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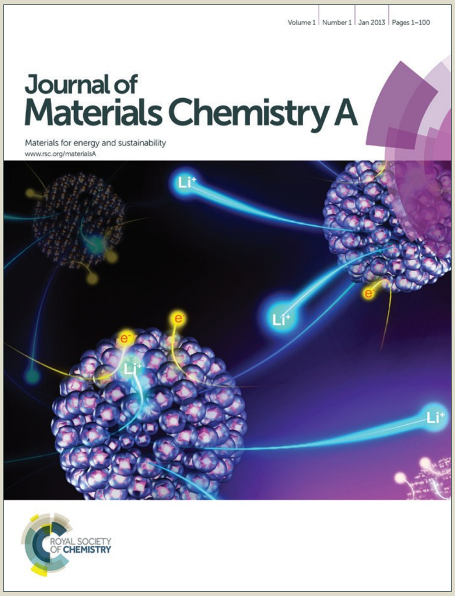

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Ultra-thin TiO_2 nanosheets decorated with Pd quantum dots for high-efficiency hydrogen production from aldehyde solution

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Herein, we demonstrate that quantum-sized Pd dots decorated ultra-thin anatase TiO_2 nanosheets with exposed (001) facets (2 wt %) exhibit the highly efficient catalytic activity for hydrogen generation from formaldehyde solution at room temperature, which is much higher than that of traditional Pd/TiO_2 (Degussa P25) and pure Pd nanoparticles. By further optimizing the reaction parameters, the hydrogen generation rates could reach up to 250 mL g^{-1} min^{-1} and keep consistent for ten hours. Owing to its high efficiency and stability, this hydrogen production reaction may serve as an alternate technique for supplying hydrogen in practical applications.

Hydrogen energy has attracted considerable attention due to the high energy efficiency and environmental benefits compared with the conventional fuels such as petroleum, natural gas, and coal, et al. However, most hydrogen production procedures available to date cannot satisfy fully the criteria of cost, safety, and purity in the future practical utilizations, especially for the mobile devices. More specifically, trace amounts of carbon monoxide presented in the commercial scale hydrogen from steam reforming of methane will make the platinum-based catalysts deactivation and result in the decrease of catalytic efficiency.[1-3] On the other hand, this hydrogen generation system requires external heat supply and high temperature, which restricts its miniaturization, simplification for on-line applications.[4-6] Recently, hydrogen generation from hydrolysis of chemical hydrides (i.e., $NaBH_4$) or hydrazine hydrate ($N_2H_4.H_2O$) under alkaline conditions has been extensively reported.[7-11] Although this process has many merits compared with other methods for room temperature hydrogen generation, the high cost is the significant barriers for its mass application. Therefore, it is highly desirable to develop a low-cost as well as high efficient hydrogen generation procedures.

It is well known that during the disproportionation of aldehydes into corresponding alcohols and carboxylic acid in strongly alkaline medium (Cannizzaro reaction),[12,13] a small quantity of gaseous hydrogen could be produced,[14-16] while this phenomena had received very little attention and only considered as the undesired byproducts during the past one hundred years.[17-21] Recently, Ashby et al.[22-25] have studied the hydrogen evolution mechanism from alkaline formaldehyde solutions by the isotopic composition analysis, demonstrating that one hydrogen atom originates in water and another in the organic moiety. Compared with present hydrogen production technologies, it provides some significant advantages: it utilizes organic reagents with low costs to generate hydrogen at room temperature;[22] the one hydrogen atom of H_2O molecule can also be utilized; the by-products such as CO and CO_2 are not contained. However, note that the efficiency of hydrogen generation is very low, producing only about 2 mL of hydrogen gas even at high temperature.[26] Thereby, such low efficiency has greatly limited its practical applications.

Herein, we demonstrate that ultra-thin anatase TiO_2 nanosheets(NS) with exposed (001) facets modified with only a 2 wt % of quantum-sized Pd dots exhibit the extremely high catalytic activity and stability for the hydrogen generation from alkaline formaldehyde at room temperature. By further optimizing the reaction parameters such as sodium hydroxide concentrations, formaldehyde concentrations, temperature, the hydrogen generation rates could be further increased up to 250 mL g^{-1} min^{-1}, while only 0.3 mg palladium amount has been practically utilized.[27] Therefore, it has been considered that this Pd/TiO_2 based hydrogen generation method may serve as an alternate hydrogen supply candidate for practical application.

