View Article Online View Journal

NJC Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Liu, P. Su, Y. Chen, B. Zhu, S. Zhang and W. Huang, *New J. Chem.*, 2018, DOI: 10.1039/C8NJ00404H.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

ROYAL SOCIETY OF CHEMISTRY

New Journal of Chemistry Accepted Manuscript

Published on 30 April 2018. Downloaded by Kaohsiung Medical University on 04/05/2018 11:08:24.

g-C₃N₄ supported metal (Pd, Ag, Pt) catalysts for hydrogenproduction from formic acid

Xiaotong Liu^a, Penghe Su^a, Ya Chen^a, Baolin Zhu^{a,c}, Shoumin Zhang^{a,c} and Weiping Huang^{a,b,c*}

Received 00th January 20xx, Accepted 00th January 20xx

Journal Name

ARTICLE

www.rsc.org/

ABSTRACT: $g-C_3N_4$ supported metal (Pd, Ag, Pt) catalysts were synthesized, and their catalytic performances for hydrogenproduction from formic acid were evaluated. The Pd catalyst can effectively turn formic acid into H₂ and CO₂ with 100% selectivity at room temperature or even lower temperature. The catalysts were characterized with TEM, XPS, PXRD, ICP, Chemisorption, IR spectra and Raman spectra. The results indicate that good catalytic performance of the catalyst was attributed to the interaction between g-C₃N₄ and metal nanoparticles that is the overlap between d-orbits of Pd and π conjugated system of g-C₃N₄. The effect of interaction was verified by the contrast analyzing the catalytic performances of Pd/g-C₃N₄, Ag-Pd/g-C₃N₄, Pt-Pd/g-C₃N₄ and Pd/HTNTs (hydrogen titanate nanotubes) for hydrogen-production from formic acid.

Introduction

A limited amount of fossil fuel in the earth drives people to develop new and renewable energy, because the fossil fuel will be used up in the foreseeable future. H_2 energy, a renewable energy, is becoming high attracting attention.¹ One of the processes of H₂ energy utilization is the hydrogen-generation. In terms of generation of H₂, besides traditional water-gas shift process etc. there are various developing methods, such as photocatalytic decomposition of water², biological hydrogen production,³ catalytic decompositions of organic compounds^{4, 5} and so on. Among those methods, catalytic decomposition of organics should be a more practical one in view of the fact that organics used can be carried conveniently, synthesized massively and decomposed efficiently. Formic acid (FA) is widely used as hydrogen source because of its hydrogen content (4.4 wt.%), nontoxicity, stability under ambient condition⁶, easy-to-gain⁷ and so on. The FA can be selective catalytically decomposed into H₂ and CO₂ by using homogeneous⁸ and heterogeneous catalysts, such as metals (e.g. Ru,⁹ Rh,¹⁰ Au,¹¹ Pd,¹² Cu¹³ Ag-Pd Alloys¹⁴ and Pt-Cu Alloys¹⁵) and supported metals¹⁶. Among them the Pd shows high activity. To make use of Pd more efficiently and increase its catalytic activity as well as selectivity for H₂, supports of supported-Pd catalysts are extensively investigated, including

hydroxyapatite,¹⁷ graphite,¹⁸ TiO₂-nanotubes (TNTs) and other supporters. g-C₃N₄ of large π -conjugated system is an interesting support, which is applied in several fields, such as decomposition of water,¹⁹ chemical hydrogen storage^{20, 21}, transfer hydrogenation²² and so on. Furthermore, g-C₃N₄ and its modified products are also used in hydrogen-production from formic acid.²³⁻²⁶ With a great template, mesoporous g-C₃N₄ can be synthesized. Using this mpg-C₃N₄, metal like Pd can be separated as single atoms.²⁷

It has been reported that the assistant of sodium formate (SF) is needed for increasing the reaction rate in the Pd catalysing dehydrogenation of FA, in which the formate ion (HCOO) binds Pd NPs firstly.^{28,29} In view of the reference 30, the promotion effect originates in the electron donation ability of HCOONa toward the Pd surface, based on which it should be theoretically reasonable and attracting to design and synthesize Pd catalyst supported by the support with π -conjugated system for the catalytically dehydrogenation of FA. In such catalyst, the electron density on Pd NPs may be reduced through the interaction between Pd and support. As the result of it, HCOO⁻ ions bind Pd NPs more smoothly, and catalytic activity of catalyst, in turn, is enhanced.

