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Visible-Light-Driven Selective Alcohol^{OI: 10.1039/C9TA13811K} Dehydrogenation and Hydrogenolysis Via the Mott Schottky Effect

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Abstract

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The Schottky barrier created at the interface between electron sinks and semiconductors can effectively optimize the electrons transfer for active photocatalysis. However, heterogeneous photocatalytic organic transformations via the Mott Schottky effect are still rare and their role in the specific photocatalytic system remains ambiguous. Here, a versatile photocatalytic system integrating the Schottky junctions into the TiO_2 particles (Degussa, P25) and Pd NPs based films has been developed. They were readily available through the facile encapsulation of P25 by Pd-H₄BINDI films using an alternating layer-by-layer (LBL) approach (H₄BINDI: N, N'-bis (5-isophthalate acid) naphthalene-diimide). After H₂ reduction process under 200 °C, the Pd NPs were obtained, denoted as P25@Pd-H₄BINDI-200. Interestingly, the resulting P25@Pd-H₄BINDI-200 photocatalyst presented an exceptionally high activity for dehydrogenation and hydrogenolysis of benzyl alcohol under visible light irradiation, which was approximately 17 times higher than that of the parent $P25@Pd-H_4BINDI$ and was superior to any other analogous systems reported to date. Specifically, the negative charges accumulated on the Pd NPs surface reduce the benzyl alcohol, while the holes left on the valence band oxidize the benzyl alcohol, effectively promoting the photocatalytic cycles with enhanced carrier separation. The deeper understanding of the reaction mechanisms unveiled that Pd NPs play a vital mediating role in storing and shuttling photogenerated electrons via the Mott Schottky effect, and revealed that the highly enhanced carrier separation by direct use of photoexcited electrons and holes for photoredox reactions. This work holds great promises for designing Mott-Schottky

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catalysts in enabling solar-driven photoredox reactions.

Keywords: Mott-Schottky, P25, photocatalysis, Pd, visible light, layer-by-layer, films

Introduction

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Photochemical reaction has become a research focus for the synthesis of various chemicals due to its environmental friendliness and sustainability.¹⁻³ The application of solar energy in challenging organic synthesis is an especially promising strategy for synthetic chemistry.⁴⁻⁷ However, these reactions are often hampered by the sluggish electrons transfer and rapid recombination of photogenerated electron (e^{-})-hole (h^{+}) pair. Integrating metal (mainly noble metal) to semiconductor materials has been recognized as a promising strategy for facilitating the electron (e^{-})-hole (h^{+}) separation for efficient photocatalysis.⁸⁻¹² Once a metal is in direct contact with a semiconductor,^{13, 14} a Schottky barrier will be formed at the metal-support interface due to their different Fermi level positions,¹⁵⁻¹⁷ which can serve as an efficient hot electrons trap to avoid the e⁻h⁺ recombination during photocatalysis.¹⁸ The Mott Schottky effect will greatly contribute to the improvement of heterogeneous photocatalytic activity in the visiblelight region and concomitant effective hot electrons transfer.¹⁹⁻²¹ However, the dispersion and stabilization of metal NPs on semiconductor is still a challenge as the metal-support interactions are not yet sufficient strong.^{11, 22-24} It is of great interest to construct effective Schottky barrier between the metal NPs and semiconductive support.^{20, 21, 25-27}

Photochemical reactions are often hampered by the sluggish electrons transfer and rapid recombination of photogenerated e⁻- h⁺ pair.²⁸⁻³³ In particular, it has become a research trend that coupling e⁻ and h⁺ induced redox reactions synergistically in one reaction system, as photogenerated e⁻ and h⁺ exhibit remarkable reducing and oxidizing

peculiarity,³⁴⁻³⁶ respectively. Earlier, Jiang's group successfully coupled H₂ production with benzylamine oxidation over a Pt/PCN-777 catalyst in a single system.³⁷ According to our recent work,³⁸ the photogenerated e⁻ and h⁺ can fully be utilized for nitrobenzene photoreduction coupled with alcohols photooxidation. Aromatic alcohols are significant and fundamental substrates for synthesizing value-added organic chemicals.^{5, 39, 40} Consequently, current interests have been directed toward the oxidation of aromatic alcohols by photoexcited holes, while reduction of aromatic alcohols over photoexcited electrons synergistically in a single system.^{27, 41} Unfortunately, related works still constitute a daunting challenge and its reaction mechanism remains ambiguous.

