

An efficient room-temperature H₂ production system containing hypophosphite and CuPd/TiO₂ catalyst

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Abstract

A safe, clean, and cost-effective H₂ production system is critically important for developing hydrogen energy. Sodium hypophosphite (NHP) represents a promising hydrogen carrier due to its high stability, low cost, and abundance. In the presence of appropriate catalysts, NHP can easily react with water under mild conditions to yield high-purity H₂ but without any gaseous by-products. In this work, we report an efficient room-temperature H₂ production system containing the supported CuPd/TiO₂ as a catalyst, and NHP and water as hydrogen carriers (hydrogen sources). The H₂ production rate is 13.53 mL·min⁻¹ (135.3 mL·min⁻¹·g⁻¹) and NHP reaches 100% conversion within 30 min. The CuPd/TiO₂ catalyst also exhibits excellent stability and recyclability toward H₂ production. Cu generates both geometric and electronic effects in CuPd/TiO₂ catalyst. Pd nanoparticles are more dispersive, and their sizes are smaller with the help of Cu. The electronic interaction between Cu and Pd leads to an increased d-band holes of Pd, which is beneficial for the adsorption of H₂PO₂⁻ and reduce the activation energy of H₂PO₂⁻ dehydrogenation. This work develops a new cost-economic and highly efficient catalytic H₂ production system, which is expected to contribute to development of hydrogen economy, especially hydrogen–oxygen fuel cell.

Introduction

Energy sources are the fundamental basis for the survival and development of the humanity. The non-renewability of fossil energy and the series of environmental problems, such as carbon emission caused by its use, have made exploring green and renewable energy systems a common pursuit worldwide. H₂ fuel is regarded as the ultimate energy source for the 21st century due to its pollution-free nature and large calorific value.^{1–4} Fuel cell is an excellent pathway to harness chemical energy of molecular hydrogen with the energy conversion efficiency of as high as 60% ~80%.^{5,6} The establishment of a safe, efficient, and cost-economic H₂ production system (HPS) is vital for the development of fuel cell-based hydrogen economy.

A HPS contains at least a hydrogen carrier and a catalyst. In theory, water is the most common and cheapest hydrogen carrier on the Earth. However, due to the thermodynamic limitation, the direct water decomposition into H₂ is extremely difficult (unless additional energy such as electricity or light are provided). In recent years, formic acid (HCOOH),^{7,8} formate salts,⁹ methanol (CH₃OH),¹⁰ metal borohydrides (e.g. NaBH₄),¹¹ boranes (e.g. NH₃BH₃),¹² and liquid organic hydrogen carriers (LOHCs, e.g. C₈H₁₈)¹³ etc. were used as hydrogen carriers for H₂ production (Table 1). However, the above hydrogen carriers suffer some disadvantages. For example, they are all classified as flammable, some of them were toxic or/and corrosive as well according to the GHS classification and labelling of chemicals. Besides, the decomposition of carbon-based hydrogen carriers including HCOOH, LOHCs and CH₃OH etc., easily generates toxic CO.^{14–16} Even if they merely undergo dehydrogenation, it will still release by-

product CO₂, which does not meet the goal of “carbon neutrality”.^{17,18} Moreover, the high cost and/or less availability of metal borohydrides and NH₃BH₃ also tremendously limit their application in the hydrogen production field.¹⁹

Sodium hypophosphite (NaH₂PO₂, NHP) is a widely used reducing agents and phosphiding agents in the electroless deposition, phosphide preparation, and foods preservation et al. fields.^{20,21} It easily reacts with water under mild conditions to yield hydrogen ($\text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{PO}_3^-$, called HPH reaction), thus it is a potential hydrogen carrier. Hydrogen production using NHP and water has multiple advantages (see the last row in Table 1): (I) NHP exhibits exceptional stability and safety (requiring no specific storage or transportation conditions), is eco-friendly (it is obtained from white phosphorus and basic solvent, and not a hazardous substance according to the GHS green), affordable (< \$20/kg), and available in bulk quantities (global production exceeding 100,000 tons/year).^{22,23} (II) It is a carbon-free reaction system, and molecular H₂ is the sole gaseous product without any other gas, which eliminates the need for gas separation and purification. This is vitally important to obtain high-purity hydrogen. (III) H₂ can be readily generated from NHP and water even at very mild conditions, and the reaction is simple, clean, and environmentally friendly (carbon-free). (IV) The unique solid product, sodium hydrogen phosphite (NaH₂PO₃), is an important reducing agent, which can be widely used in the reduction of metal salts, the preparation of chemical reagents, and the synthesis of microporous materials.^{24,25} NaH₂PO₃ is also a promising phosphorus fertilizer.²⁶ Moreover, in

Table 1 Comparisons of different chemical hydrogen carriers.¹⁹

Hydrogen carrier	Price ^a (\$/Kg)	GHS classification ^b	Hydrogen production reaction	
			Equation	By-products
HCOOH (l)	15		$\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$	CO_2 (g)
CH_3OH (l)	14		$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$	CO_2 (g)
C_8H_{18} (l)	36		$\text{C}_8\text{H}_{18} \rightarrow 5\text{H}_2 + \text{C}_8\text{H}_8$	C_8H_8 (l)
NH_3BH_3 (s)	1600		$\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{NH}_4\text{BO}_2$	NH_4BO_2 (s)
NaBH_4 (s)	270		$\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{NaBO}_2$	NaBO_2 (s)
NaH_2PO_2 (s)	20	Not a hazardous substance or mixture	$\text{NaH}_2\text{PO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{NaH}_2\text{PO}_3$	NaH_2PO_3 (s)

^a This is the reagent price based on China market.

^b The information is from GESTIS Substance Database. <https://gestis-database.dguv.de>

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recent years, some reports have demonstrated the phosphite can be re-hydrogenated to access NHP through electrocatalytic reduction,^{27,28} this will allow for sustainable NHP synthesis.

Up to now, rare-infrequent works have focused on the hydrogen production using NHP as hydrogen sources. Recently, Ron Shirman reported the hydrogen release from NHP using noble metal Pd supported graphitic carbon nitride (Pd/GCN, with ~ 10 wt% Pd) at elevated temperature (50 ~ 60°C).^{29,30} However, the reaction mechanism still needs to be further studied. Moreover, the catalysts only consist of high-content noble metal encounter substantial obstacles in large-scale practical applications due to their high costs and low natural reserves.

