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Article

Pyroelectricity effect on photoactivating palladium nanoparticles in PbTiO_3 for Suzuki coupling reaction

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ABSTRACT

Combining microwave radiation with photocatalytic systems is a promising method to inhibit photogenerated electron-hole recombination and enhance the photocatalytic reaction performance. In this study, we have designed Pd/PbTiO_3 catalysts that can use both microwave fields and photocatalysis. Benefiting from the synergistic effect of microwave field and UV light, the PbTiO_3 crystals convert thermal energy into electrical energy via the pyroelectricity effect, generating positive and negative charges (q^+ and q^-), while Pd nanoparticles significantly improve the quantum efficiency of the photocatalytic process. The composite catalyst significantly enhances the reaction rate and selectivity of the model Suzuki coupling reaction performed with bromobenzene. Microwave fields can directly act on chemical systems, promoting or changing various chemical reactions in unique ways.

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1. Introduction

Photocatalytic technology is considered a potential green technology because of the following advantages: environmental protection and low energy consumption [1–4]. The conditions required for photocatalytic redox reactions are milder than the conventional catalytic conditions; moreover, the use of certain strong oxidants and harmful reducing materials can be avoided [5,6]. Therefore, many researchers have applied photocatalysis in the field of organic synthesis [7–12]. However, in many reactions, the time required for the conversion of organics is long, and the selectivity is poor [13]. This is attributed to the low solar energy utilization efficiency and easy recombination of

photogenerated electrons and holes. Recently, the photocatalytic performance has been significantly improved by using external fields such as microwave, thermal, electric, magnetic, and ultrasonic fields [14–20].

In recent years, microwave technology has been applied in environmental science, pollution control engineering, environmental monitoring and analysis, clean production, and green technology; moreover, it has been used to achieve technological innovation and breakthroughs [21]. Microwaves strongly penetrate materials and start heating directly from the inside of the materials, resulting in uniform and efficient heating, which makes microwave heating environmentally friendly [22,23]. The essence of microwave heating is the conversion of

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microwave energy into thermal energy. Pyroelectric materials can convert absorbed thermal energy into electrical energy. The pyroelectric effect is a natural physical effect observed in crystals [24]. In this phenomenon, charge is released when the polarization intensity changes with temperature [25–30]. When a crystal with spontaneous polarization is heated or cooled, a spontaneous polarization change (ΔP_s) occurs due to the temperature change (ΔT), resulting in the generation of surface polarization charges in a certain direction in the crystal [31]. Macroscopically, temperature changes will produce positive and negative charges (q^+ and q^-) at both ends of the material, which are then transferred from the surface of the catalyst to the reactant molecules, promoting the reaction [32].

Tetragonal perovskite PbTiO_3 is a ferroelectric material with a high Curie temperature and a low dielectric constant [33–35]. With a change in the temperature, the spontaneous polarization of PbTiO_3 becomes more intense, resulting in a stronger pyroelectric effect [36]. In addition, PbTiO_3 exhibits another important characteristic: birefringence, making it an important material for photovoltaic applications [37]. However, as a photocatalyst, the excessively wide band gap of PbTiO_3 is not conducive to the formation of photogenerated electrons and holes [38].

In this work, we have designed a Pd/PbTiO_3 photocatalyst to promote organic synthesis under the synergistic effect of microwave field and UV light. The Pd nanoparticles (Pd NPs) promote the separation of photogenerated electrons and holes of PbTiO_3 . Furthermore, we have achieved a highly active and selective Suzuki coupling reaction by exploiting the photocatalytic performance and pyroelectric effect of PbTiO_3 . Combining photocatalysts with microwave radiation opens up new possibilities for interdisciplinary research.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of PbTiO_3 nanosheets by the hydrothermal method

In this study, analytical grade chemicals (Sigma Aldrich) were used without further purification. PbTiO_3 nanosheets were synthesized by the hydrothermal method. Typically, 0.4 g of Degussa P25 was dispersed in 17.5 mL of potassium hydroxide aqueous solution (7 mol L^{-1}), and the mixture was uniformly dispersed under vigorous stirring. Next, a certain amount of lead acetate was added to the above solution (Pb:Ti molar ratio = 1.25:1) and rapidly stirred for 2 h. Finally, 3 mL of polyethylene glycol and 14.5 mL of deionized water were added and stirred for 10 min. Then, the resulting solution was subjected to hydrothermal reaction in an oven at 200 °C for 12 h. The obtained product was washed several times with deionized water and dried for future use; the final product was a pale-yellow powder.