Bearing the above considerations in mind, a promising approach was developed to enhance the e⁻h⁺ separation via the Mott Schottky effect in a thin film photocatalyst. The Pd-H₄BINDI films were successfully coated on P25 surface through an alternating layer-by-layer self-assembly method.⁴² After H₂ reduction process under 200 °C . the well dispersed Pd NPs were obtained, denoted as P25@Pd-H₄BINDI-200. The ingeniously integration of H₄BINDI ligand resisted the aggregation of Pd NPs and extended the light absorption region of P25. Interestingly, the negative charges accumulated on the Pd NPs surface reduce the benzyl alcohol, while the holes left on the VB (valence band) band oxidize the benzyl alcohol, promoting photocatalytic cycles. The simultaneous exploitation of photogenerated holes and electrons greatly enhance the e-h⁺ separation for efficient photocatalysis. This work realizes the conversions of biomass-relevant substrates and holds great promises for applying Mott-

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Schottky catalysts in enabling solar-driven organic transformations.

Experimental Section

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Synthesis Procedures of ligand

N, N'-bis (5-isophthalic acid) naphthalenediimide (H₄BINDI) was synthesized according to some reported literatures.⁴³ In a typical process, a mixture of 1,4,5,8-tetracarboxydianhydride (5.0 mmol) and acetic acid (25 mL) was stirred for 10 min. Then, 5-aminoisophthalic acid (10 mmol) was added into the above mixture. The reaction mixture was refluxed for 12 h, and 20 mL water was added. The product was collected by filtration washed with ethanol and dried at 70 °C under vacuum for 12 h. Finally, the H₄BINDI compound was recrystallized from DMF.



Fabrication of Pd-H₄BINDI metal-organic films on different substrates

P25, mixture of anatase and rutile (82/18) particles (size, 24 nm; BET surface area, 57 $m^2 g^{-1}$) was purchased from Sinopharm Chemical Reagent Co., Ltd. In a typical procedure, the P25 pre-coated with Poly(ethylenimine) (PEI, 50 wt% aqueous solution) as a metal-ion adhesive layer were immersed in an aqueous solution containing K₂PdCl₄ (5 mM, 5 mL) and an H₄BINDI DMF solution (0.5 mM, 5 mL) for 30 min, respectively.

After each immersion, the powders were centrifuged and washed with ethanol.^{DOI} ¹⁰ By^{O39/C9TA13811K}

repeating the above steps for several times and finally dried in a vacuum, the catalyst film P25@Pd-H₄BINDI was prepared. The SiO₂-Pd-H₄BINDI-200 and quartz@Pd-H₄BINDI were prepared in the same manner, but the Pd-H₄BINDI composite films were adsorbed on the surface of the quartz slides (size 25 mm × 12 mm × 1 mm) or SiO₂.

Preparation of P25@Pd-H₄BINDI-T

The prepared P25@Pd-H₄BINDI sample (100 mg) in a ceramic boat was reduced in a 5 % H₂/N₂ atmosphere by raising the temperature in a heating rate of 3 °C min⁻¹ to appropriate pyrolysis temperature to afford P25@Pd-H₄BINDI-T, in which T denotes the pyrolysis temperature (150 °C, 200 °C and 300 °C) and maintaining for 5 h to yield Pd nanocomposites. The as-obtained black powders were applied for further characterizations and catalytic reactions. the P25@Pd was prepared according the former reported process with some modification. In detail, the K₂PdCl₄ was dissolved into acetone to disperse P25 and the mixture was ultrasonic agitation for intensive mixing. The P25@Pd was obtained by the same reduction process as that for P25@Pd-H₄BINDI-200. The resulting P25@Pd was mixed with an DMF solution of H₄BINDI and stirred for 6 h. The P25@Pd/H₄BINDI-200 was collected by centrifugation and dried for the following photocatalysis.

