

The enhanced catalytic performance of Pd/SiC for the hydrogenation of furan derivatives at ambient temperature under visible light irradiation†

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By using semiconductive SiC as the support, palladium exhibits a tremendous promotion of its intrinsic catalytic activity for the hydrogenation of furan derivatives at ambient temperature under visible light irradiation. The promotion in the catalytic activity results from the fact that the Mott–Schottky contact between SiC and Pd enhances the quick transfer of the photo-generated electrons from SiC to Pd nanoparticles.

Photocatalysis has received a large interest since it can exploit solar energy. The early studies focused on the photodegradation of organic pollutants and then photocatalytic hydrogen production.^{1,2} Recently, photocatalytic selective transformations of organics are becoming increasingly noticeable.^{3,4} Metal oxide semiconductors and plasmonic metals are widely employed as photocatalysts to catalyze the oxidation of alcohols and amines, C–H bond activation and the reduction of nitroaromatics.^{5,6} Palladium (Pd) is widely used as a catalyst in heterogeneous catalytic reactions.⁷ The improvement of the catalytic activity of Pd catalysts is generally achieved by precisely dispersing Pd particles on solids with a high surface area to expose as many Pd atoms as possible. Recent work indicates that the catalytic activity of Pd can be significantly increased by alloying gold, a plasmonic metal whose nanoparticles absorb light and produce energetic electrons due to the localized surface plasmon resonance.⁸ Cubic SiC (β -SiC) is a non-oxide semiconductor with a band gap of ~ 2.4 eV,^{9,10} which enables it to absorb visible light. Since the conduction band of SiC is very negative (-1.3 V),² it will produce energetic photo-generated electrons under light irradiation. If the energetic electrons can efficiently transfer to Pd nanoparticles supported on SiC by means of a Mott–Schottky contact, then the intrinsic catalytic activity of Pd is expected to be enhanced significantly.

Furan and its derivatives can be massively obtained from biomass and therefore they are important platform molecules to produce energy and chemicals.¹¹ These molecules usually contain C=C, C=O, and C–O–C bonds, and they need hydrogenation or hydrogenolysis using metal catalysts before utilization.^{12,13} For example, the selective hydrogenation of furfural generates tetrahydrofurfural or methyltetrahydrofuran.¹⁴ The former can be converted into diesel fuel components by self-aldol condensation and the latter is a principal component of P-series fuel.¹² Pd is one of the most extensively studied catalytic metals for furan hydrogenation.¹⁵ The reaction is generally carried out under the conditions of high temperature and pressure to achieve a high yield and efficiency.¹⁶ Herein, we demonstrate that the catalytic activity of Pd for furan hydrogenation can be greatly promoted by using photoactive SiC as the support under irradiation of visible light.

The powder-like β -SiC support with a specific surface area of 48 m² g⁻¹ was prepared by a sol–gel and carbothermal reduction route.¹⁷ The 3 wt% Pd/SiC catalyst was prepared *via* a liquid phase reduction method. Firstly, 291 mg of SiC and 22.5 mg of palladium nitrate were dispersed into absolute ethanol under sonication, then the suspension was magnetically stirred to get a mixture of palladium nitrate and SiC. Secondly, the mixture was reduced using diethylene glycol for 2 h at 180 °C to obtain the Pd/SiC catalyst. For comparison, Pd/SiO₂ and Pd/TiO₂ with the same Pd loading of 3 wt% were also prepared by a similar method.