Transition metals (the fourth period) have been extensively studied as the catalysts in numerous reactions due to their potential activities and cost-effectiveness. Incorporating transition metals into noble metals with an alloy structure may boost catalytic properties while reducing noble metal consumption.^{31,32}

Herein, we report a supported bimetallic CuPd catalyst (CuPd/TiO₂) synthesized by a facile co-reduction method using NaBH₄ as reductants. The prepared CuPd/TiO₂ with relatively low-level noble metals possesses a high catalytic activity and excellent durability for H₂ production from NHP and water at room temperature (RT) without any other additives. The catalyst preparation and catalytic H₂ production from NHP and water were schematically illustrated in Scheme 1, and the experimental set-up for H₂ production was presented in Fig. S1 (Supporting Information). Cu boost the well-distribution of Pd on TiO₂, and a uniform pared-sites were identified, combined with the increased d-band holes of Pd induced by electronic interaction between Cu and Pd, are beneficial for adsorption and dehydrogenation of H₂PO₂⁻ ions so as to harvest fast H₂ production dynamics. This work develops a clean, efficient and cost-effective HPS, which will have great application potential in hydrogen–oxygen fuel cell.

Results and discussions

Catalysts characterization

Figure 1a shows the XRD results of CuPd/TiO₂, Pd/TiO₂, Cu/TiO₂ and TiO₂. The diffraction patterns of all the samples are almost identical. The peaks with 2θ at 25.26 °, 37.80, 38.50, 47.98, 53.90, 55.04, 62.72, 70.24 and 75.02 belong to the anatase phase.³³ The ones at 27.38, 36.04, 41.24 and 56.58 belong to the rutile phase.³⁴ The Pd and Cu species related peaks cannot be observed possibly due to the good dispersions and small sizes of their crystalline grains. To elucidate the crystal phase of the Pd and Cu particles, 10% CuPd/TiO₂, 10%Pd/TiO₂, 10%Cu/TiO₂ were prepared by the same mothed. 10%Cu/TiO₂ shows a new peak at 43.26° while 10%Pd/TiO₂ shows a new weak feature at 40.13° (Fig. S2), which could be attributed to the (111) plane of face-centered cubic (fcc) Cu (PDF # 04-0836) and Pd (PDF #46-1043), respectively.³⁵

XPS spectra were shown in Fig. 1b and c. There are two group peaks (3d_{5/2} and 3d_{3/2}) in Pd 3d spectra. For Pd/TiO₂, the Pd exhibits a binding energy (BE) of 335.05 eV for 3d_{5/2} and 340.37 eV for 3d_{3/2}, indicating that Pd in the Pd/TiO₂ sample mainly exists in the metallic state (Pd⁰), besides, the BE of 3d_{5/2} is 342.06 eV and that of 3d_{3/2} is 336.25 eV, ascribing to oxidation state (such as Pd²⁺).^{36,37} In the CuPd/TiO₂ sample, the BE of Pd⁰ and Pd²⁺ shifts to a higher-energy direction (336.40 and 337.57 eV for 3d_{5/2}, 341.74 and 343.66 eV for 3d_{3/2}). A significant shift (more than 1.3 eV) in BE of Pd is usually associated with alloying/interface interaction with Cu. The introduction of Cu changes the chemical

environment of Pd, possibly forming CuPd alloy phases. Moreover, the remarkable positive shift in BE of Pd suggests an electron transfer from Pd to Cu after forming CuPd alloy, resulting into an increase in d-band holes of Pd, which is beneficial for adsorption and catalytic reaction on Pd surface. For Cu 2p spectra (Fig. 1c), there are also two states (Cu^0 and Cu^{2+}), the Cu 2p of CuPd/TiO₂ exhibits a negative shift (0.2 ~ 0.3 eV) in BE compared with that of Pd/TiO₂, ascribing to interface interaction between Cu and Pd, and Cu accepts electron from Pd. This is in agreement with the XPS results of Pd. The electron transfer from Pd and Cu were further supported by the Ti and O XPS analyses (Fig. S3).

The CO-IR spectra were shown in Fig. 1d. In general, the vibrational frequencies of adsorbed CO molecules can be identified as three categories:^{38,39} i) $> 2100 \text{ cm}^{-1}$, is cationic carbonyls ($\text{M}^{\delta+}\text{-CO}$, M represents a metal) on oxidation-state metal; ii) $2000 \sim 2100 \text{ cm}^{-1}$, is linearly adsorbed CO on a M^0 atom; iii) $1800 \sim 2000 \text{ cm}^{-1}$, is a bridge (including two-fold and three-fold) adsorbed CO on M^0 atoms. Cu/TiO₂ exhibits a strong CO adsorption at 2107 cm^{-1} , belonging to $\text{Cu}^{\delta+}\text{-CO}$ state,⁴⁰ whilst the other wide and weak adsorption band with the center at 2170 cm^{-1} is $\text{Ti}^{\delta+}\text{-CO}$ from the support Ti atom.⁴¹ For Pd/TiO₂, CO exhibits four different adsorptions on Pd sites, the band at 1928 cm^{-1} is three-fold bridged CO, 1976 cm^{-1} is two-fold bridged CO, 2093 cm^{-1} is linear CO adsorption (Pd-CO), and the rest 2127 cm^{-1} is cationic carbonyls ($\text{Pd}^{\delta+}\text{-CO}$).⁴² For CuPd/TiO₂, except for the $\text{Cu}^{\delta+}\text{-CO}$ band (2109 cm^{-1}), there is almost only one adsorptions band, two-fold bridged CO at 1986 cm^{-1} on Pd sites, the other three adsorption bands were not observed. This result is quite different from previous reports, the latter thought that the adsorption of CO by Pd was mainly linear in CuPd catalysts.^{35,43-45} This was because the dispersion of Cu enabled Pd to form more isolated Pd species. In our study, it is demonstrated that the CO adsorption on Pd become uniform two-fold bridged in CuPd/TiO₂, this is a more stable adsorption mode compared with the linear adsorption,⁴⁶ indicating that the Pd sites in CuPd/TiO₂ display stronger adsorption interaction with adsorbates or reactants due to the introduction of Cu. Since this adsorption mode involves two adjacent sites, we called paired sites, these paired sites are highly conducive to the hydrogen production from NHP and water (see below). In addition, it was found that two-fold bridged adsorption of CO on CuPd/TiO₂ has a blue shift compared with that of Pd/TiO₂, indicating an electron transfer from Pd to Cu,^{47,48} this result is consistent with the XPS analysis. As a result, the d-band holes of Pd increases, which should enhance the bonding interaction between CO and Pd. The above discussion confirms that Cu has simultaneously exerted geometric and electronic effects on the CuPd/TiO₂ catalyst.

The morphologies and distributions of Pd and Cu were observed by TEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The TiO₂ support exhibits irregular nanoparticles with the size of 10 ~ 40 nm (Fig. 2a and d). As shown in Fig. 2b, Pd nanoparticles are nonuniformly distributed on the TiO₂ support with a mean diameter of 5.68 nm for Pd/TiO₂. The HR-TEM of Pd/TiO₂ (Fig. 2c) reveals an obvious lattice fringe and the spacing is 0.225 nm, belonging to the (111) plane of fcc Pd. In the case of CuPd/TiO₂, CuPd nanoparticles are relatively uniformly dispersed on the TiO₂ with a mean diameter of 3.13 nm (Fig. 2e), the size is smaller than that Pd nanoparticles in Pd/TiO₂.