Electrochemical characterization

The electrochemical analysis was carried out on a Zahner Instruments electrochemical station in a traditional three electrode quartz cell. Briefly, Pt foils plate was used as the

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counter electrode, and Ag/AgCl as the reference electrode. The fluoride-tin $oxide (FTO)^{COTAI3BILK}$ glass had been thoroughly cleaned by ethanol and acetone and acted as working electrode. The catalyst (10 mg) was ultrasonicated in 0.5 mL of DMF to obtain slurry. Then, 40 mL of the slurry was spread onto the prepared FTO glass, and the side of the glass was previously protected using scotch tape to ensure the exposed area of the working electrode was controlled at 1 cm². Then, the coated working electrode was dried at room temperature in air without any heating process. The electrolyte was a 0.2 M aqueous Na₂SO₄ solution without additives. The Nyquist plots were measured covering the frequency of 1 × 10⁵ to 0.1 Hz intervals. The Mott-Schottky plots were measured at 800 and 1000 Hz.

Typical experimental procedure for photocatalytic test

In a general procedure for photocatalytic selective oxidation and reduction of alcohol, 10 mg of film photocatalyst was added into 1.5 mL trifluorotoluene (BTF) containing 0.1 mmol alcohol in a quartz tube equipped with a magnetic stirrer. The reaction system was evacuated and backfilled with oxygen at 1 atm pressure for five times before the reaction. The reaction system was stirred vigorously (500 rpm) and irradiated with a 300 W xenon lamp equipped with an ultraviolet cut-off filter (> 420 nm). After the reaction was finished, a certain amount of reaction solutions (60 μ L) was filtered by a one-time plastic filter and extracted with ethanol for GC analysis (Agilent 7890A). Controlled photoactivity experiments using various radical scavengers were performed in a similar manner to the photocatalytic experiment with radical scavengers (0.3 mmol) added to the reaction system.



General procedures for recyclability test

After photocatalysis, the reacted photocatalyst in the aqueous phase was separated by filter membrane and washed with ethyl alcohol. The recycled photocatalyst was dried at 70 °C under vacuum conditions. Then the collected photocatalyst was reused for another catalytic cycle with the addition of fresh benzyl alcohol and BTF.

Computational methods

The main calculations based on density functional theory (DFT) were carried out using the Vienna Ab initio Simulation Package (VASP). The kinetic cut-off energy of the plane-wave expansion was set to 500 eV. The effects of van der Waals interactions were considered by using the dispersion-corrected vdW-DF2 functional, and the dipole correction in the surface normal direction was applied. A six-layer slab with a (4×2) supercell was adopted to simulate TiO_2 (101) and (001) surface. To avoid the interactions between the neighboring slabs, the vacuum between adjacent slabs was set to 20 Å. A part calculation of H₄BINDI was carried out by G03 with 6-31G** basis set.

Results and discussion

The synthetic route of Mott-Schottky-type P25@Pd-H₄BINDI-T (T denotes the pyrolysis temperature) film photocatalyst was shown in Scheme 1. In a typical process, various number layers of Pd-H₄BINDI were readily encapsulated on TiO₂ substrate (Degussa, P25) through a facile alternating layer-by-layer (LbL) deposition method.

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The H₄BINDI (N, N'-bis (5-isophthalate acid) naphthalene-diimide) ligand was coordinated with Pd²⁺ using an LBL approach, which dually provides driving force for the efficient assembly of the thin films. The well-dispersed Pd NPs were obtained followed by mild calcination under an 5% H₂/N₂ atmosphere, affording P25@Pd-H₄BINDI-T as black powders. Unless otherwise specified, the P25 based film catalyst used in this work was coated with eight layers of Pd-H₄BINDI. The Pd content was determined to be 3.69 wt% by inductively coupled plasma atomic emission spectroscopy (ICP). FT-IR spectra were compared in P25@Pd-H₄BINDI and P25@Pd-H₄BINDI-200 (Fig. S9a) which showed almost no significant change. In more detail (Fig. S9b), the band at 1580 cm⁻¹, 1670 cm⁻¹ and 1708 cm⁻¹ can be ascribed to the carboxylate carbonyl functionalities, amide functionalities and imide carbonyl of free H₄BINDI,⁴³ respectively. Such characteristic peaks were also appeared in P25@Pd-H₄BINDI and P25@Pd-H₄BINDI-200, indicting the stability of the H₄BINDI during the reduction process (Scheme 1)

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Scheme 1. Schematic illustration for the synthesis of P25@Pd-H₄BINDI-T.