Ultra-thin anatase TiO_2 nanosheets with high percentage of the exposed (001) facets were fabricated by a modified hydrothermal reaction. Fig. 1a shows the typical transmission electron microscopy (TEM) images of as-prepared TiO_2 nanoproducts, indicating that well-defined rectangular sheet-structures with an average side length of ca. 50-80 nm and thickness of about 5 nm have been obtained. The high-resolution TEM (HRTEM) image (Fig. 1b) clearly indicates that the lattice spacing parallel to the top and bottom facets is 0.235 nm, corresponding to the (001) planes of anatase TiO_2 crystals. Furthermore, the exposure proportion of (001) planes

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as well as morphology of TiO_2 nanoproducts could be further rationally tailored by simply adjusting the amount of HF. As shown in the Fig. S1b, when the amount of HF has been reduced down to 2 mL, the thickness of as-prepared TiO_2 nanosheets has been increased. Further decreasing the HF amount to 1 mL, only octahedral bipyramid TiO_2 structures with an average side length of ca. 100 nm and width of ca. 80 nm have been synthesized. In contrast, with increasing the amount of HF up to 6 mL, the ultra-thin TiO_2 nanosheets with an irregular morphology have been prepared (Fig.S1d). Fig. 1c and Fig. S2 show the TEM images of the Pd quantum dots modified ultra-thin anatase TiO_2 nanosheets that were obtained by directly reducing the H_2PdCl_4 with $NaBH_4$ at room temperature. It can be clearly seen that the Pd nanoparticles with diameters of 2-5 nm have been successfully grown on the ultra-thin TiO_2 nanosheets. The HRTEM image (Fig. 1d) clearly reveals that the lattice spacing of the quantum-sized Pd nanoparticles is ca. 0.223 nm, which is consistent with the lattice spacing of (111) plane of metallic Pd. For comparison, the TiO_2-P25 supported Pd samples and pure Pd nanoparticles have also been prepared by the same reduction process and shown in Fig. S3 and Fig. S4.

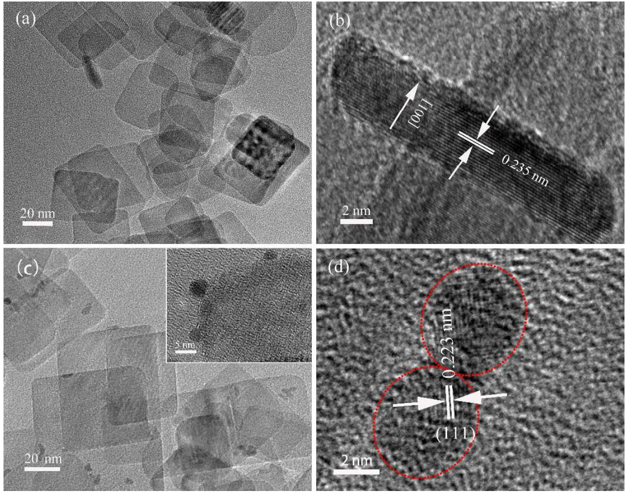


Fig. 1 (a) TEM images of TiO_2 nanosheets, (b) HRTEM image of TiO_2 nanosheets, (c) TEM images of Pd/TiO_2 nanosheets, (d) HRTEM images of Pd nanoparticles.

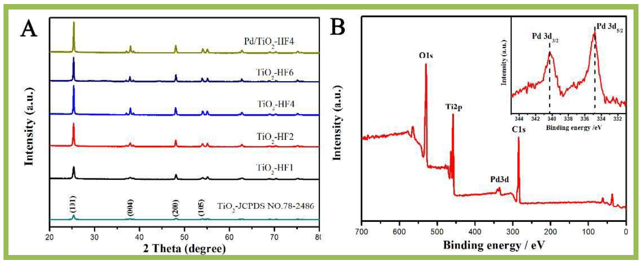


Fig. 2 (A) XRD patterns of TiO_2 nanosheets and Pd/TiO_2 nanosheets; (B) XPS spectra of Pd/TiO_2 nanosheets.