In the present contribution, we design and synthesize g-C₃N₄ supported metal (Pd, Ag, Pt) catalysts, in which the large π -conjugated system of g-C₃N₄ can accept the electron transfer of palladium etc. nanoparticles by d-p π action. The interaction between Pd NPs and g-C₃N₄ not only effectively disperse Pd NPs, but also obviously promote electron flowing. As a result, the catalyst can catalyse hydrogen-production from formic acid at room temperature with a high selectivity.

Experimental section

Synthesis of catalyst

^{a.} College of Chemistry, Nankai University, Tianjin 300071, China.

^{b.} Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, China.

^c The Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China.

⁺ Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

ARTICLE

Published on 30 April 2018. Downloaded by Kaohsiung Medical University on 04/05/2018 11:08:24

(1) Synthesis of $g-C_3N_4$. $g-C_3N_4$ was synthesized by direct pyrolysis of carbamide according to the previous report.³¹ The procedure is described as follows: 10 g of carbamide power was put into a crucible with a cover and then heated at 500°C (with a heating rate 10°C min⁻¹) for 2 h in a muffle furnace. The product was washed with deionized water and dried at 80°C.

(2) Synthesis of Pd/g-C₃N₄. 1 g of g-C₃N₄ was dispersed in 15 mL acetic acid, which was saturated solution of palladium diacetate. This mixture was stirred for 6 h at room temperature. After centrifuged and dried, the solid was dispersed and reduced in 20 mL 20% sodium formate (SF) solution, and pH of the solution was adjusted to 10 with 1 M NaOH solution. After vigorous stirred for 3 h, the solid was centrifuged, washed with deionized water, dried and labeled as Pd/g-C₃N₄.

(3) Synthesis of Pt/g-C₃N₄. Platinum nanoparticles were deposited on the g-C₃N₄ by photo-reduction.³² 0.5 g g-C₃N₄ powder was dispersed in 40 mL 90% ethanol solution, and 5 mL of H₂PtCl₆ solution (0.01 M) was added. Then the mixture was irradiated by visible light from 500 W Xenon lamp for 2 h. Solid was collected and washed with deionized water. After dried, product was labeled as Pt/g-C₃N₄.

(4) Synthesis of Ag/g-C₃N₄. Silver nanoparticles were deposited on the g-C₃N₄ by the same procedure as synthesis of Pt/g-C₃N₄, besides that 5 mL H₂PtCl₆ solution was replaced by 5 mL AgNO₃ solution (0.01 M), and product was labeled as Ag/g-C₃N₄.

(5) Synthesis of Pt-Pd/g-C₃N₄. Platinum nanoparticles were deposited on the Pd/g-C₃N₄ by the same procedure as synthesis of Pt/g-C₃N₄, besides that 0.5 g g-C₃N₄ was replaced by Pd/g-C₃N₄, and product was labeled as Pt-Pd/g-C₃N₄.

(6) Synthesis of Ag-Pd/g-C₃N₄. Silver nanoparticles were deposited on the Pd/g-C₃N₄ by the same procedure as synthesis of Pt-Pd/g-C₃N₄, besides that 5 mL H₂PtCl₆ solution was replaced by 5 mL AgNO₃ solution (0.01 M), and product was labeled as Ag-Pd/g-C₃N₄

(7) Synthesis of Pd/HTNTs. Hydrogen titanate nanotubes (HTNTs) are synthesized according to the previous report.³³ To obtain Pd/HTNTs, photo-reduction was applied. 0.5g HTNTs powder was dispersed in 35 mL 90% ethanol solution, and 10 mL of $(NH_4)_2PdCl_4$ solution (0.05 M) were added. Then the mixture was irradiated by UV-light from 300 W mercury lamp for 2 h. Product was labeled as Pd/HTNTs.

(8) Synthesis of Pt-Pd/HTNTs. Platinum nanoparticles were deposited on the Pd/HTNTs by the same procedure as synthesis of Pt/g-C₃N₄, besides that 0.5 g g-C₃N₄ was replaced by Pd/HTNTs, and xenon lamp was replaced by the mercury lamp. Product was labeled as Pt-Pd/HTNTs.