2.1.2. Preparation of Pd/PbTiO_3 by photoreduction

Typically, 150 mL of deionized water and 50 mL of ethanol (sacrificial agent) were placed in a 250 mL beaker at room

temperature and uniformly stirred. Then, 1.0 g of PbTiO_3 powder was added to the above solution, sonicated for 10 min, and a certain amount of PdCl_2 aqueous solution was added. The resulting mixture was stirred for 30 min under irradiation with a 300 W xenon lamp (1050 mW cm^{-2}). The obtained solution was centrifuged, washed with deionized water for four times, and then, dried in a vacuum oven at 80 °C. The resulting gray particles were ground and sieved to obtain a gray powder: Pd/PbTiO_3 catalyst (theoretical load: 0.5 wt%).

2.2. Characterization

The crystal structure was characterized by X-ray diffraction (XRD, Rigaku D/MAX-2000) using a $\text{Cu K}\alpha$ source at 40 kV and 20 mA (scan rate: 5° min^{-1}). The UV-Vis diffuse reflectance spectra were recorded on a spectrophotometer (Shimadzu, UV2600) with an integrating sphere attachment in the range of 200–800 nm using BaSO_4 as the reflectance standard. The morphology was characterized with a scanning electron microscope (SEM, Hitachi S4800) and a transmission electron microscope (TEM, JEOL JEM-2010, operated at 200 kV). The surface electronic states were determined by X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI 5000C, Al $\text{K}\alpha$).

2.3. Photocatalytic activity

We selected the Suzuki carbon-carbon coupling reaction as the probe reaction. Typically, certain amounts of halobenzene (0.5 mmol), phenylboronic acid (1.2 equiv.), tetrabutylammonium bromide (TBAB, 0.5 equiv.), K_3PO_4 (3.0 equiv.), and $\text{EtOH/H}_2\text{O}$ (1:1) were placed in a quartz reactor. Then, a certain amount of the Pd/PbTiO_3 catalyst was added and the reactor was placed in a microwave-photocatalytic reaction device. The reaction conditions were UV light (300 W mercury lamp), 600 W microwave power, 80 °C, and 500 rpm. A Shimadzu GCMS-QP2010 SE gas chromatograph-mass spectrometer (GC-MS) was used to determine the biphenyl yield. An Rxi-5MS column with a diameter of 0.25 mm was used. The spectra were collected in the SIM mode and quantitatively analyzed using 1,3,5-trimethylbenzene as the internal standard.

3. Results and discussion

All the peaks in the XRD patterns of the PbTiO_3 and Pd/PbTiO_3 samples (Fig. 1(a)) were assigned to the tetragonal perovskite PbTiO_3 phase (PDF #06-0452), confirming the successful synthesis of PbTiO_3 . The strong and sharp diffraction peaks indicated that the prepared samples were highly crystalline [39]. The absence of Pd diffraction peaks was probably due to the small loading amount of Pd. In addition, as observed from the UV-Vis diffuse reflectance spectra, the single crystalline PbTiO_3 samples exhibited strong absorption in the UV region and weak visible absorption at 400–450 nm (Fig. 1(b)). Notably, the absorption in the visible light region was significantly enhanced after Pd NPs loading, which demonstrated the high photocatalytic reaction potential of the sample. The prepared perovskite single crystalline PbTiO_3 sample consisted of

Fig. 1. (a) XRD patterns and (b) UV-Vis diffuse reflectance spectra of PbTiO_3 and Pd/PbTiO_3 . SEM images of (c) PbTiO_3 and (d) Pd/PbTiO_3 .

nanosheets and cubic crystals, as shown in the SEM image in Fig. 1(c). It could be clearly observed from Fig. 1(d) that the Pd NPs were supported on the surface of PbTiO_3 , confirming the successful synthesis of Pd/PbTiO_3 . More importantly, Pd NPs were selectively deposited on one side of single crystalline PbTiO_3 , because of surface polarization charge screening. This was attributed to the fact that the metal ions coordinated to Cl⁻ were concentrated on the positive electrode surface of the single crystal and were reduced to a simple substance on the positive electrode surface, resulting in the selective deposition of the noble metal NPs.