View Article Online In the present work, the ligand N, N'-bis (5-isophthalate acid) naphthalene-dilmide (H₄BINDI) (Fig. S1) ⁴⁴ was chosen to act as a useful building unit for the fabrication of LBL films. The clear evidence of loading of H₄BINDI in multilayer films was obtained by UV/vis spectra. As expected, the UV/vis absorption of guartz@Pd-H₄BINDI films was aroused from H₄BINDI, and its intensity increased systematically with the number of growth cycles (Fig. 1a). The result indicated the successful adsorption of the H₄BINDI into every layer of film through consecutive, alternating adsorption steps. The microstructure of films was further investigated by Powder X-ray diffraction (XRD) analyses. As Fig. 1b showed, the major peaks for films can be perfectly indexed as its substrate P25. It was noteworthy that the feature diffraction peaks of Pd at 40.1° (JCPDS no. 46-1043) also displayed on the XRD pattern of P25@Pd-H₄BINDI-200, revealing the successful reduction of Pd NPs on the films. In addition, the Pd valence state in P25@Pd-H₄BINDI film before and after reduction process were investigated by the Xray photoelectron spectroscopy (XPS), respectively. As Fig. 1c showed, P25@Pd- H_4 BINDI dominating Pd (II) due to two obvious binding energies of the Pd 3d5/2 and 3d3/2 electrons at 338.02 and 343.18 eV, corresponding to Pd²⁺ ions. After H₂ reduction process under 200 °C, the Pd 3d signal of P25@Pd-H4BINDI-200 can be fitted to two pairs of doubles: 340.95/335.65 eV and 343.13/337.89 eV, which can be assigned to Pd (0) and Pd (II),³⁹ respectively. These results indicated that the Pd (0) NPs were successfully inlayed into the P25@Pd-H₄BINDI-200 multilayer films. The distinct color change of samples also confirmed the successful adsorption of Pd-H₄BINDI films onto the P25 (Fig. S2). Furthermore, the optical properties of films were investigated

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by UV-vis diffuse reflection spectra, and the reflectance date of all samples were converted into absorbance by the Kubelka-Munk function (Fig. 1d). It was found that H₄BINDI not only provided driving force for the efficient assembly of the thin films, but also played a key role in extending the photo response of the film catalyst system to the abundant visible region. Notably, the resulting P25@Pd-H₄BINDI-200 film retained the intrinsic absorption of substrate P25 in the UV region, with remarkably broaden light adsorption cross section in the whole visible light region.



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Fig. 1. (a) Absorbance of P25@Pd-H₄BINDI films with various numbers of layer. (b) XRD patterns and (c) XPS spectra of Pd in P25@Pd-H₄BINDI and (d) P25@Pd-H₄BINDI-200 catalysts. (d) UV-vis diffuse reflection spectra of P25@Pd-H₄BINDI-200, P25@Pd-H₄BINDI, P25, and H₄BINDI.

The scanning electron microscopy (SEM) revealed the microsphere morphology of bare P25 (Fig. S4). The morphology and particle size of the P25@Pd-H₄BINDI-200 films were investigated by transmission electron microscopy (TEM) images. As shown in Fig. 2a, the well-dispersed Pd NPs within the multilayer films were detected. The

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high-resolution TEM (HRTEM) images showed that the lattice fringe of 0.235 and 2.35 and 2.35 and 3.235 and 3.2350.350 nm were matched (101) and (001) facets of P25, respectively (Fig. 2b). In addition, Pd NPs dispersed within P25 and H₄BINDI layers, and the intervals between two lattice fringes in Pd were 0.224 nm, corresponding to (111) plane of face-centered cubic Pd (Fig. 2c, d). HRTEM results revealed the close contact and lattice correlations between P25 and (Pd-H₄BINDI) films. Moreover, the interfacial part of the Pd NPs had been partially buried in a thin layer of P25 and H₄BINDI. Obviously, the P25 acted as a support and H₄BINDI as organic stabilizers for well-dispersed Pd NPs. These results certainly indicated that strong interactions have been established in P25@Pd-H₄BINDI-200 film, which ensured the formation of compact Schottky contact.