2 | J. Name., 2012, 00, 1-3

(9) Synthesis of Ag-Pd/HTNTs. Silver nanoparticles were deposited on the Pd/HTNTs by same procedure as synthesis of Ag/g-C₃N₄, besides that 0.5 g g-C₃N₄ was replaced by Pd/HTNTs, and xenon lamp was replaced by the mercury lamp. Product was labeled as Ag-Pd/HTNTs.

Scheme 1. Schematic Representation for the Synthesis and Catalysis of $Pd/g\mbox{-}C_3N_4$ Catalyst

Characterizations of catalyst

The metal contents in catalysts were determined by inductively coupled plasma spectrometers (X7 Thermo Fisher Scientific). Powder X-ray diffraction (XRD) measurements were performed on D/max-2500 X-ray diffraction analyzer of Rigaku Corporation, with Cu K α , $\lambda = 0.154$ nm radiation as source with nickel filter (18 KW, 60 KV, 300 mA). Data were recorded at a scan rate of $0.02^{\circ} 2\theta \text{ s}^{-1}$ and the 2 θ range from 3° to 80°. X-ray photoelectron spectroscopy (XPS) analysis was performed on Esalab 250Xi, using an Al X-ray source, and the binding energy was calibrated by taking C₁₅ peak at 284.6 eV as reference. Transmission electron microscopy (TEM) image was recorded using a JEOL Model JEM-2100 instrument at an accelerating voltage of 200 kV.

Nitrogen adsorption-desorption isotherms were collected on Autosorb-1-MP 1530VP automatic surface area and porosity analyzer. The sample was degassed at 200 °C for 5 h and then analyzed at -196 °C. The relative pressure (P/P_0) range used for calculation of BET surface area was from 0.05 to 0.30. The H₂ chemisorption was carried out on Autosorb IQ C-XR (Quantachrome Instruments). Prior to measurements, 0.410 g of Pd/g-C₃N₄ was thermally treated under a He stream at 100 °C for 60 min to remove physically adsorbed water and other impurities. The sample was cooled down to room temperature and heated to 150 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C min⁻¹ using pure H₂ at 50 mL min⁻¹. The oxides on the sample surface were then reduced in a pure H_2 flow at 150°C for 60 min. After the reduction at 150 °C, the sample was purged with a He gas at the same temperature for 30 min. After cooling to 40 °C, a pure H_2 was introduced for the combination of H_2 chemisorption and physical adsorption (the pressure range was from 5332.89 to 106657.89 Pa), and after evacuated, He was introduced for the physical adsorption. Then we can get the H₂ chemisorption data by using combined adsorption minus weak adsorption (physical adsorption). The metal dispersion of $Pd/g-C_3N_4$ was then calculated from the amount of H_2 adsorbed, taking the stoichiometry factor (S_F: Pd/H₂) as 2. The metal dispersion could be calculated as follows:

$$Dispersion (\%) = \frac{V_{ads} \times S_F \times M_W}{S_W \times F_n \times 22.414} \times 100\%$$
 (1)

where V_{ads} is the cumulative volume of adsorbed H₂ (cm³ at STP). M_W is the molecular weight of Pd metal (g mol⁻¹). S_W is the weight of the sample, and F_n is the Pd fraction in relation to the total catalyst sample weight.³⁴

Fourier transform infrared (FTIR) spectra were recorded on a Bio Rad FTS 6000 spectrometer, and the samples were prepared as KBr pellets. Raman spectra were recorded on a

This journal is C The Royal Society of Chemistry 20xx

Journal Name

Bruker RFS 100/S FT-Raman Spectrometer. The wavelength of excitation light is 1064 nm.

Evaluation of catalytic performance of catalyst.

0.1 g catalyst and 2 mL deionized water were mixed in a flask, which was placed in a water bath at 25 °C. 15 mL buffer solution, in which the ratio of SF to FA is 9 and the total concentration is 6 mol/L, was added into the flask and the time was recorded as starting point of reaction. The volume of released gas was measured by displacement method and the gas was analysed by gas chromatography (Beifen 3420A, with thermal conductivity detector, and mixture of H₂ and CO was used as reference standard, nitrogen as the carrier gas).