The PbTiO_3 nanosheets had lateral dimensions of about 500 nm, as shown in the TEM image Fig. 2(a). The high-resolution TEM (HRTEM) image in Fig. 2(b) shows lattice fringes with a spacing of 0.390 nm, which was assigned to the (100) facet.

Fig. 2. TEM images of Pd/PbTiO_3 (insert in (b): SAED pattern).

Furthermore, the corresponding selected area electron diffraction (SAED) pattern (inset in Fig. 2(b)) confirmed that the PbTiO_3 nanosheet was monocrystalline and had the advantage of the (100) facet. Fig. 2(c) confirmed the presence of Pd NPs; as observed, the Pd NPs were mainly concentrated on one side of single crystalline PbTiO_3 . The HRTEM image of the selected area showed a different interplanar spacing, which corresponded to the (111) facet of Pd (Fig. 2(d)).

XPS was performed to determine the chemical state and elemental composition of 0.5 wt% Pd/PbTiO_3 . The XPS profile showed peaks due to Ti, O, Pd, and Pb; no impurity peak was detected, indicating the high purity of the sample (Fig. S1(a)). Furthermore, to further explore the existence of Pd and its chemical state, the high-resolution Pd 3d spectrum was recorded. Two sets of spin-orbit coupling peaks were observed (Fig. S1(b)). The Pd ($3d_{5/2}$, $3d_{3/2}$) peaks at 334.8 and 340.3 eV were attributed to Pd^{2+} and those at 336.5 and 342.4 eV were attributed to Pd^0 respectively, indicating that the valence and zero-valent metal Pd existed on the surface of PbTiO_3 [40].

In addition, a comparison of the spectra of the catalysts before and after the loading (Fig. 3(a–c)) showed that the Ti 2p, O 1s, and Pb 4f peak binding energies were significantly different. The Ti 2p and O 1s peaks shifted to higher binding energies after Pd deposition. This was possibly due to the interaction between the Pd NPs and PbTiO_3 substrate, indicating that the binding between supports was stronger. The change in the binding energy measured by XPS could be attributed to the bending of the electron band near the surface. When the Pd NPs were in contact with the PbTiO_3 crystal, the Fermi levels of Pd and PbTiO_3 reached equilibrium via consumption of most of the carriers near the dielectric interface, which resulted in the bending of the electron band and formation of a Schottky bar-

Fig. 3. XPS profiles of PbTiO_3 and Pd/PbTiO_3 . (a) Ti 2p, (b) O 1s, and (c) Pb 4f spectra.

rier junction [41].

To study the generation of pyroelectric charges, the thermal current responses for PbTiO_3 and Pd/PbTiO_3 with respect to the change in temperature were measured. The temperature change curve recorded during the heating process, which was controlled by a constant temperature heater, is shown in Fig. 4(a). The electrolyte temperature remained constant after reaching 60 °C. For both PbTiO_3 and Pd/PbTiO_3 , the current increased with increasing temperature at the beginning, and it decreased when the temperature was constant (Fig. 4(b)). This indicated that the change in temperature generated charges at both ends of the materials. Moreover, after PbTiO_3 was loaded with Pd NPs, the current intensity significantly increased, reaching 0.73 μA . The results showed that Pd NPs contributed to charge migration, carrier recombination inhibition, and catalyst activity improvement.

We performed the Suzuki coupling reaction using bromobenzene (Fig. 5(a)). The biphenyl yield obtained in the presence of Pd/PbTiO_3 was much higher than that obtained in the presence of PbTiO_3 , under the same reaction conditions (Fig. 5(b)). To investigate the cause of the increased reactivity, we

conducted exploratory experiments. Firstly, the influence of the pyroelectric effect (induced by the microwave field on the catalyst) on the photocatalytic organic synthesis process and the possible mechanism were investigated under five different conditions (CH, MW, UV, UV + CH, and UV + MW). It was found that the reactivity under the UV and microwave co-irradiation condition was the highest (Fig. 6(a)). The yield of biphenyl reached 78.2% within 20 min, which was 14 times higher than that obtained under only the UV irradiation condition. In addition, the catalyst could promote the reaction under only heating, without UV and microwave irradiation. This was attributed to the thermal nature of the Suzuki coupling reaction and heating-induced pyroelectric effect of the catalyst, enabling the catalyst to be excited in the absence of light. Under microwave irradiation, the activity was significantly higher than that under separate heating conditions. This was due to the unique heating properties of microwave, which enabled the material to release more charges, thus promoting the reaction. The reactivity significantly decreased when PbTiO_3 was replaced with TiO_2 , because TiO_2 does not exhibit any pyroelectric effect (Fig. S2).