Fig. 2. (a) TEM and (b-d) HRTEM images for P25@Pd-H₄BINDI-200.

The application of solar energy in challenging organic synthesis is an especially promising strategy for synthetic chemistry. Encouraged by the remarkable absorption property of P25@Pd-H₄BINDI-200 in visible light, photocatalytic dehydrogenation and hydrogenolysis of benzyl alcohol was further explored. As Table 1 showed, the P25@Pd-H₄BINDI-200 demonstrated remarkable conversion of benzyl alcohol under mild conditions, affording a benzaldehyde yield of 66% and a toluene yield of 33% (entry 1), respectively. The activity was more than 17 times higher than those P25@Pd-H₄BINDI (entry 4) and was superior to the reported result on photocatalytic dehydrogenation and hydrogenolysis of aromatic alcohols in one reaction system.^{27, 41}

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The activity of our work also could compete with other reported analogous systems for the photocatalytic oxidation of benzyl alcohol (Fig. S7). It's worth mentioning that, the ratio of benzaldehyde and toluene remained unchanged even extended the reaction time. This suggested that dehydrogenation and hydrogenolysis of benzyl alcohol occurred simultaneously with high selectivity. The recent advances on reactive oxygen species of photocatalysts has emphasized that molecular oxygen is significant for alcohols photooxidation to aldehydes.⁴⁵ In addition, the photocatalytic activity was decreased under air atmosphere (entry 2). There were no byproducts without visible light irradiation (entry 3), indicating that the photoredox reaction over the P25@Pd-H₄BINDI-200 catalyst was due entirely to a photocatalytic process. P25@Pd-H₄BINDI-150 showed only 10% conversion under the same conditions (entry 5) due to the inadequate reduction of Pd. However, P25@Pd-H₄BINDI-300 showed much inferior catalytic activity (entry 6). The quartz@Pd-H₄BINDI-200 showed no conversion of benzyl alcohol (entry 7), indicting indispensable role of P25.

The quartz@Pd-H₄BINDI-200 showed no conversion of benzyl alcohol (entry 7), indicting indispensable role of P25. To further demonstrate the key role of P25 for photocatalytic activity, the contrast photocatalyst of SiO₂@Pd-H₄BINDI-200 was prepared. Due to the poor photoactivity of SiO₂, SiO₂@Pd-H₄BINDI-200 photocatalyst shows only 15 % conversion of benzyl alcohol under the identical conditions (entry 10), indicting the key role of P25 during the photocatalytic process. Nevertheless, bare P25 exhibit negligible activity, due to its wide band gap (entry 8). Although the H₄BINDI ligand can respond to the visible light, it gives only a minor mount of products

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under the same condition (entry 9). P25@Pd/H₄BINDI-200 with low photocatalytic activity indicted that the ingeniously integration of H₄BINDI ligand through layer-bylayer method also contributed to the efficient photocatalysis (entry 11). The relationship between catalytic activities and the number of films were further explored. The results showed that the conversion of benzyl alcohol correlated with the number of bilayers (Fig. S8). In other words, catalytic activity was related to loading amount of Pd-H₄BINDI. It can be concluded that the catalyst with more Pd-H₄BINDI bilayers has higher efficiency, and the conversion of benzyl alcohol realizes the maximum content of 100 % with eight layers of Pd-H₄BINDI.

Table 1. Photocatalytic dehydrogenation and hydrogenolysis of benzyl alcohol for 2 h under various conditions ^a

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Entry	Catalyst	Con. A/% ^b	Yield B/% ^b	Yield C/% ^b
1	P25@Pd-H ₄ BINDI-200	100	66	33
2°	P25@Pd-H ₄ BINDI-200	73	49	23
3 ^d	P25@Pd-H ₄ BINDI-200	0	0	0
4	P25@Pd-H ₄ BINDI	6	6	0
5	P25@Pd-H ₄ BINDI-150	10	10	0

6	P25@Pd-H ₄ BINDI-300	20	20	View Article Online DOI: 10.1039/C9TA13811K 0
7	quartz@Pd-H ₄ BINDI-200	0	0	0
8	P25	trace	trace	0
9	H ₄ BINDI	5	5	0
10	SiO ₂ @Pd-H ₄ BINDI-200	15	15	0
11	P25@Pd/H ₄ BINDI-200	8	8	0

^a Reaction conditions: 0.1 mmol benzyl alcohol, O₂ (1 atm), 1.5 mL BTF, 10 mg photocatalyst, and visible light illumination ($\lambda > 420$ nm).