To further confirm the compositions of the hybrid nanostructure, the X-ray diffraction (XRD) pattern has been performed and presented in Fig. 2A. The diffraction peaks could be indexed to anatase-phase TiO_2 (JCPDS No. 78-2486), indicating that the as synthesized products were pure anatase TiO_2. It is noteworthy that with increasing amount of HF, the XRD peak intensities of the samples steadily increase and the (001) peaks of the TiO_2 nanosheets become enhanced. As compared with pure TiO_2 nanoplates, all the diffraction peaks of Pd/TiO_2 samples have no evident changes after the modification process, indicating that the Pd quantum dot deposition did not cause any damage to the crystalline TiO_2 nanoplates. Moreover, note that no obvious diffraction peaks of metallic Pd have been observed in the Pd/TiO_2 nanosheets, which may due to its low loading (2 wt%), quantum-sizes, and well dispersion. Thereby, X-ray photoelectron spectroscopy (XPS) was further applied to study the surface composition and shown in Fig. 2B. All the peaks corresponding to Ti, O, Pd and C element (in which the C element was used to calibration) can be detected. The high-resolution Pd 3d spectra of the Pd/TiO_2 samples (Fig. 2B inset) show two peaks at ca. 334.9 eV and 340.1 eV, which could be assigned to Pd $3d_{5/2}$ and Pd $3d_{3/2}$ of metallic Pd, respectively. Furthermore, Fig. S5 shows the energy dispersive X-ray (EDX) result of Pd/TiO_2 samples. Except for the elements of Cu and C from the fundus, all the Ti, O, and Pd elements have been clearly observed, indicating that Pd nanoparticles have been successfully deposited on the TiO_2 nanoplates.

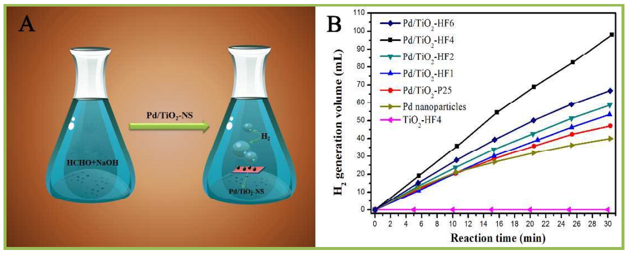


Fig. 3 (A) Schematic illustration of the hydrogen production process form formaldehyde over Pd/TiO_2-NS; (B) Hydrogen production over Pd/TiO_2 and Pd nanoparticles, NaOH: 1 mol/L, HCHO: 0.6 mol/L, catalyst: 15 mg, reaction temperature: 25 ^oC.

Furthermore, the as-prepared Pd/TiO_2 samples as well as pure Pd nanoparticles were utilized as the catalysts in the hydrogen production reaction from alkaline formaldehyde solution at room temperature, and the schematic illustration has been shown in Fig. 3A. It can be seen that in the presence of pure TiO_2 nanoplates, almost no any hydrogen could be detected. Surprisingly, when Pd/TiO_2-NS catalysts were introduced in this reaction system, the catalytic reaction of hydrogen production started immediately without any induction period. It can be clearly seen from Fig. 3B that Pd/TiO_2-HF4 exhibit highest catalytic activities than pure Pd nanoparticles and other Pd/TiO_2 (Pd/TiO_2-HF6, Pd/TiO_2-HF2, Pd/TiO_2-HF1, Pd/TiO_2-P25) samples. Moreover, as shown in Fig. S6, the 2 wt % weight ratios between Pd to TiO_2 exhibit the best catalytic performance. Herein, it was considered that the improved activity of Pd/TiO_2-HF4 might be due to the high specific surface area (Table S1) and high surface energies of

TiO_2 (001) facets. More specifically, the unique plate-like structure could effectively provide more absorption sites in comparison to conventional solid particles. In contrast, the rapid aggregation of pure Pd nanoparticles during the catalytic reactions generally result in the decrease of the catalytic activities.[28] The above results clearly demonstrate that the rational construction of Pd/TiO2 catalysts could serve as an effective approach for enhancing their catalytic performances.

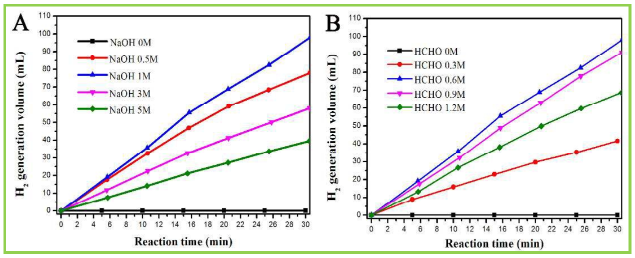


Fig. 4 (A) The effect of NaOH concentrations on H_2 production, Pd/TiO_2 catalyst: 15 mg, HCHO: 0.6 mol/L, temperature: 25 °C; (B) The effect of HCHO concentrations on H_2 production, Pd/TiO_2 catalyst: 15 mg, NaOH: 1 mol/L, temperature：25 °C.