Fig. 1A and B show the transmission electron microscopy (TEM) images of the Pd/SiC catalyst. Homogeneous Pd nanoparticles are uniformly dispersed on the SiC surface, and their mean diameter is ~ 5 nm. From the X-ray diffraction (XRD) patterns (Fig. 1C), all the strong diffraction peaks can be indexed to β -SiC. The diffraction peak at $2\theta = 46.7^\circ$ is attributed to cubic Pd. Fig. 1D shows the ultraviolet (UV) and visible absorption spectra of the pure SiC and Pd/SiC catalyst. The spectra indicate that β -SiC has strong UV and visible absorption. The maximal peak appears at about 375 nm,

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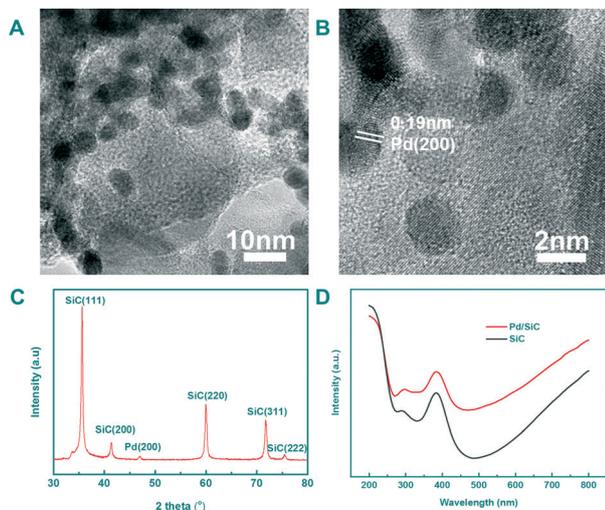


Fig. 1 The TEM images (A, B), XRD patterns (C) and UV-vis absorption spectra (D) of the 3 wt% Pd/SiC catalyst.

which is similar to that previously reported.¹⁰ However, the Pd/SiC catalyst displays stronger absorption in the UV and visible range, indicating that the light energy can be better exploited by the catalyst. The visible absorption spectra of Pd/SiC above 530 nm are gradually strong resulting from the infrared absorption of SiC and the reflection of the sample in the measurement.

The photocatalytic performances of the 3 wt% Pd/SiC catalyst for the hydrogenation of furan and its derivatives were conducted in an *n*-amyl alcohol solution under the irradiation of a 300 W Xe lamp, whose wavelengths range from 400 to 800 nm. The reaction results are summarized in Table 1. The Pd/SiC exhibits a high activity and selectivity under light irradiation, suggesting that the catalyst has the general applicability for these reactions. Over the Pd/SiC photocatalyst, the

Table 1 The photocatalytic hydrogenation of furan derivatives over a Pd/SiC catalyst^a

Reactant	Main product	Conv. (%)	Select. (%)	TOF (h ⁻¹)
		99	99	70
		99	99	70
		99	99	70
		95	81 ^b	56
		89	78 ^b	49
		81	70 ^b	40

^a Reaction conditions: 4 mmol reactant, 80 mg 3 wt% Pd/SiC catalyst in *n*-amyl alcohol (10 ml) at 25 °C and 1 MPa of H₂, reaction time 2.5 h, and irradiation intensity 0.15 W cm⁻². ^b The other products are alcohols, acids and esters due to the ring hydrogenolysis of furan derivatives.

yield of tetrahydrofuran (THF) from furan hydrogenation is 99% and the turnover frequency (TOF) is 70 h⁻¹. These are comparable to the thermal catalytic results (the yield and TOF are 98% and 16 h⁻¹, respectively, at 40 °C and 8 MPa H₂).¹⁶ The control experiment reveals that the Pd/SiC catalyst in the dark can only achieve a furan conversion of 37%, suggesting that the high activity of the Pd/SiC under irradiation mainly results from the light driving.

Under the same temperature and pressure conditions, increasing the light intensity resulted in a nearly linear increase for the conversion of furan (Fig. 2A). To ensure that a thermal effect could be discounted, the reaction temperature was carefully controlled and maintained at 25 °C. The contribution of the light induced conversion was calculated by subtracting the conversion in the dark (thermal effect) from the total one under irradiation. The relative contributions of the irradiation and thermal effect to the total conversion are shown in Fig. 2A. The contribution of the light induced conversion increases with the light intensity. For instance, only 42% of the total conversion results from the light irradiation when the light intensity is 0.1 W cm⁻²; while that is 62% when the light intensity is 0.15 W cm⁻². This suggests that the promotion in the catalytic activity of Pd/SiC originates from the light irradiation.