Furthermore, the effect of microwave power on the

Fig. 4. Thermal current measurement results: (a) temperature curve recorded during heating and (b) the corresponding thermal current response graph.

Fig. 5. (a) Suzuki coupling reaction. (b) Biphenyl yield obtained using PbTiO₃ and Pd/PbTiO₃ under the same reaction conditions. Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (1.2 equiv.), TBAB (0.5 equiv.), K₃PO₄ (3.0 equiv.), EtOH/H₂O (1:1), UV light (300 W Hg lamp), 600 W microwave power, 80 °C, 500 rpm, 1 h. The yield was determined using GC-MS with 1,3,5-trimethylbenzene as the internal standard.

Pd/PbTiO₃-catalyzed Suzuki coupling reaction was investigated. As shown in Fig. 6(b), as the microwave power increased, the activity significantly improved, reaching a maximum value at 600 W. To save energy, powers >600 W were not used. Thus, in this process, microwave irradiation led to not only thermal effects but also non-thermal effects, which possibly influenced the catalyst or directly the reactants. Moreover, experiments were performed to determine the stability of the catalyst. The results showed that the activity of the catalyst decreased after three reaction cycles. This was possibly due to the adsorption of organic substances on the catalyst surface, which hindered the reaction. To remove the organic matter from the surface, the catalyst was calcined at 400 °C, thereby the catalyst activity was restored (Fig. S3). On comparing the XPS profiles of

Pd/PbTiO₃ before and after the reaction under different conditions, we found that the binding energy of the Pd/PbTiO₃ catalyst did not significantly change, which reflected the excellent stability of the catalyst (Fig. S4).

To broaden the application potential of the Pd/PbTiO₃ catalyst, we performed the Suzuki coupling reaction with different substrates. High yields were obtained for different substrates in this reaction system, as shown in Table S1. Overall, microwave-assisted photocatalytic organic synthesis is an efficient and environmentally friendly method.

To determine the mechanism of the Suzuki coupling reaction catalyzed by Pd/PbTiO₃, we measured the coupling reaction activity after adding a capture agent. In the presence of ethylenediaminetetraacetic acid, the yield of biphenyl decreased from 78% to 38%, while in the presence of AgNO₃, the yield was only 28% (Fig. S5). It was found that both e⁻ and h⁺ influenced the reaction, with e⁻ playing the major role. Fig. 7 shows the schematic of a probable mechanism for the Suzuki coupling reaction using Pd/PbTiO₃ under microwave-photocatalytic conditions. Under UV light irradiation, the Pd/PbTiO₃ catalyst generated electron-hole pairs, and the generated electrons were immediately transferred between PbTiO₃ and Pd. A change in temperature resulted in a net change in the electric dipole moment of the high-temperature catalyst, which resulted in charge compensation on the surface of the thermal catalyst. The positive and negative charges (q⁺ and q⁻) generated at the high temperature were transferred from the surface of the pyrolysis catalyst to the reactant molecules to participate in the reaction. At thermodynamic equilibrium ($\Delta T = 0$), the compensated charges on the surface completely shielded the polarization charge. When PbTiO₃ was heated, the polarization density decreased ($\Delta P_s < 0$), resulting in the formation of uncompensated charges on the surface of PbTiO₃, which were then transferred to the reactant molecules to form an intermediate state. When the temperature was constant ($\Delta T = 0$), the system returned to the initial state. When PbTiO₃ cooled down, the polarization density increased ($\Delta P_s > 0$), and PbTiO₃ absorbed the charges from the solution, thereby promoting the formation of the product. At the same time,

Fig. 6. Biphenyl yield obtained using Pd/PbTiO₃ under different (a) reaction conditions (conventional heating (CH), microwave (MW), UV irradiation (UV), UV + CH, and UV + MW; 20 min) and (b) microwave power conditions.

Fig. 7. Schematic of biphenyl synthesis using Pd/PbTiO₃ cocatalyst.