Fig. 4A shows the effect of NaOH concentrations on hydrogen generation rates. As can be seen from Fig. 4A, no hydrogen can be produced in the absence of NaOH, while quantitative hydrogen was production immediately when only a small quantity of NaOH was introduced into the reaction system, indicating that the alkaline condition is indispensable for this catalytic process. As NaOH concentrations increased from 0.5 to 1.0 mol L^{-1}, the average rates of hydrogen production obviously increased. However, further increasing NaOH concentration up to 3 mol L^{-1} and 5 mol L^{-1}, the rate of hydrogen production decreased obviously, which may be due to the competition with the Cannizzaro reaction for transforming formaldehyde into the corresponding methanol and formic acid under highly alkaline conditions. Furthermore, the effects of HCHO concentrations on hydrogen generation have also been studied and shown in Fig. 4B. It can be clearly seen that the HCHO concentrations play a crucial role in determining the hydrogen production rates, and the highest rate of hydrogen generation was obtained at 0.6 mol L^{-1}. However, with increasing the HCHO concentrations (0.9 or 1.2 mol L^{-1}), the rate of hydrogen generation slightly decreased. Thereby, these demonstrations clearly reveal that in order to achieve high hydrogen generation rates, both HCHO and NaOH should be controlled in the appropriate concentrations.

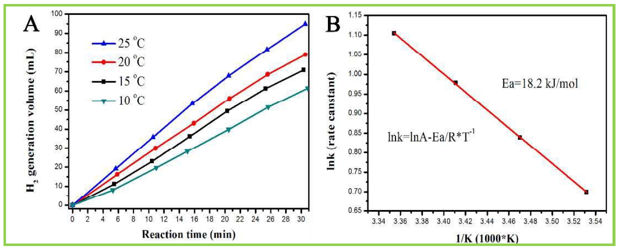


Fig. 5 The effect of reaction temperature on H_2 production, Pd/TiO_2 catalyst: 15 mg, HCHO: 0.6 mol/L, NaOH: 1 mol/L; (B) The calculation of activation energy for Pd/TiO_2.

The effects of reaction temperature on H_2 generation rates were shown in Fig. 5A. As the temperature increased from 10 to 25 °C，the hydrogen generation rate increased rapidly from 132.7 to 217.8 mL min^{-1} g^{-1}, suggesting that the increasing temperature could facilitate this hydrogen generation reaction. Furthermore, it can be seen that the amount of hydrogen generated is linearly dependent on the reaction time at each temperature, which demonstrates that this hydrogen generation reaction could be considered zero order reaction. Thereby, the reaction rate equation can be written as follows:

$$k = A \exp(-E/RT), \quad \text{Eq.(1)}$$

where E is the activation energy, R is the gas constant, and T is the absolute temperature, k is the rate constant. Following Eq.(1), lnk versus 1/T, which was plotted in Fig. 5B from the experimental data shown in Fig. 5A. Hence, form the slop of Fig. 5B, the calculated activation energy for the hydrogen generation reaction over Pd/TiO_2 catalysts was 18.2 kJ mol^{-1}, which was lower than the previously reported value, 65 kJ mol^{-1}, for non-catalytic cases.

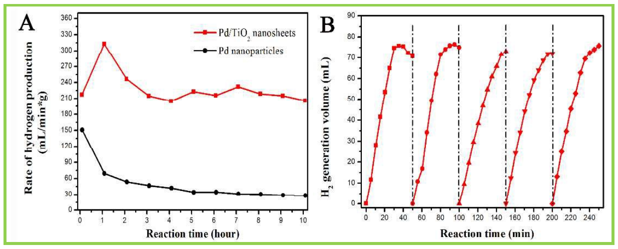
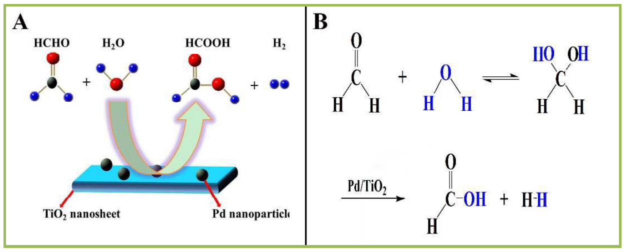


Fig. 6 (A) Stability of the Pd/TiO_2 catalyst and Pd nanoparticles for the H_2 production, catalyst: 15 mg, NaOH: 1 mol/L, HCHO: 0.6 mol/L, temperature：25 °C; (B) Continuity of the Pd/TiO2 catalyst for the H_2 production, catalyst: 15 mg, NaOH: 1 mol/L, HCHO: 0.6 mol/L, temperature：25 °C.