The HR-TEM of CuPd/TiO₂ (Fig. 2f) reveals two distinct lattice fringes with spacing of 0.225 and 0.210 nm, belonging to (111) planes of fcc Pd and Cu, respectively. The above observation perfectly agrees with the result of XRD. Compared with Pd in Pd/TiO₂, CuPd nanoparticles in CuPd/TiO₂ is more dispersive, indicating it can provide more active sites for reactants adsorption and surface reaction. The elemental mapping images (Fig. 2g) confirms that the CuPd/TiO₂ sample contains Pd, Cu, O, and Ti elements, Pd and Cu elements are uniformly dispersed on the TiO₂. Based on the ICP-OES measurement, the real content of Pd and Cu in CuPd/TiO₂ is 2.11 and 2.68 wt%, respectively, while the content of Pd in Pd/TiO₂ is 4.16 wt%. The real contents of Pd roughly agree with the designed contents of Pd.

Figure S4 reveals the adsorption isotherms of CuPd/TiO₂, Pd/TiO₂, Cu/TiO₂ and TiO₂ samples. All the isotherms could be identified as type III (BDDT classification) with weak interaction of N₂ with different catalysts. The loading of Cu, Pd, and CuPd on TiO₂ has no significant impacts on the isotherm, indicating the homogeneous dispersion of Cu and Pd on TiO₂.⁴⁹ The BET-specific surface areas of CuPd/TiO₂, Pd/TiO₂, and Cu/TiO₂ were determined to be 48.9, 52.3, and 51.2 m² g⁻¹, respectively. The similar specific surface area of supported catalysts eliminates the influence of specific surface areas on catalytic properties.

Catalytic H₂ production

The catalytic performance of the prepared catalysts in aqueous NHP solution for hydrogen production was performed under RT. As shown in Fig. 3a, no hydrogen is generated over the Cu/TiO₂ catalyst without Pd, indicating that the catalyst has no catalytic activity. This result is consistent with what has been reported in previous literature, namely that Cu cannot catalyze the oxidation of NHP due to unstable intermediates. The Pd/TiO₂ displays remarkable catalytic activity with a H₂ production rate of 5.76 mL·min⁻¹ and a TOF of 6.3 min⁻¹. Moreover, the H₂ production rate could be increased to as high as 13.53 mL·min⁻¹ (135.3 mL·min⁻¹·g⁻¹) by using CuPd/TiO₂ catalyst, and the TOF is 29.1 min⁻¹, indicating that the CuPd bimetallic catalyst exhibits higher catalytic activity while reducing the usage of noble metal. Figure 3a also shows the effect of initial ratio of Cu:Pd on catalytic activity, both the Cu_{0.5}Pd/TiO₂ and Cu₂Pd/TiO₂ display lower hydrogen production rate than CuPd/TiO₂. The possible reason is that when the amount of Cu is inadequate, it cannot effectively play the role of dispersing Pt. On the other hand, if the proportion of Cu is too high, it will result in insufficient Pd active sites, leading to reduced activity. Therefore, the optimized initial Cu:Pd is 1:1. Figure 3b depicts the time course of H₂ production and NHP conversion (%) over CuPd/TiO₂ and Pd/TiO₂ catalysts. It is obvious that the CuPd/TiO₂ catalyst demonstrates phenomenal activity, and the H₂ production rate is relatively stable within 20 min. NHP reaches 100% conversion within 30 min under RT, the activity surpasses the Pd/GCN (~ 10 wt% Pd) catalyst where the 100% conversion of NHP was obtained in 60 min at elevated 60 °C.³⁰ The results demonstrate that the CuPd/TiO₂ is a highly effective catalyst for HPH reaction. The Pd/TiO₂ catalyst reaches 78% conversion after reaction for 50 min and growth of H₂ amount is limp. The effects

of the loading content of CuPd in the CuPd/TiO₂ on the catalytic performance were revealed in Fig. 3c, the activity first increases and then decreases with the loading content, and the highest activity is obtained by adding 5.0 wt% CuPd. Excessive loading may cause the aggregation of active components, thereby reducing the activity of catalysts. The recyclability of the CuPd/TiO₂ catalyst in the HPH reaction was tested, and the results are shown in Fig. 3d. The catalytic activity is maintained with perfect constancy although six cycles reaction were conducted, indicating that the CuPd/TiO₂ is a reusable and durable catalyst for HPH reaction. To elucidate the stability of CuPd/TiO₂ catalyst itself, XPS spectra and TEM micrographs of used catalyst after six cycles reaction were recorded. The Pd and Cu XPS spectra of CuPd/TiO₂ before and after the reaction are very similar (Fig. S5a-b). TEM reveals that the CuPd nanoparticles are uniformly dispersed on the TiO₂ after the reaction, and their sizes do not change significantly (the mean 3.42 nm) (Fig. S5c). Those demonstrate the excellent durability of CuPd/TiO₂ catalyst, and it can be used repeatedly for a long time. The effects of second metals (MPd/TiO₂) and supports on H₂ production were discussed in the Supporting Information (Fig. S6 and S7).

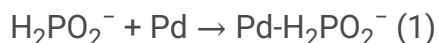
The kinetics of CuPd/TiO₂ catalyzed HPH reaction was investigated. We changed the NHP concentration ([NHP]) and obtained a series of kinetic curves (Fig. 4a). When the [NHP] increases from 0.05 to 0.3 mol·L⁻¹, the amount (volume) of H₂ production increases from 109.7 to 413.2 mL, but the hydrogen production rate (*r*) in initial stage (the first 5 min) is slightly affected by the [NHP] (Fig. 4b). The linear fitting result of $\ln r$ against $\ln[\text{NHP}]$ spots was revealed in Fig. 4c, the slope of the line is 0.24, indicating that the HPH reaction obeys to quasi zeroth-order kinetics concerning the [NHP].⁵⁰ Fig. 4d-f shows the effects of catalyst dosage on the H₂ production. In the absence of catalyst, no H₂ is released even reaction for 60 min. The NHP conversion is about 40% by using 0.02 g catalysts, and it increases to 91%, 100%, and 100% by increasing the catalyst dosage to 0.05, 0.1, and 0.2 g, respectively (Fig. 4d). Figure 4e shows the effect of catalyst dosage on initial activity, the *r* linearly increases with increasing catalyst dosage. More active sites can be provided by increasing the catalyst dosage, and thus the H₂ production is boosted. The linear fitting slope of the $\ln r$ and $\ln [\text{cat}]$ is 1.01 (Fig. 4f), indicating that the HPH is a first-order reaction relative to catalyst concentration.