Calculation method. The TOF and TON of catalytic reaction were calculated based on the following formulas.

$$TON = \frac{PV_{gas}/RT}{n_{Pd}}$$
(2) $TOF = \frac{PV_{gas}/RT}{tn_{Pd}}$ (3)

where *P* is the atmospheric pressure (101325 Pa), V_{gas} is the volume of H₂ generated, *R* is the universal gas constant (8.3145 m³ Pa mol⁻¹ K⁻¹), *T* =25°C (298.15 K), n_{Pd} is the total mole number of Pd atom in catalyst, and *t* is the time of gas generation.

Result and discussion

 $g-C_3N_4$ was prepared by direct pyrolysis of carbamide and welldispersed Pd nanoparticles were anchored on $g-C_3N_4$ by an impregnation method coupled with subsequent reduction with HCOONa. Pt and Ag NPs were well dispersed on Pd/g-C₃N₄ by photo-reduction method.

Composition and structure of catalyst

The compositions of catalysts were determined by ICP and the results are listed in Table 1. The SSA of catalysts are also listed in Table 1. The SSA of catalysts are slightly reduced compared with that of supports. Table 2 shows the metal dispersions and metal surface areas of the as-prepared and used $Pd/g-C_3N_4$. The dispersion degree of Pd NPs analyzed by static chemical adsorption is 72.7% and the average particle size is 1.54 nm in the as-prepared Pd/g-C_3N₄, which matches the result obtained by TEM. However, the size of Pd particles increased in the used Pd/g-C_3N_4.

Table 1. Metal contents and SSA of catalysts.

Comple	Contents (%)			$CCA(m^2/r)$
Sample	Pd	Pd Pt Ag		SSA (m /g)
$Pd/g-C_3N_4$	1.09	—	_	65.21
$Pt/g-C_3N_4$	—	0.65	—	62.34
$Pt-Pd/g-C_3N_4$	1.01	0.50	—	65.09
$Ag/g-C_3N_4$	—	_	0.44	64.53
$Ag-Pd/g-C_3N_4$	1.02	_	0.61	65.01
g-C ₃ N ₄	—	_	—	65.54
Pd/HTNTs	0.97	_	—	202.1
Pt-Pd /HTNTs	0.95	1.33	_	136.4
Ag-Pd /HTNTs	0.97	_	0.61	199.4
HTNTs	_	-	_	287.5

Table 2. Metal dispersion and particle size of the Pd/g-C₃N₄ catalyst

	Catalyst	Metal	dispersion ^a	Average particle size (nm)		
		(%)		Chemisorption ^a	TEM ^b	
	Pd/g-C ₃ N ₄ (before)	72.7		1.54	2.9	
	Pd/g-C ₃ N ₄ (after)	50.4		4.28	5.7	
a.	Calculated from the H2 ch	emisorption.				

Analyzed from the TEM images



Figure 2. Raman spectra of $g-C_3N_4$ and as-prepared Pd/g-C₃N₄ (1064 nm)

Several methods were used to characterize catalysts; the following discussion is mainly related to the catalysts that have good catalytic performance. FT-IR spectra of the $g-C_3N_4$ and catalysts are shown in Fig. 1. Both of pure $g-C_3N_4$ and asprepared Pd/g-C_3N_4 exhibit similar FT-IR vibration modes. The peaks at 814 cm⁻¹ and 1240-1640 cm⁻¹ are the characteristic breathing and stretching vibration modes of aromatic CN heterocycles, confirming the existence of thiazine units; the broad and weak bands at 3100–3250 cm⁻¹ are typical signals of N-H or C-H vibrations, which are attributable to the uncondensed amino groups as the surface terminal groups.³⁵ It can be seen from Fig. 1a and b that the structure of $g-C_3N_4$ did not change in the catalytic reaction process.

Fig. 2 displays Raman spectra of $g-C_3N_4$ and as-prepared Pd/g-C₃N₄ (1064 nm). As is known to all, $g-C_3N_4$ of large π conjugated system has a band gap of 2.7 eV,³⁶ it can absorb visible light (457-532nm) and generate fluorescence. The Raman spectrum of $g-C_3N_4$ (Fig. S1) using 532 nm laser source as excitation light shows strong fluorescence. Using near infrared laser source (1064 nm) as excitation light, the fluorescence of $g-C_3N_4$ can be efficiently decreased. Two Raman peaks at 707.02cm⁻¹ and 1233.50cm⁻¹ of $g-C_3N_4$ (Fig. 2a)

DOI: 10.1039/C8NJ00404H

ARTICLE

Published on 30 April 2018. Downloaded by Kaohsiung Medical University on 04/05/2018 11:08:24.

