–329.
- [2] A. Muthurasu, V. Maruthapandian, H. Y. Kim, *Appl. Catal. B* **2019**, *248*, 202–210.
- [3] S. Lee, S. Oh, M. Oh, *Angew. Chem. Int. Ed.* **2020**, *59*, 1327–1333; *Angew. Chem.* **2020**, *132*, 1343–1349.
- [4] C. Van Nguyen, S. Lee, Y. G. Chung, W.-H. Chiang, K. C. W. Wu, *Appl. Catal. B* **2019**, *257*, 117888.
- [5] M. Zhang, Q. Dai, H. Zheng, M. Chen, L. Dai, *Adv. Mater.* **2018**, *30*, 1705431.
- [6] J. Ying, J. Li, G. Jiang, Z. P. Cano, Z. Ma, C. Zhong, D. Su, Z. Chen, *Appl. Catal. B* **2018**, *225*, 496–503.
- [7] a) S. Demirci, A. K. Sunol, N. Sahiner, *Appl. Catal. B* **2020**, *261*, 118242; b) J. Lai, B. Huang, Y. Chao, X. Chen, S. Guo, *Adv. Mater.* **2019**, *31*, 1805541.
- [8] a) G. Bozkurt, A. Özer, A. B. Yurtcan, *Energy* **2019**, *180*, 702–713; b) J. Guo, B. Wang, D. Yang, Z. Wan, P. Yan, J. Tian, T. T. Isimjan, X. Yang, *Appl. Catal. B* **2020**, *265*, 118584; c) L. Shi, Z. Chen, Z. Jian, F. Guo, C. Gao, *Int. J. Hydrogen Energy* **2019**, *44*, 19868–19877.
- [9] a) S. M. Sadeghzadeh, R. Zhiani, S. Emrani, *New J. Chem.* **2018**, *42*, 988–994; b) L. Jin, X. Zhao, J. Ye, X. Qian, M. Dong, *Catal. Commun.* **2018**, *107*, 43–47.
- [10] a) M. I. Din, R. Khalid, Z. Hussain, T. Hussain, A. Mujahid, J. Najeeb, F. Izhah, *Crit. Rev. Anal. Chem.* **2020**, *50*, 322–338; b) G. Eichenbaum, M. Johnson, D. Kirkland, P. O'Neill, S. Stellar, J. Bielawne, R. DeWire, D. Areia, S. Bryant, S. Weiner, D. Desai-Krieger, P. Guzzie-Peck, D. C. Evans, A. Tonelli, *Regul. Toxicol. Pharmacol.* **2009**, *55*, 33–42.
- [11] N. Pradhan, A. Pal, T. Pal, *Colloids Surf. A* **2002**, *196*, 247–257.
- [12] a) F. Coccia, L. Tonucci, D. Bosco, M. Bressan, N. d'Alessandro, *Green Chem.* **2012**, *14*, 1073–1078; b) R. Liu, S. M. Mahurin, C. Li, R. R. Unocic, J. C. Idrobo, H. Gao, S. J. Pennycook, S. Dai, *Angew. Chem. Int. Ed.* **2011**, *50*, 6799–6802; *Angew. Chem.* **2011**, *123*, 6931–6934.
- [13] a) Y. Sun, L. Xu, Z. Yin, X. Song, *J. Mater. Chem. A* **2013**, *1*, 12361–12370; b) C. Tang, F. Qu, A. M. Asiri, Y. Luo, X. Sun, *Inorg. Chem. Front.* **2017**, *4*, 659–662.
- [14] X.-H. Li, X. Wang, M. Antonietti, *Chem. Sci.* **2012**, *3*, 2170–2174.
- [15] a) L. Cui, Y. Xu, L. Niu, W. Yang, J. Liu, *Nano Res.* **2017**, *10*, 595–604; b) Q. Yao, Z.-H. Lu, Y. Yang, Y. Chen, X. Chen, H.-L. Jiang, *Nano Res.* **2018**, *11*, 4412–4422.
- [16] a) X. Cheng, D. Wang, J. Liu, X. Kang, H. Yan, A. Wu, Y. Gu, C. Tian, H. Fu, *Nanoscale* **2018**, *10*, 22348–22356; b) Y. Yang, K. Jiang, J. Guo, J. Li, X. Peng, B. Hong, X. Wang, H. Ge, *Chem. Eng. J.* **2020**, *381*, 122596.
- [17] a) Y. Sun, Y. Zhou, C. Zhu, W. Tu, H. Wang, H. Huang, Y. Liu, M. Shao, J. Zhong, S.-T. Lee, Z. Kang, *Appl. Catal. B* **2019**, *244*, 795–801; b) S.-J. Choi, H.-J. Choi, W.-T. Koo, D. Huh, H. Lee, I.-D. Kim, *ACS Appl. Mater. Interfaces* **2017**, *9*, 40593–40603.
- [18] Y. Tong, H. Mao, Y. Xu, J. Liu, *Inorg. Chem. Front.* **2019**, *6*, 2055–2060.