The influence of the reaction temperature on the catalytic performance was shown in Fig. 4g-i. It is noted that temperature (*T*) exhibits a significant influence on H₂ production. When the *T* increases from 25 °C to 55 °C, the time for complete conversion reduces from ~ 30 min to ~ 10 min (Fig. 4g), and the initial rate for hydrogen generation is accelerated from 13.53 to 29.49 mL·min⁻¹ (Fig. 4h). The apparent activation energy (*E*_a) of the HPH reaction was estimated by plotting $\ln r$ against 1/*T* based on the Arrhenius equation.⁵¹ The *E*_a on CuPd/TiO₂ is 26.87 kJ·mol⁻¹ (Fig. 4i) while the value is 46.62 kJ·mol⁻¹ on Pd/TiO₂ catalyst (Fig. S8). The CuPd/TiO₂ catalyst noticeably reduces the *E*_a of the HPH reaction, thus greatly boosting the H₂ production activity.

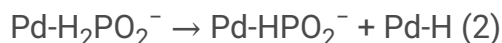
Catalytic reaction mechanism

In the electroless deposition field, NHP, as a widely used reducing agent, has been extensively reported regarding its oxidation mechanism, wherein the target metal act as a catalyst. In this work, except for oxidation of H_2PO_2^- , we are more focused on the hydrogen production process, a possible reaction mechanism is speculated.

The first step is adsorption of H_2PO_2^- . Since the adsorption of H_2PO_2^- on Cu surface is very weak and unstable (Cu/TiO₂ is inactive for the HPH reaction), H_2PO_2^- is preferentially adsorbed on the Pd sites,⁵²



The second step is dehydrogenation of adsorbed H_2PO_2^- to form intermediate HPO_2^- , meanwhile the H atom is dissociated and adsorbed on an adjacent Pd site through migration, two H atoms immediately bond and H_2 is generated for the first time. The dehydrogenation of adsorbed H_2PO_2^- (Eq. 2) was thought as a rate-determining step for the whole reaction.^{52–54}

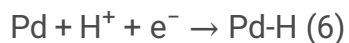


Obviously, the rich paired sites in the CuPd/TiO₂ catalyst are highly conducive to the simultaneous adsorption of the intermediate HPO_2^- and dissociated H atom.

The next is HPO_2^- oxidation by the OH^- from H_2O dissociation,



At the same times, the H^+ generated from H_2O ionizing accept the e^- to form atomic H, immediately, two H atoms bond to produce molecular H_2 (this is the second time that hydrogen has been produced).



The oxidative product H_2PO_3^- is simultaneously obtained after H_2PO_3^- desorption from the catalyst surface.

To confirm the above reaction mechanism, some related experiments were conducted. Firstly, the key intermediate HPO_2^- radical was verified by the ESR spectroscopy. Employing N-tert-Butyl- α -phenylnitrone

(PBN) as the spin trapping agent, the ESR spectrum of the H₂ production system exhibits four-group and sixteen-fold peaks ($g = 2.0060$) (Fig. 5a), which is exactly consistent with those previous reports.^{55,56} The ESR test confirms the existence of HPO₂⁻ radicals in the HPH reaction system.

Secondly, the effect of pH of the NHP solution on H₂ production was investigated. The results (Fig. S9) showed that, compared with the H₂ production activity under natural (pH 7.1) condition, the activity remarkably decreases whether under alkaline (pH 10.2, adjusting by adding NaOH) or acidic (pH 3.6, adjusting by adding HCl) conditions, supporting that the H₂O ionizing step is not the rate-determining step for the HPH reaction.

Thirdly, to identify the source of the produced H₂, an isotope labelling experiment was performed in HPH reaction by using deuterium oxide (D₂O) instead of H₂O. The generated gas was detected by the gas chromatography-mass spectrometry (GC-MS) technology, it is noticeable that the D₂ ($m/z = 4$) and H₂ ($m/z = 2$) is the main species, and only a small amount of HD ($m/z = 3$) was discovered (Fig. 5b). The isotope labelling experiments demonstrate that the H source in the generated H₂ gas is both the NHP and H₂O. The initial atomic H (Eq. 2) generated by dehydrogenation of H₂PO₂⁻ tends to bond with each other to produce H₂ rather than reacts with the H from H₂O during the HPO₂⁻ oxidation (Eq. 6).

Finally, the solid product of HPH reaction was analyzed by FTIR (Fig. S10a) and ³¹P-NMR (Fig. S10b), and the results confirmed that NaH₂PO₃ is the sole oxidative product.

In addition, the mole ratio of produced H₂ and the added NHP is 1:1, since only the 0.5 equivalent H₂ can be obtained from the oxidation of H₂PO₂⁻, it is certified that the rest 50% H₂ has to origin from the H₂O reduction. Thus, the overall reaction can be expressed as:



To elucidate the origin of the enhanced catalytic property of CuPd/TiO₂ catalyst, DFT calculations were performed to estimate the Gibbs free energy profiles for the adsorption of the reaction-related species on Pd (111) sites in both CuPd/TiO₂ and Pd/TiO₂ catalysts. The optimized structure models and the Gibbs free energy profiles were revealed in Fig. S11-12 and Fig. 5c, respectively. In the H₂PO₂⁻ adsorption step, an optimized model expresses that H₂PO₂⁻ ion with a pseudo-tetrahedra structure tends to adsorb onto the surface through its oxygen atoms, which induces electron transfer from the P–O bond to the substrate, renders the P atom more positively charged and thereby withdraws greater electron density from adjacent H atoms,⁵⁷ this is in favor of the next dehydrogenation of the absorbed H₂PO₂⁻. The adsorption exhibits a negative adsorption energy, indicating that the process is thermodynamically spontaneous. Moreover, the free energy change (ΔG) of H₂PO₂⁻ adsorption on CuPd/TiO₂ is more negative (-1.99 eV) than that on Pd/TiO₂ (-1.63 eV), manifesting a stronger adsorption for the bimetallic CuPd/TiO₂ catalyst due to the increased d-band holes of Pd induced by the electronic transfer from Pd to

Cu. In the dehydrogenation step, H dissociates from the center P atom to produce the adsorbed H atom (then immediately forms molecular H_2 on the Pd sites) and HPO_2^- , the free energy of this step both on Pd/TiO₂ and CuPd/TiO₂ are uphill, proving it is a thermodynamically sluggish process thus a rate-determining step. The calculational result consists with our previous speculation. Obviously, the energy barrier of the dehydrogenation on CuPd/TiO₂ is smaller (from - 1.99 to - 1.64 eV, $\Delta G = 0.35$ eV) than that on Pd/TiO₂ (from - 1.63 to - 1.06 eV, $\Delta G = 0.57$ eV), which may also be ascribed to the Pd of CuPd/TiO₂ with a stronger adsorption could effectively contribute to stabilizing the HPO_2^- radical intermediate. In the third step, the $H_2PO_3^-$ is formed after OH^- (from H_2O) attack and the atomic H is generated by H^+ accepting an electron from the central P atom. It is noted that the step is thermodynamically downhill due to a negative ΔG . These DFT calculation results suggest that the CuPd/TiO₂ could accelerate the H_2 production from NHP and water mainly by promoting the absorption $H_2PO_2^-$ and reduce the activation energy of $H_2PO_2^-$ dehydrogenation step (the rate-determining one).