^b Calculated by GC analysis.

^c Under air atmosphere.

^d In the dark.

The recyclability of a photocatalyst is very meaningful for its practical application. The stability of P25@Pd-H₄BINDI-200 was examined in the dehydrogenation and hydrogenolysis of benzyl alcohol under direct visible light exposure for 2 h. Strikingly, the photocatalytic activity of P25@Pd-H₄BINDI-200 could be maintained at least 5 runs, indicting the excellent recyclability and photostability of P25@Pd-H₄BINDI-200 in this coupled system (Fig. 3a). In addition, the time-resolved photoluminescence (TRPL) spectra in Fig. 3b showed that the emission induced by the P25@Pd-H₄BINDI-200 exhibited a much longer lifetime than that of P25 and P25@Pd-H₄BINDI-300, indicting the most efficient e⁻-h⁺ separation efficiency. It was very promising for the target reactions under visible light irradiation.



Fig. 3. (a) Recyclability of P25@Pd-H₄BINDI-200 in the dehydrogenation and hydrogenolysis of benzyl alcohol upon direct visible light exposure for 2 h. (b) Photoluminescence decay curve of the P25@Pd-H₄BINDI-200 and P25@Pd-H₄BINDI-200-T.

The efficient photogenerated charge separation contributes to the prominent photocatalytic activity. In this regard, the photocurrent and electrochemical impedance spectroscopy (EIS) measurements were explored to prove the rapid charge separation efficiency. As Fig. 4a showed, the photocurrent measurements featured good reproducibility over several on/off cycles of intermittent irradiation ($\lambda > 420$ nm). Moreover, the P25@Pd-H₄BINDI-200 produced the highest photocurrent response, indicating the most efficient transfer and longest lifetime of photoexcited charges. Inversely, P25 showed no visible light responsiveness due to its wide band gap. Furthermore, the rapid charge separation efficiency was also proved by open circuit photovoltaic measurements (Fig. 4b). The P25@Pd-H₄BINDI-200 indicated the smallest radius at high frequencies, suggesting a lowest resistance in charge transportation and an efficient mechanism for e⁻h⁺ separation. The more favorable electron contacts between Pd and P25 was attributed to the Mott-Schottky effect. These results clearly revealed that the synergistic constitution of films accelerated the trapping and transferring of the photoinduced electrons, which should be beneficial for the

View Article Online efficient photocatalysis. These results obviously matched well with the measured $UV^{39/C9TA13811K}$ visible absorption spectra and photocatalytic activity order. The remarkable photocatalytic dehydrogenation and hydrogenolysis of benzyl alcohol over $P25@H_4BINDI-Pd-200$ was initiated by the Schottky junctions of Pd NPs, which significantly promoted the electrons transfer and reduced the recombination of photogenerated electron-hole pair. It has been reported that the Schottky junction will be formed between Pd NPs and TiO₂ due to their different Fermi level positions (Fig. 3c-d).^{46, 47} In general, the work functions of noble metals are usually larger than those of n-type semiconductor.^{48, 49} That is, the Fermi level (E_F) of P25 is higher than the E_F of Pd NPs. When Pd NPs is in direct contact with a P25 (Fig. 4c), the electrons of the CB P25 will transfer to the Pd NPs (entitled "metal island") at the lower energy level to build up an equilibrium state between their Fermi level. It was mainly attributed the formation of Mott-Schottky heterojunction at the interface of P25 and metallic Pd that increased the electron density of Pd NPs, promoting the injection of hot electrons from photoactivated P25 to Pd NPs (Fig. 4d).