According to the above discussions, Pd/TiO_2 could serve as a highly efficient catalyst for catalyzing hydrogen production form formaldehyde solution at room temperature. Besides, the catalytic stability should also be considered due to their future practical application. Thus, the catalytic stability has been investigated under identical reaction conditions for 600 min (shown in Fig. 6A). The average speed of the hydrogen production has no dramatic decline and kept at about 250 mL^{-1} min^{-1} g^{-1}. However, the hydrogen production rates of pure Pd nanoparticles have been markedly decreased even at 30 min, which should be due to the rapid aggregation of Pd nanoparticles during the catalytic reactions. In contrast, the loading Pd nanoparticles on TiO_2 nanosheets could efficiently prevent agglomeration, and TiO_2 nanosheets exposed with the (001) facets could promote formaldehyde molecules adsorbed to the active site of the catalysts. Thereby, Pd/TiO_2 could catalyze formaldehyde to produce hydrogen with excellent catalytic activity and stability in alkaline aqueous solutions during a long-term reaction process. In order to further verify that the hydrogen evolution from formaldehyde solution at room temperature, and the consecutive hydrogen generations were shown in Fig. 6B. Under the first 50 min, a total amount of 75 mL H_2 is produced without noticeable deterioration of the activity until the completely transformation of 2.5 mL formaldehyde. More meaningful, once the formaldehyde is continued to supply, the hydrogen evolution will start immediately, and the rates of hydrogen production still keep constant. Thereby, it has been considered that this hydrogen production system may offer the potential to provide on-line hydrogen supply.



Scheme 1 (A) Schematic illustration of the hydrogen generation over Pd/TiO_2; (B) Reaction sequences for the hydrogen from formaldehyde aqueous solution.

On the basis of the experimental results, we proposed a possible pathway for hydrogen production from formaldehyde catalyzed by Pd/TiO_2, which has been shown in Scheme 1. Firstly, it was extensively reported that compared with (101) and (100), the (001) facets of anatase TiO_2 possess higher surface energy as a result of more undercoordinated atoms and resulting surface defects,[29,30] which assures the higher adsorption of reactant molecules. Furthermore, as shown in Scheme 1A, the Pd nanoparticles were supported on TiO_2 nanosheets with exposed (001) facets, which were surrounded by the formaldehyde and water molecules with high concentrations.[31-34] Accordingly, the hydrogen generation reaction from formaldehyde and water over Pd catalytic active-sites could be effectively accelerated, and a high rate of hydrogen generation has been achieved. More specifically, Scheme 1B demonstrated the separate steps of the hydrogen generation reaction. It has been well recognized that in aqueous solution, formaldehyde is mostly hydrated to methylene glycol intermediate,[22-25,34] which has no relationship with the catalysts. Subsequently, when Pd/TiO_2 catalysts has been introduced in this system, which facilitate the transform reaction of methylene glycol intermediate under alkaline condition into hydrogen and formic acid. However, the exact mechanism for hydrogen generation over Pd/TiO_2 catalysts cannot be completely understood until now.

In summary, we have demonstrated a facile and efficient strategy for facilitating the hydrogen production from formaldehyde aqueous solution by using quantum-sized Pd dots decorated ultra-thin anatase TiO_2 nanosheets as the catalysts at room temperature. Moreover, by further optimizing the formaldehyde concentrations, sodium hydroxide concentrations and reaction temperature, the highly efficient hydrogen generation over the Pd/TiO_2 catalyst could be achieved. In this hydrogen production system, H_2 was the only gaseous product in all catalytic experiments, and other gases such as CO or CO_2 were not generated. Thereby, we consider that owning to the low costs of reagents and the high rate of the hydrogen production, this hydrogen generation system may serve as an alternate technique for supplying hydrogen.

Acknowledgements

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Ultra-thin TiO_2 nanosheets decorated with Pd quantum dots for high-efficiency hydrogen production from aldehyde solution

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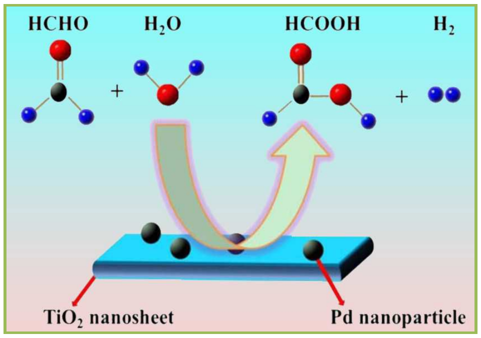

We demonstrate that quantum-sized Pd dots decorated ultra-thin anatase TiO_2 nanosheets with exposed (001) facets exhibit the highly efficient catalytic activity for hydrogen generation from formaldehyde solution at room temperature