Comprehensively understanding the reasons for the enhanced activity of CuPd/TiO₂ catalyst, we think it is the combination result of the geometric and electronic effects of Cu. The geometric effect is that the Pd nanoparticles are more dispersive, and their sizes are smaller. Moreover, the Pd active sites in the CuPd/TiO₂ catalyst are changed and a great deal of paired sites are beneficial for the simultaneous adsorption of the intermediate HPO_2^- and dissociated H atom (Eq. 2). The electronic effect of Cu in the enhanced activity of CuPd/TiO₂ compared to that of Pd/TiO₂ is strong electronic interaction between Cu and Pd. The notable electron transfer from Pd to Cu is supported by the XPS and CO-IR analyses, leading to an increased d-band holes of Pd. The vacant d-bands induce bonding interaction between not only initial $H_2PO_2^-$ but also intermediate HPO_2^- and the surface Pd, where vacant d-band could promote electron transfer from the HOMO (the highest occupied molecular orbital) of $H_2PO_2^-$ or HPO_2^- to the d-band of Pd,^[47] on the other hand, the d-band also promotes back-donation from the d-band to the latter LUMO (lowest unoccupied molecular orbital), which stabilizes the hypophosphite species on the catalyst surface and facilitates P-H bond cleavage.²⁰ The above-mentioned mechanism of H_2 production from NHP and water over CuPd/TiO₂ catalyst is exhibited in Fig. 5d.

Conclusion

In this work, an efficient room-temperature H_2 production system with NHP and water as hydrogen carriers and CuPd/TiO₂ as a catalyst was studied. Pd nanoparticles in the CuPd/TiO₂ are more dispersive, and their sizes are smaller than that in Pd/TiO₂. The electronic interaction between Cu and Pd leads to an increased d-band holes of Pd, which promotes the adsorption of reactant $H_2PO_2^-$ and reduce the activation energy of $H_2PO_2^-$ dehydrogenation. In addition, Co-IR demonstrates that there are rich paired sites on the CuPd/TiO₂. which is beneficial for the simultaneous adsorption of the intermediate

HPO₂⁻ and H atom. As a result, the CuPd/TiO₂ exhibits the high activity and excellent stability toward H₂ production from NHP and water without any additives at room temperature.

Methods

Preparation of catalysts

CuPd/TiO₂ was prepared by a co-reduction method using NaBH₄ as reductants. Typically, 8.3 mg of PdCl₂ and 19.0 mg of Cu(NO₃)₂·3H₂O were dissolved in 80 mL of deionized water under stirring for 10 min, followed by the addition of 200.0 mg of TiO₂ (P25). After ultrasonic treatment for 10 minutes, stirring was continued for 30 minutes. A certain amount of NaBH₄ was then added, and the reaction system was stirred overnight at RT. The product was collected after vacuum filtration and washing with water and EtOH, then dried at 60°C for 8 h. The resultant product was named CuPd/TiO₂, where the theoretical loading content of Pd and Cu on the catalysts is 2.5 wt% and 2.5 wt% (Cu:Pd = 1:1), respectively. When the initial Cu:Pd is altered as 0.5:1, 2:1 (the total loading contents of 5.0 wt%), the obtained samples were labelled as Cu_{0.5}Pd/TiO₂ and Cu₂Pd/TiO₂, respectively.

If only PdCl₂ or Cu(NO₃)₂·3H₂O is added in the above process, while keeping other conditions unchanged, the prepared product would be Pd/TiO₂ or Cu/TiO₂. For comparison, the pristine TiO₂ was also treated by the same process but without PdCl₂ and Cu(NO₃)₂·3H₂O.

H₂ production experiment

Catalytic H₂ production experiments were carried out at RT. Typically, 100.0 mL of 0.1 mol·L⁻¹ aqueous NHP solution was added to a 150-mL three-necked flask. The solution was stirred for 10 min. Then, 0.100 g of catalysts was quickly added to the three-necked flask under stirring, the volume of released H₂ was recorded with a flow-meter system. The experimental set-up was presented in Fig. S1 (Supporting Information).

In cyclic experiments, the catalyst was separated by centrifugation when one reaction was completed, washed thoroughly using water and acetone, dried overnight at 70°C, and recycled for the next run.

The catalytic turnover frequency (*TOF*) was employed as a measure to characterize the catalytic efficiency of the catalysts. It was defined as the ratio of the mole of produced hydrogen (*n*_{H₂}) to the mole of added Pd (*n*_{Pd}) within unit time (h⁻¹) as the following Eq. (9).

$$TOF = \frac{n_{H_2}}{n_{Pd} \cdot t}$$

The conversion (%) of sodium hypophosphite was calculated as the mole ratio of the produced hydrogen to the added sodium hypophosphite, according to the following Eq. (10).

$$Conversion = \frac{n_{H_2}}{n_{NHP}}$$

10

Declarations

Data availability

The original contributions presented in the study are included in the article and its Supplementary Information, further inquiries can be directed to the corresponding author.

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Scheme 1

Scheme 1 is available in the Supplementary Files section.