The dependence of the catalytic activity on the irradiation wavelength is illustrated in Fig. 2B. A series of optical low-pass filters were employed to block light below a specific cut-off wavelength. Without any filters, the irradiation of light with wavelengths ranging from 400 to 800 nm gives a furan

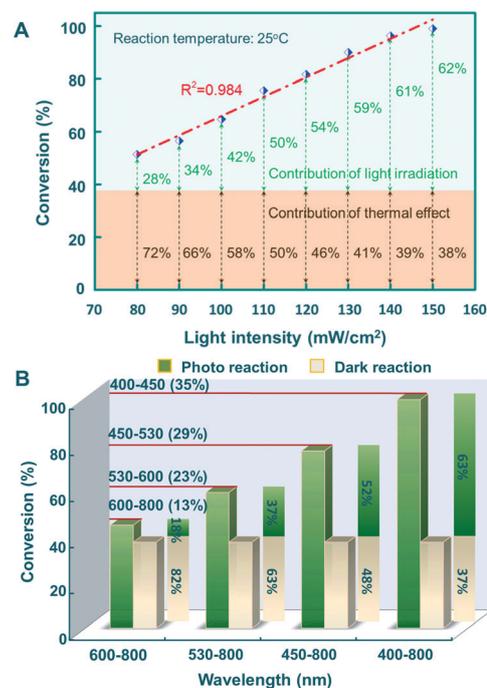


Fig. 2 The dependencies of the catalytic activity of Pd/SiC for furan hydrogenation on the intensity (A) and wavelength range (B) of light irradiation, respectively.

conversion of 99%. The conversion decreases to 77%, 59% and 45% when the wavelength range of the irradiation is 450–800, 530–800, and 600–800 nm, respectively. Since the conversion of furan in the dark is 37%, the light in the 600–800 nm wavelength range contributes 8 percentage points (45–37%), accounting for 18% ($8/45 \times 100\%$) of the total conversion and 13% ($8/(99 - 37) \times 100\%$) of the light-induced conversion. Similarly, the contributions from other specific wavelength ranges to the overall and the light-induced conversion were calculated. Because the Pd/SiC catalyst has a strong absorption to the light with wavelengths below 460 nm, the light in the 400–450 nm wavelength range contributes the highest light-induced conversion (35%). While the irradiation in the wavelength ranges of 450–530 and 530–600 contributes 29% and 23% to the conversion, respectively. Although Pd/SiC has a strong infrared absorption above 530 nm, the reaction temperature was strictly controlled at 25 °C resulting in the fact that the photothermal effect from the infrared absorption hardly has a great contribution in the light-induced conversion.

The results of the control experiments show that the furan conversions over Pd/SiO₂ and Pd/TiO₂ with the same Pd loading of 3 wt% are 41% and 49%, respectively, under the same conditions. However, the Pd/TiO₂ catalyst can achieve a nearly 100% conversion for furan hydrogenation under UV irradiation of 0.15 W cm⁻² at 25 °C. The UV-vis spectra of Pd/SiO₂ and Pd/TiO₂ reveal that both catalysts exhibit a very weak absorption in the wavelength range from 400 to 800 nm and the Pd/TiO₂ exhibits a strong absorption to light with wavelengths below 400 nm (Fig. 3A). The slight catalytic activity improvement of Pd/SiO₂ and Pd/TiO₂ under visible light is mainly because those Pd nanoparticles absorb the light through interband electronic transitions to produce photo-excited electrons, which interact with the reactant molecules on the particles and accelerate these reactions.¹⁸ These results further confirm that the intrinsic catalytic activity of Pd is significantly enhanced by visible light irradiation when using SiC as the support.