Pd/PbTiO₃ was excited by UV light, leading to the formation of photogenerated electrons and holes, which further promoted the reaction. Under the action of the double charge, the catalyst exhibited high activity and selectivity for the Suzuki coupling reaction regardless of the substrate.

4. Conclusions

In summary, we successfully prepared Pd/PbTiO₃ nanosheets by a simple hydrothermal reaction. Because of the combination of photocatalytic and pyroelectric effects, Pd/PbTiO₃ showed excellent activity and selectivity for the Suzuki coupling reaction. Experimental results showed that positive and negative charges (q⁺ and q⁻) were generated on both ends of PbTiO₃ at high temperatures, and then, were transferred from the catalyst surface to the reactant molecules to participate in the reaction. The Pd NPs further promoted charge migration and increased the activity of the catalyst. The Pd/PbTiO₃ showed great potential in organic synthesis under microwave-light irradiation, and also promotes the development of photocatalytic organic synthesis.

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Graphical Abstract

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The pyroelectric effect of PbTiO_3 crystal promotes organic reaction and enhances reactivity under the action of microwave field and ultraviolet light. The effect of microwave on the catalyst was studied by performing the model Suzuki coupling reaction with bromobenzene.

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Pd/PbTiO₃表面的热电效应增强光催化Suzuki偶联反应闻洁雅^a, 凌丽丽^b, 陈瑶^a, 卞振锋^{a,*}^a上海师范大学, 资源化学教育部重点实验室, 稀土功能材料上海重点实验室, 上海200234^b上海电力大学, 上海201303

摘要: 发展绿色化学技术是21世纪化学研究的一个重要方向, 其主要目标是取代那些对环境有害的耗能过程, 其中新能源尤其是太阳能开发利用的重要性愈加突显。光催化作为一种低能耗、高效、无二次污染的技术, 以其反应条件温和、能直接利用太阳能转化为化学能的优势而备受科研人员关注。光催化技术是利用半导体材料作为催化剂的光催化过程, 当能量高于半导体禁带宽度的光子照射半导体材料时, 半导体材料上的价带电子发生带间跃迁, 从价带跃迁到导带, 从而产生带正电荷的光致空穴和带负电荷的光生电子。光致空穴的强氧化能力和光生电子的还原能力导致半导体光催化剂引发一系列光催化反应的发生。光催化选择性氧化还原体系的出现和应用极大地满足了人们对能源和环境的要求。在光催化选择性氧化还原体系中, 反应发生所需要的条件比传统催化温和, 同时它也避免了一些危险的强氧化剂和还原性物质的使用。但是在一些过程中, 催化反应常常需要在高温下进行。传统加热是由外部热源通过热辐射由表及里的热传导的方式进

行的, 并且为了达到催化温度, 需使催化剂床层整体升温. 而微波诱导的催化方法与常规不同, 微波不仅加热速度快、能源利用率高, 而且加热均匀、温度梯度小, 因此微波化学作为一门新兴的前沿交叉学科, 已在广泛的实际应用中显示出强大的生命力. 将光催化技术与微波联用可能会取得意想不到的成果.

微波与光催化系统相结合是抑制光生电子–空穴复合并增强光催化反应性能的一种有效方法. 本文通过简单的水热反应制备了单晶 PbTiO_3 纳米片. 由XRD谱可以看出, 所有衍射峰均归属于四方钙钛矿相 PbTiO_3 , 紫外-可见漫反射光谱表明单晶 PbTiO_3 在紫外光区域有强吸收, 在400–450 nm处还存在微弱的可见光吸收. 另外, 负载了Pd纳米颗粒之后, 在可见光区域吸收明显增强. 这说明我们成功制备了一种既能利用微波又能利用光催化的Pd/ PbTiO_3 催化剂. 利用 PbTiO_3 晶体的热释电效应在微波场下与紫外光协同促进以溴苯引导的Suzuki偶联反应发生, 反应速度和选择性显著提高. 在微波场和紫外光的协同作用下, PbTiO_3 晶体的热电效应可以将热能转换为电能, 产生正电荷和负电荷(q^+ 和 q^-), 而Pd纳米粒子则显著提高了光催化过程的量子效率. 光催化技术协同微波场可以直接作用于有机化学反应, 以独特的方式促进甚至改变各种化学反应过程.

关键词: 光催化; 热释电; 微波; Suzuki偶联反应

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