Figures

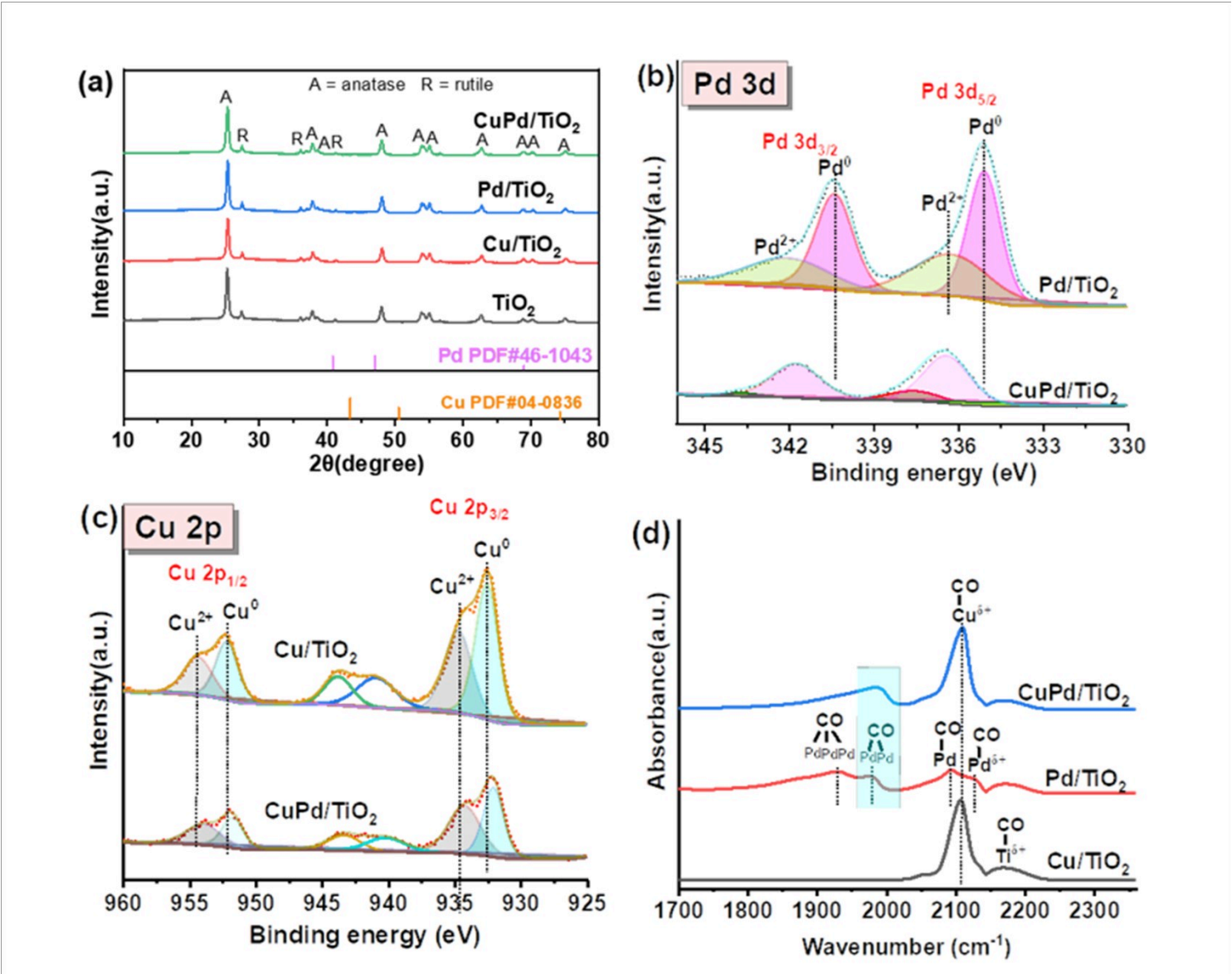


Figure 1

(a) XRD patterns of various samples, (b, c) XPS spectra of CuPd/TiO₂ and Pd/TiO₂, (d) CO-IR spectra of CuPd/TiO₂, Pd/TiO₂ and Cu/TiO₂ after desorption under Ar atmosphere for 5 min at room temperature.

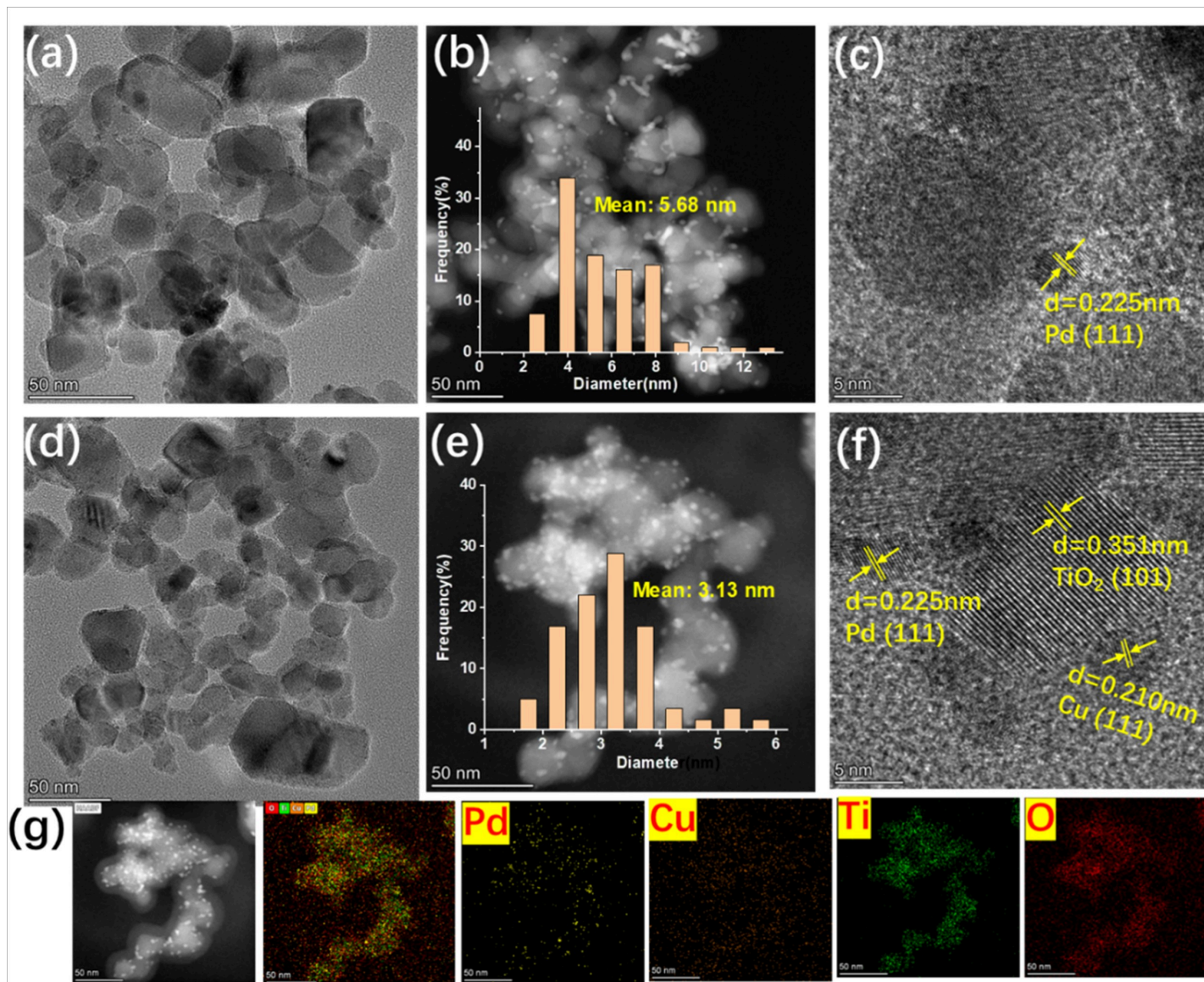


Figure 2

(a) TEM, (b) HAADF (the inset is particle size distribution), (c) HRTEM micrographs of Pd/TiO₂, (d) TEM, (e) HAADF-STEM (the inset is particle size distribution), (f) HRTEM micrographs of CuPd/TiO₂, and (g) elemental mapping of CuPd/TiO₂. The inset is particle size distribution.