The activity of pure β-SiC for the photocatalytic hydrogenation of furan is very low. In our case, only a furan conversion of 7.4% can be achieved using the β-SiC powders as the photocatalyst while it can reach up to 99% over the Pd/SiC. No reaction product was detected in the experimental system when using argon instead of H₂. A 46% and 8.4% conversion of furan can be achieved when isopropanol and *n*-amyl alcohol, respectively, act as the hydrogen donor in the presence of KOH at 25 °C and 1 atm of argon. The photocatalytic hydrogenation mechanism of furan over the Pd/SiC catalyst can be interpreted by a simple model (Fig. 4). When the metallic Pd nanoparticles are dispersed on the SiC surface a metal–semiconductor contact (Mott–Schottky contact) can form between Pd and SiC.¹⁹ The work function (WF) of SiC is about 4.0 eV²⁰ and the WF of Pd is 5.12 eV. Therefore, a built-in potential of 1.12 eV can be formed at the interface of SiC and Pd. The built-in potential impels the transfer of electrons in SiC to the Pd nanoparticles. The XPS spectra

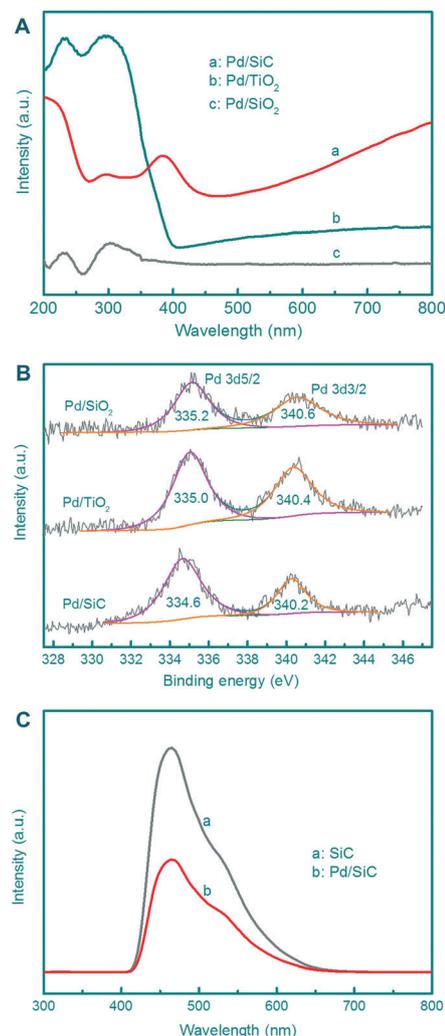


Fig. 3 The UV-vis spectra (A) and X-ray photoelectron spectroscopy results (B) of Pd/SiO₂, Pd/TiO₂ and Pd/SiC; and the photoluminescence spectra of pure SiC and Pd/SiC (excitation wavelength, 320 nm) (C).

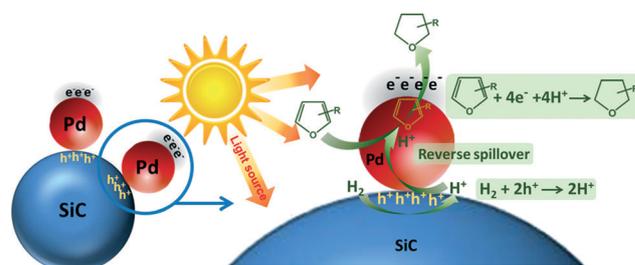


Fig. 4 A proposed mechanism for the photocatalytic hydrogenation of furan derivatives on the Pd/SiC catalyst.