- [19] a) X. C. Huang, Y. Y. Lin, J. P. Zhang, X. M. Chen, *Angew. Chem. Int. Ed.* **2006**, *45*, 1557–1559; *Angew. Chem.* **2006**, *118*, 1587–1589; b) H. Hu, B. Guan, B. Xia, X. W. Lou, *J. Am. Chem. Soc.* **2015**, *137*, 5590–5595.
- [20] B. Coşkuner Filiz, A. Kantürk Figen, S. Pişkin, *Appl. Catal. B* **2018**, *238*, 365–380.
- [21] Y. Zhao, H. Zhou, W. Chen, Y. Tong, C. Zhao, Y. Lin, Z. Jiang, Q. Zhang, Z. Xue, W.-C. Cheong, B. Jin, F. Zhou, W. Wang, M. Chen, X. Hong, J. Dong, S. Wei, Y. Li, Y. Wu, *J. Am. Chem. Soc.* **2019**, *141*, 10590–10594.
- [22] a) H. Lee, X. Wu, Q. Ye, X. Wu, X. Wang, Y. Zhao, L. Sun, *Chem. Commun.* **2019**, *55*, 1564–1567; b) H.-C. Li, Y.-J. Zhang, X. Hu, W.-J. Liu, J.-J. Chen, H.-Q. Yu, *Adv. Energy Mater.* **2018**, *8*, 1702734.
- [23] J. Huang, Y. Xiao, Z. Peng, Y. Xu, L. Li, L. Tan, K. Yuan, Y. Chen, *Adv. Sci.* **2019**, *6*, 1900107.
- [24] Y. She, Z. Lu, W. Fan, S. Jewell, M. K. H. Leung, *J. Mater. Chem. A* **2014**, *2*, 3894–3898.
- [25] W. Chen, B. Han, C. Tian, X. Liu, S. Liang, H. Deng, Z. Lin, *Appl. Catal. B* **2019**, *244*, 996–1003.
- [26] a) J. Sun, N. Guo, Z. Shao, K. Huang, Y. Li, F. He, Q. Wang, *Adv. Energy Mater.* **2018**, *8*, 1870121; b) S. Gao, F. Liao, S. Ma, L. Zhu, M. Shao, *J. Mater. Chem. A* **2015**, *3*, 16520–16527.
- [27] Y. Tong, P. Chen, M. Zhang, T. Zhou, L. Zhang, W. Chu, C. Wu, Y. Xie, *ACS Catal.* **2018**, *8*, 1–7.
- [28] a) T.-J. Wang, F.-M. Li, H. Huang, S.-W. Yin, P. Chen, P.-J. Jin, Y. Chen, *Adv. Funct. Mater.* **2020**, *30*, 2000534; b) C. Wu, J. Guo, J. Zhang, Y. Zhao, J. Tian, T. T. Isimjan, X. Yang, *Renew. Energy* **2019**, *136*, 1064–1070.
- [29] B. Wang, H. Huang, M. Huang, P. Yan, T. T. Isimjan, X. Yang, *Sci. China Chem.* **2020**, *63*, 841–849.
- [30] F. Fu, C. Wang, Q. Wang, A. M. Martinez-Villacorta, A. Escobar, H. Chong, X. Wang, S. Moya, L. Salmon, E. Fouquet, J. Ruiz, D. Astruc, *J. Am. Chem. Soc.* **2018**, *140*, 10034–10042.
- [31] J. Guo, C. Wu, J. Zhang, P. Yan, J. Tian, X. Shen, T. T. Isimjan, X. Yang, *J. Mater. Chem. A* **2019**, *7*, 8865–8872.
- [32] H.-L. Wang, J.-M. Yan, Z.-L. Wang, S.-I. Oh, Q. Jiang, *J. Mater. Chem. A* **2013**, *1*, 14957–14962.
- [33] D. D. Tuan, K.-Y. A. Lin, *Chem. Eng. J.* **2018**, *351*, 48–55.
- [34] C. Wu, J. Zhang, J. Guo, L. Sun, J. Ming, H. Dong, Y. Zhao, J. Tian, X. Yang, *ACS Sustainable Chem. Eng.* **2018**, *6*, 7451–7457.
- [35] U. B. Demirci, P. Miele, *C. R. Chim.* **2014**, *17*, 707–716.
- [36] M. Fan, W. D. Wang, Y. Zhu, X. Sun, F. Zhang, Z. Dong, *Appl. Catal. B* **2019**, *257*, 117942.
- [37] a) L. Tan, B. Tan, *Chem. Eng. J.* **2020**, *390*, 124485; b) E. Park, J. Jack, Y. Hu, S. Wan, S. Huang, Y. Jin, P.-C. Maness, S. Yazdi, Z. Ren, W. Zhang, *Nanoscale* **2020**, *12*, 2596–2602.
- [38] Q. Sun, N. Wang, T. Zhang, R. Bai, A. Mayoral, P. Zhang, Q. Zhang, O. Terasaki, J. Yu, *Angew. Chem. Int. Ed.* **2019**, *58*, 18570–18576; *Angew. Chem.* **2019**, *131*, 18743–18749.
- [39] B. Baruah, G. J. Gabriel, M. J. Akbashev, M. E. Booher, *Langmuir* **2013**, *29*, 4225–4234.