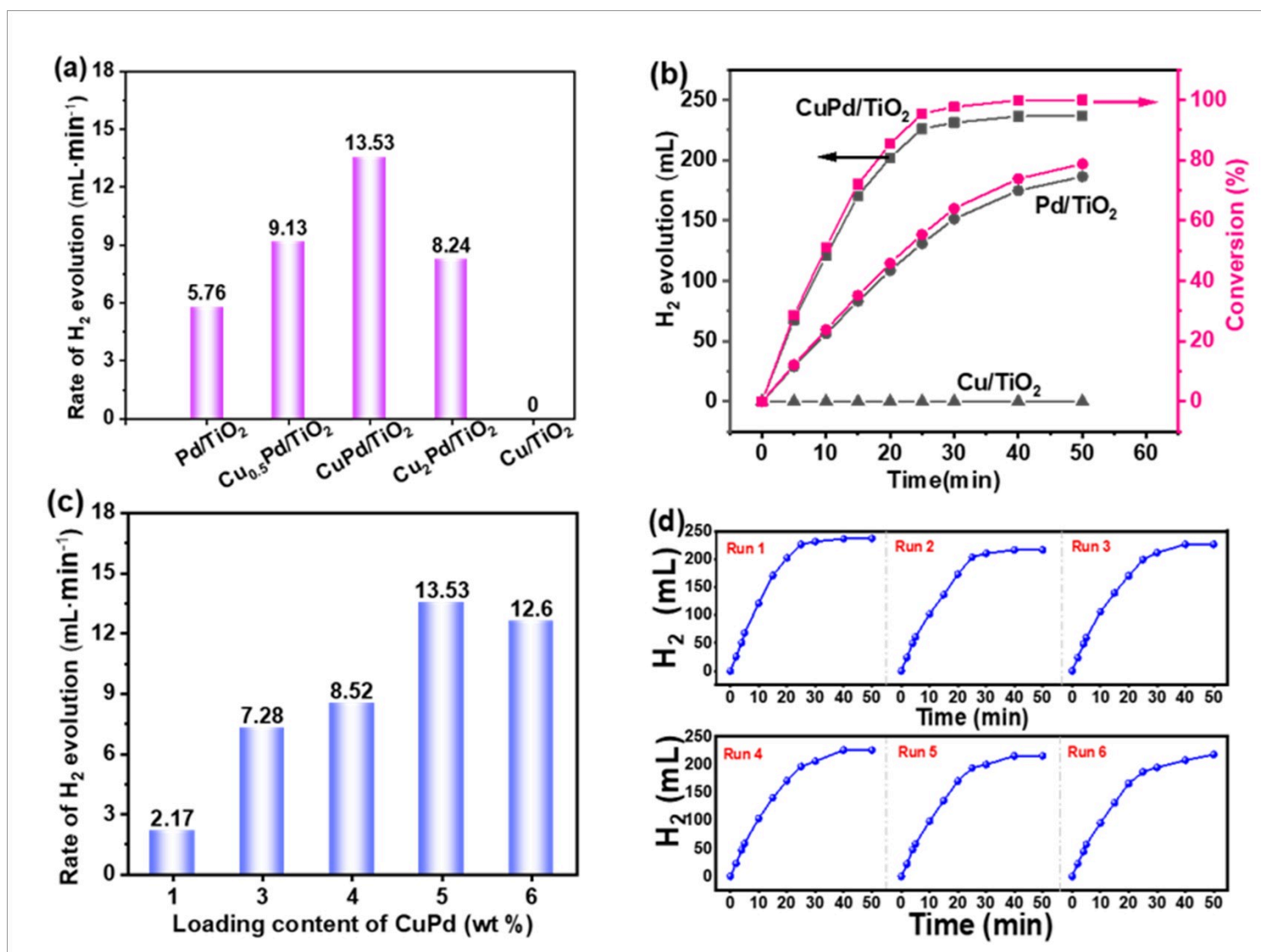


Figure 3

(a) H₂ production rate from aqueous NHP solution catalyzed by various catalysts, (b) Time course of H₂ production and NHP conversion (%), (c) The effects of loading content of CuPd on catalytic activity, and (d) The cyclic performance of CuPd/TiO₂. Reaction conditions: 0.100 g catalysts, 100.0 mL 0.1 M NHP water solution, reaction temperature is RT (298 K).