A detailed investigation of energy levels of photocatalysts were explored by electrochemical Mott-Schottky measurements in conjunction with Tauc plot (Fig. S5-S6). Evidently, the positive slope of the obtained C⁻²-V value demonstrated the n-type character of P25 and H₄BINDI ligand. The conduction band (CB) position for P25 and H₄BINDI, which was determined from the intersection with value of -0.58 V, -0.77 V versus Ag/AgCl (-0.38 V, -0.57 V *vs*. normalized hydrogen electrode (NHE)), respectively. With assistant of Tauc plot, the valance band value of P25 and H₄BINDI

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was then calculated to be 2.74 V and 2.23 V, respectively.



Fig. 4. (a) Photocurrent tests and (b) EIS plots of P25, P25@Pd-H₄BINDI-200 and P25@Pd-H₄BINDI-300. (c) The potential diagram of H₄BINDI, P25 and Pd. (d) Schematic illustration of the Mott-Schottky-type contact of Pd NPs and P25. (E_F : work function; E_{CB} : conduction band; E_{VB} : valence band)

Based on the above experimental and theoretical results, the illustration of carrier dynamics in selective reduction-oxidation of benzyl alcohol was proposed in Scheme 2. Firstly, the H₄BINDI ligand was excited by visible light ($\lambda > 420$ nm) to produce energetic electrons and holes. Density functional theory (DFT) calculations were performed and the bandgap of H₄BINDI and P25 were corrected according to the experiment results (Fig. S5), respectively. The results noted that (Fig. 3c), the lowest unoccupied molecular orbital LUMO value of H₄BINDI (-3.72 V) was more positive than that of P25 (-4.33 V), which was thermodynamically allowed for electrons transfer. Evidently, the photogenerated electrons will inject from the H₄BINDI into the P25 conduction band. The unique route for wide band-gap P25 to use visible light is similar

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to the traditional dye-sensitized mechanism. Ultimately, amounts of electrons Wilf be accumulated in the CB of P25, making them "hot" enough to diffuse to the Pd NPs surface due to the Mott Schottky effect. Pd NPs play a vital mediating role in storing and shuttling photogenerated hot electrons. Finally, the electrons accumulated on the Pd NPs surface will be consumed by hydrogenolysis process of benzyl alcohol, which inhibited the recombination of e-h⁺ pairs and induced the holes to participate in dehydrogenation of benzyl alcohol continuously. In return, the Schottky barrier also effectively restrained the electron drift from the NPs back to the P25. Synergistically, the photogenerated holes left on the valance band (VB) of H₄BINDI will participate in oxidation reactions, promoting photocatalytic cycles. As a result, the dehydrogenation reaction consumed two holes and released two protons to produce benzaldehyde. This process essentially separated and synchronously utilized the photogenerated electrons and holes, which further improved the activity for the photocatalytic reductionoxidation of benzyl alcohol. Under visible light irradiation, benzyl alcohol consumes the photo-generated holes and releases two protons to produce benzaldehyde. In addition, Pd is reported as a famous protons catcher which can facilely form Pd-H catalytic sites to promote the reduction half reaction.²⁷ As a result, the benzaldehvde further depletes two protons to generate toluene and molecular oxygen. Finally, the production of benzaldehyde and toluene were realized in one single system.²⁷ It was worth mentioning that, the hydroxyl group is a poor leaving group, it is of great significance to transform hydroxyl group into its corresponding alkyl group under mild photocatalysis condition.



Scheme 2. The proposed reaction mechanism for the photocatalytic selective reductionoxidation of benzyl alcohol over P25@H₄BINDI-Pd-200 under visible light irradiation.

Conclusions

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In summary, a promising strategy for coupling the unique properties of Pd NPs with the functionality of P25 was proposed through utilization of the LBL technique. The resulting P25@Pd-H₄BINDI-200 photocatalyst displayed a drastically enhanced photocatalytic performance benefitting from accelerated electrons transfer. This work realized dehydrogenation and hydrogenolysis of benzyl alcohol simultaneously. The Schottky barrier created at the interface between Pd NPs and P25 greatly prompted the hot electrons transfer. The concept demonstrated here will provide a novel solar-driven catalyst platform for utilizing Mott-Schottky effect for promoting solar-to-chemical conversion.

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This work realized dehydrogenation and hydrogenolysis of benzyl alcohol simultaneously.