Manuscript received: August 15, 2020

Revised manuscript received: September 11, 2020

Accepted manuscript online: September 15, 2020

Version of record online: ■■■■■ 0000

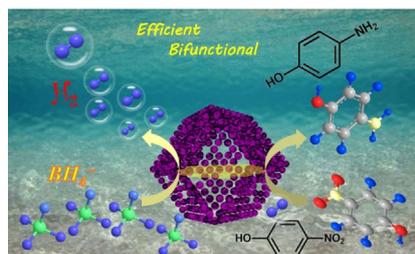
## FULL PAPER

## Bifunctional Catalysts

S. Dou, S. Zhou, H. Huang, P. Yan,  
E. Shoko, T. T. Isimjan,\* X. Yang\*



  **Metal–Organic Framework (MOF)-Derived Electron-Transfer Enhanced Homogeneous PdO-Rich  $\text{Co}_3\text{O}_4$  as a Highly Efficient Bifunctional Catalyst for Sodium Borohydride Hydrolysis and 4-Nitrophenol Reduction**



**$\text{NaBH}_4$  hydrolysis for  $\text{H}_2$  generation:** A homogeneously dispersed Pd oxide-rich  $\text{Co}_3\text{O}_4$  polyhedral catalyst with concave structure has been used as a highly active catalyst for  $\text{NaBH}_4$  hydrolysis and 4-nitrophenol reduction. The excellent catalytic performance is attributed to the unique structure and the synergy between the PdO and  $\text{Co}_3\text{O}_4$  species.