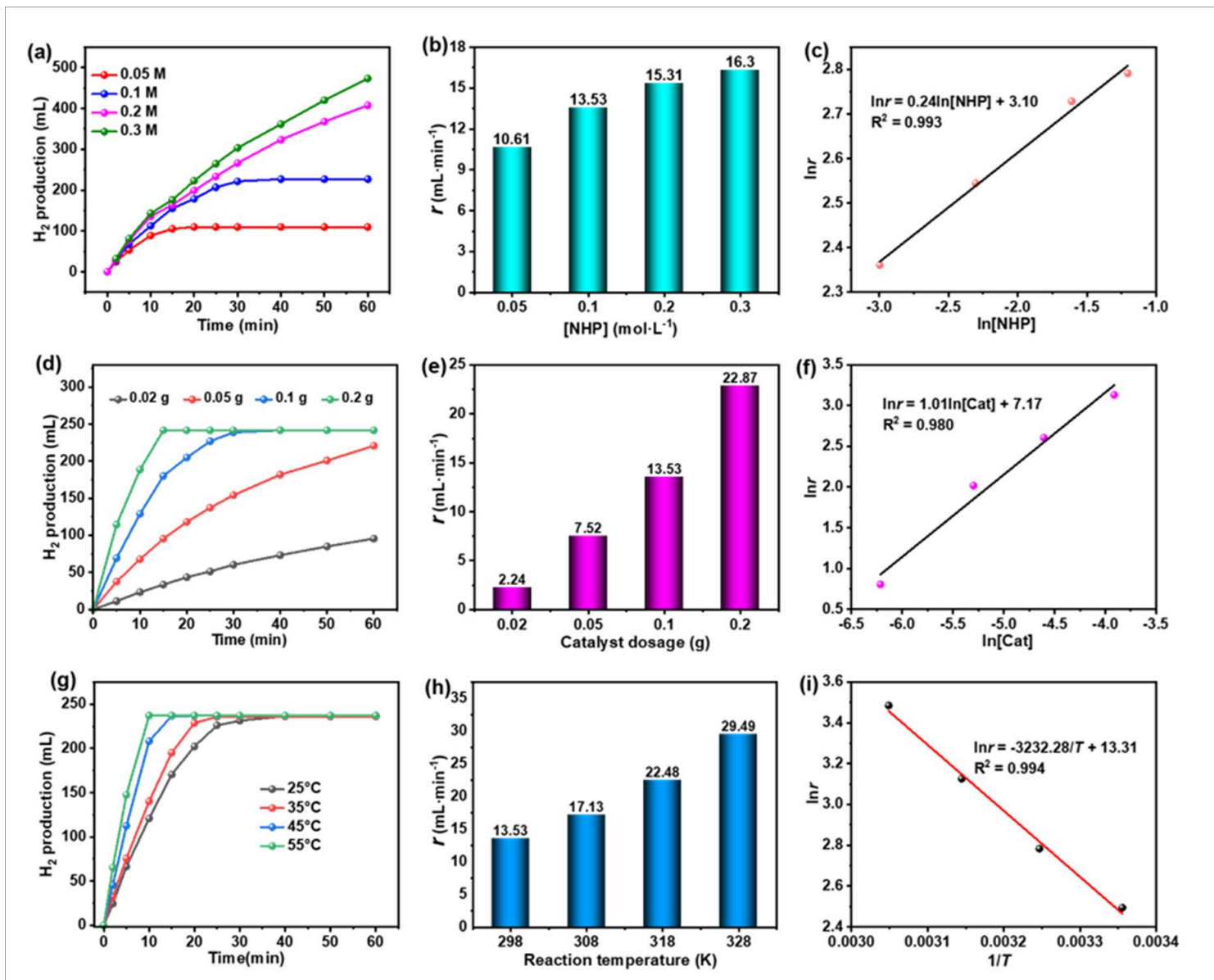


Figure 4

Kinetic investigation on H_2 production from NHP and water catalyzed by $CuPd/TiO_2$. (a) kinetic curves of H_2 production with various $[NHP]$, (b) the effects of $[NHP]$ on initial activity, (c) the corresponding plots of $\ln r$ against $\ln[NHP]$, (d) kinetic curves of H_2 production with various catalyst dosage, (e) the effects of catalyst dosage on initial activity, (f) the corresponding plots of $\ln r$ against $\ln[Cat]$, (g) kinetic curves of H_2 production at various reaction temperature, (h) the impacts of temperature on initial activity, and (i) the corresponding plots of $\ln r$ against $1/T$.

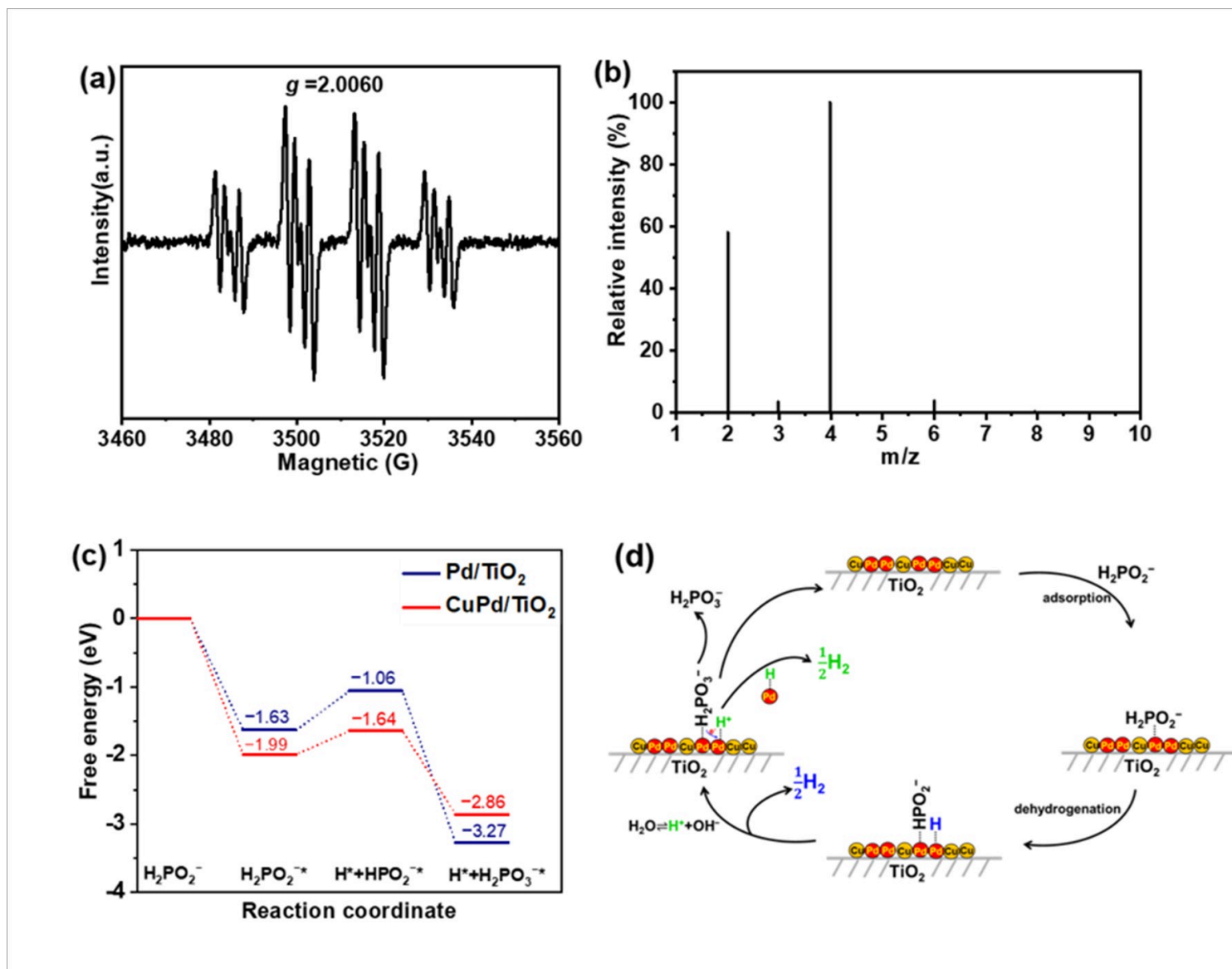


Figure 5

(a) ESR spectrum of hydrogen production system (PBN as a pin trapping agent), (b) MS spectrum of gas product from the hydrogen isotope labeling experiment, (c) The relative Gibbs free energy profiles of the reaction-related species on Pd (111) sites in CuPd/TiO₂ and Pd/TiO₂, and (d) Proposed reaction mechanism of H₂ production from NHP and water over CuPd/TiO₂ catalyst.

Supplementary Files

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