of Pd/SiO₂, Pd/TiO₂ and Pd/SiC (Fig. 3B) confirm the transfer. Generally, the binding energy (BE) values of metallic Pd are in the range of 334.7–335.5 eV for Pd 3d_{5/2} and 340.3–340.8 eV for Pd 3d_{3/2}. Therefore, the Pd particles in the three catalysts are metallic. However, the lower BE (334.6 eV) of Pd_{3d} in the Pd/SiC suggests an electron enrichment on the Pd particles. Fig. 3C shows the photoluminescence (PL)

spectra of pure SiC and Pd/SiC under the 320 nm excitation wavelength at room temperature. The PL peaks of both samples range from 400 to 550 nm, which are consistent with the literature.²¹ The PL intensity of Pd/SiC has an obvious decrement comparing with that of pure SiC, indicating that the recombination of the photogenerated electrons and holes has been effectively suppressed. This further confirms the transfer of electrons from SiC to the Pd particles. The electron transfer results in a positively charged region in SiC and a negatively charged Pd nanoparticle.¹⁹ The light irradiation can effectively amplify the directed electron transfer. Therefore, the photogenerated electrons can quickly transfer from SiC to Pd and thus avoid recombination with the holes.²² Furan molecules usually adsorb with its molecular plane lying parallel to the surface of the Pd particles, and its C–C and C=C bonds are located respectively on the top of a Pd atom.²³ So, the negatively charged Pd nanoparticles with more energetic electrons activate the C=C bonds in the furan rings by donating electrons back to the C=C anti-bonds. Kamat's group studied the photocatalytic performances of the Au–TiO₂ and Ag@TiO₂ composites and suggested that the photogenerated electrons can transfer from TiO₂ to the metal nanoparticles and the holes left on TiO₂ are scavenged by ethanol.^{24,25} In our case, the holes left on the SiC support are filled by oxidizing H₂, which generates active hydrogen. The active hydrogen then migrates to the Pd nanoparticles by reverse spillover²⁶ and reacts with the C=C bonds in furan to produce THF. When the furan rings have substituent groups, the steric effect of the substituent groups can decrease the hydrogenation activity of the C=C bonds in the furan rings but promote the hydrogenolysis of the furan rings. As a result, both the activity and selectivity for the hydrogenation of furan derivatives slightly decrease, as shown in Table 1.

Because the reaction just reaches equilibrium at 2.5 h (Fig. S1†), the activity of the Pd/SiC catalyst was monitored for five successive rounds to test the stability and the reaction time of every round is 2.5 h. No activity decrease was found during the five reaction rounds (Fig. 5). The TEM images of the used catalyst after 5 rounds (Fig. S2†) show no obvious change in morphology and aggregation of the Pd nanoparticles, indicating that the Pd/SiC catalyst has excellent

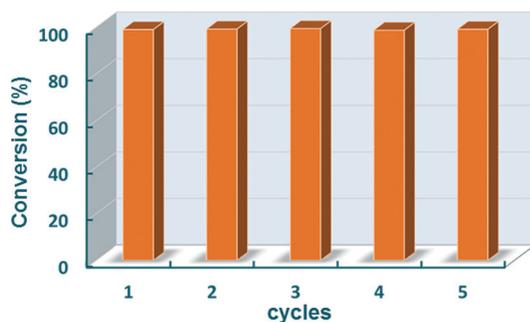


Fig. 5 The photocatalytic stability of 3 wt% Pd/SiC in 5 rounds.

stability for the photocatalytic hydrogenation of furan and its derivatives.

Conclusions

The present work suggests a new class of photocatalysts, photo-active-semiconductor supported metal nanoparticles, which can make some chemical reactions performing usually at high temperature and pressure occur under moderate light irradiation. SiC-supported Pd nanoparticles can greatly promote the hydrogenation of furan derivatives at a lower temperature (25 °C) and pressure (1 Mpa of H₂) by visible light irradiation. The yield of tetrahydrofuran from furan hydrogenation is 99% and the turnover frequency is 70 h⁻¹. The heterojunction between SiC and Pd can facilitate the quick transfer of the photogenerated electrons from SiC to Pd. These energetic electrons on the surface of the Pd nanoparticles significantly enhance their intrinsic catalytic activity. The novel processes using the Pd/SiC photocatalyst have the potential to utilize solar energy and are greener than conventional catalytic processes driven by heating.

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