are attributed to the D and G bands of a typical graphitic structure.³⁷ However, exciting Pd/g-C₃N₄ with the same excitation light, the Raman spectrum of Pd/g-C₃N₄ (Fig. 2b) shows a strong broad fluorescence peak rather than D and G bands of the typical graphitic structure, which illustrates clearly that as Pd NPs were introduced into $g-C_3N_4$, the fluorescence appeared again. It may be explained that the interaction between Pd NPs and $g-C_3N_4$, that is, the electron transfers between Pd and $g\text{-}C_3N_4$ by the d-p π interaction between Pd and g-C₃N₄ increased the electron density of g- C_3N_4 , which results in the fluorescence reappearance. We also used HTNTs without π system as the support to explore the Raman spectrum. In the Raman spectrum of Pd/HTNTs, there is no fluorescence, which confirms that Pd NPs themselves do not cause the fluorescence if there is no d-p π interaction between Pd NPs and support that does not have π -conjugated system. PXRD pattern of as-prepared Pd/g-C₃N₄ (Fig. 3a) displays the typical diffraction peaks of g-C₃N₄ (110) and Pd (111) at 27.48° (PDF#50-1512) and 40.02° (PDF#46-1043), respectively. Ag-Pd/g-C₃N₄ (Fig. 3b) not only shows peaks of g-C₃N₄ and Pd, but also peak of Ag (111) at 38.68° and peak of Ag (200) at 44.96° (PDF#04-0783), which interprets that no alloy forms in the bimetallic catalyst.

XPS was used to characterize the chemical state of metal in catalysts, as well as the interactions between metals or metal and support (Fig. 4). The Pd in samples exists as Pd⁰ and Pd²⁺, but the Pd⁰ is the dominant component based on the peak area ratio (S III, ESI). The peaks of Pd $3d_{5/2}$ and $3d_{3/2}$ located at 334.4 and 339.60 eV, respectively, in Pd/HTNTs (Fig. 4a) are associated with normal Pd(0).³⁸ Compared with Fig. 4a, Fig. 4b shows that the binding energy of Pd 3d in as-prepared Pd/g-C₃N₄ increases slightly, which means that the electron density on Pd reduces and there is certainly an interaction between the Pd NPs and g-C₃N₄, where electrons are transferred from Pd NPs to $g-C_3N_4$ by the overlap of d-orbits of Pd and empty π conjugated orbits of $g-C_3N_4$, which is consistent with the strong fluorescence in Raman spectra. Similarly, the shift of Pd 3d peaks also exists in Fig. 4c and Fig. 4d. However, by comparison with Fig. 4a and 4b, it can be found that the presence of Ag and Pt affects the shift of Pd 3d peaks differently, which can be interpreted by different work functions of metals. The work functions of Ag, Pd and Pt are 4.26 eV, 5.12 eV and 5.65 eV, respectively. It is well known that the electrons are inclined to flow from the lower work function metal to the higher one when metals with different work functions are fitted together.³⁹ Accordingly, the binding energies of Pd $3d_{5/2}$ and $3d_{3/2}$ in Pd-Ag/g-C₃N₄ (335.1 eV, 340.4eV) and Pd-Pt/g-C₃N₄ (335.35 eV, 340.65eV) are relatively lower and higher, respectively, than that in as-prepared Pd/g-C₃N₄ (335.20 eV, 340.5eV).

TEM images of the catalysts are showed in Figure 5 and supplymentary information S IV. HRTEM images (Fig. 5a inset) show that the interlayer spacing of Pd NPs in Pd/g-C₃N₄ is 0.22 nm, which agrees with that of Pd (111). The interlayer spacings of NPs in Ag-Pd/g-C₃N₄ (Fig. 5c inset) are agreement with those of Pd (111) and Ag (111), and the interlayer spacings of NPs in Pt-Pd/g-C₃N₄ (Fig. 5d inset) are agreement with those of Pd

(111) and Pt (111). As is shown in Fig. 5e and 5f, HTNTs with a diameter of about 8 nm has good tubular nanostructure and the Pd NPs are well dispersed on the HTNTs. Though the SSA of HTNTs is much larger than that of g-C₃N₄ (Table 1), all metallic particles on the g-C₃N₄ are smaller than those on the HTNTs (S V, ESI). Comparing Fig 5a and Fig. 5e, the Pd deposited on the g-C₃N₄ is highly dispersive, however, the Pd well-distributed on the surface of the HTNTs shows graininess, which can be interpreted as that π -conjugated system in g-C₃N₄ makes a great deal of contribution to disperse electrons in Pd, as a result, the aggregation of Pd NPs becomes much more difficult because of the feature of metal crystal formed maintained by metallic bond.



Figure 3. XRD partterns of as-prepared Pd/g-C $_3N_4$ and Ag-Pd/g-C $_3N_4$



Figure 4. XPS spectra of Pd/HTNTs (a), Pd/g- C_3N_4 (b), Ag- Pd/g- C_3N_4 (c) and Pt-Pd/g- C_3N_4 (d)



Figure 5 TEM images of Pd/g-C₃N₄ (a, b), Ag-Pd/g-C₃N₄ (c), Pt-Pd/g-C₃N₄ (d), Pd/HTNTs (e), and HTNTs (f)

DOI: 10.1039/C8NJ00404H

ARTICLE

Pd NPs are well dispersed on the HTNTs. Though the SSA of HTNTs is much larger than that of g-C₃N₄ (Table 1), all metallic particles on the g-C₃N₄ are smaller than those on the HTNTs (S V, ESI). Comparing Fig 5a and Fig. 5e, the Pd deposited on the g-C₃N₄ is highly dispersive, however, the Pd well-distributed on the surface of the HTNTs shows graininess, which can be interpreted as that π -conjugated system in g-C₃N₄ makes a great deal of contribution to disperse electrons in Pd, as a result, the aggregation of Pd NPs becomes much more difficult because of the feature of metal crystal formed maintained by metallic bond.

Evaluation of catalysts

The released gas in the catalytic decomposition of FA was detected by GC and no CO was found in the released gas (S VI, ESI).

The catalytic performances of catalysts are listed in Table 3. As shown in Table 3, Figure S16 and S17, for Pd, Pt and Ag, only Pd can catalyse the dehydrogenation of FA efficiently; all g- C_3N_4 supported catalysts (Entry 1-3, 7) show far higher activity than HTNTs supported ones (Entry 4-6). The TOF of asprepared Pd/g- C_3N_4 (Entry 1) is more than 8 times that of Pd/HTNTs (Entry 4). Compared with as-prepared Pd/g- C_3N_4 , the calcinated catalyst shows higher activity (Entry 7), which is mainly ascribed to the enhanced interaction between metal Pd and g- C_3N_4 . These results clearly indicate that the π -conjugated system of support, by which the electron density of metal can be efficiently reduced, is a key factor that makes catalysts have high activity, which should be utilized as much as possible in developing high efficient catalyst for hydrogen-production from formic acid.

For the as-prepared catalysts that have the same support, g- C_3N_4 , the order of the catalytic activity is as follows: Pt-Pd/g- C_3N_4 >Pd/g- C_3N_4 >Ag-Pd/g- C_3N_4 (Tab. 3), which agrees with the binding energy order of Pd determined by XPS. This order implies that anions e.g. HCOO⁻ bind to Pd NPs firstly in the catalytic processes. In the previous reports ^{19, 20}, researchers believe that the catalytic decomposition of FA proceeds a transformation from bidentate formate combined with metal NPs to monodentate one, followed by decomposition into CO₂ and H atom. Consequently, reducing the electron density on the surface of Pd NPs is benefit to the combination between formate ions and catalyst, and then enhances the catalytic activity of catalyst. Among all catalysts, Pt-Pd/g-C₃N₄ shows the highest activity, for which two factors are responsible: one is the flow of electron between Pt and Pd NPs because of the different work functions; and the next is that the Pt has lower hydrogen over potential than the Pd, which should be favour to the H₂-release.

The effect of FA/SF molar ratio on the catalytic activity of the Pd/g-C₃N₄ for FA dehydrogenation was investigated. As pure FA is used, the rate of gas generation is very slow (TOF=87 h^{-1}). However, increasing the molar percentage of SF (FA/SF = 1 and 0.1) may induce a rapid increase in rate of gas generation or

the catalytic activity of $Pd/g-C_3N_4$ (TOF=142.17 h⁻¹ and 189.56 h⁻¹), which further confirms that HCOO⁻ binds Pd NPs firstly, SF is an important promoter. However, no matter how to change

the ratio of buffer solution, the lifetime of catalysts lasts for 8-12 h in the reaction system.

Table 3.	Evaluation	of catalytic	performances	of catalysts	at room	temperature

Entry	Catalyst	Content of Pd (%)	Volume of gas released (mL)	Composition of gas	TON	TOF (h^{-1})
1	$Pd/g-C_3N_4$	1.09	96	H ₂	383.12	191.56
2	Ag-Pd/g-C ₃ N ₄	1.02	60	H ₂	255.88	127.94
3	Pt-Pd/g-C ₃ N ₄	1.01	111	H ₂	478.08	239.04
4	Pd/HTNTs	0.97	10	-	44.84	22.42
5	Ag-Pd/HTNTs	0.97	0	-	-	-
6	Pt-Pd/HTNTs	0.95	0	-	-	-
7	Pd/g-C ₃ N ₄ ^b	1.09	102	H ₂	407.7	203.54
8	Pt/g-C ₃ N ₄	0	0	-	-	-
9	Ag/g-C ₃ N ₄	0	0	-	-	-

 a The data were collected when the reaction lasted for 2 h; b The catalyst was calcinated at 150 $^{\circ}$ C for 1 h in H₂ atmosphere.

Conclusion

Published on 30 April 2018. Downloaded by Kaohsiung Medical University on 04/05/2018 11:08:24.

In this study, g-C₃N₄ supported metal (Pd, Ag, Pt) catalysts were synthesize. Among them, the catalysts containing Pd have high catalytic activity and selectivity in hydrogen-generating from formic acid. The combination of Pd, supports with π -conjugated system, and metals with higher work function and lower hydrogen overpotential should be a good option in developing high efficient catalyst for hydrogen-production from formic acid. Though g-C₃N₄ supported catalysts containing Pd show excellent catalytic performance in hydrogen-generating from formic acid, improving their reusability should be the next focus.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (21373120, 21301098, 21071086 and 21271110), and project IRT13022, B12015.

Notes and references

- Cheng, J.; Gu, X. J.; Liu, P. L.; Zhang H.; Ma, L. L. and Su, H. Q. Applied Catalysis B: Envrionmental, 2017, 218, 460.
- 2 Zong, X.; Yan, H. J.; Wu, G. P.; Ma, G. J.; Wen, F. Y.; Wang, L. and Li, C. J. Am. Chem. Soc., 2008, 130, 7176.
- 3 Das, D. and Veziroglu, T. N. International Journal of Hydrogen Energy, 2001, 26, 13.
- 4 Haruta, M. Gold Bulletin, 2007, 37, 27.
- 5 Pingping, Z.; Nan, C.; Wei, L. and Gongzhen, C. J. Mater. Chem. A, 2015, 3, 12468.
- 6 Bi, Q. Y.; Lin, J. D.; Liu, Y. M.; He, H. Y.; Huang, F. Q. and Cao, Y. Angew. Chem. Int. Ed., 2016, **55**: 11849.
- 7 Ciftci, A.; Ligthart, D.A.J. M.; Pastorino, P. and Hensen, E. J.M. *Applied Catalysis B: Environmental*, 2013, **130**, 325.
- 8 Mellmann, D.; Sponholz, P.; Junge, H. and Beller, M. Chem. Soc. Rev., 2016, 45, 3954.
- 9 Kübler, M.; Jurzinsky, T.; Ziegenbalg, D. and Cremers, C. Journal of Power Sources, 2018, 375, 320.
- Himeda, Y.; Miyazawa, S. and Hirose, T. ChemSusChem, 2011, 4, 487.
- 11 Bi, Q. Y.; Du, X. L.; Liu, Y. M.; Cao, Y.; He, H. Y. and Fan, K. N. J. Am. Chem. Soc., 2012, **134**, 8926.

- 12 Ruthven, D. M. and Upadhye, R. S. J. Catal., 1971, 21, 39.
- 13 Marcinkowski, M. D.; Murphy, C. J.; Liriano, M. L.; Wasio, N. A.; Lucci, F. R. and Sykes E. C. H. ACS Catal., 2015, **5**, 7371.
- 14 Lan, Y.; Xing, H.; Jun, S.; Wei, L.; Shengli, C. and Gongzhen, C. Applied Catalysis B: Environmental, 2015, **168-169**, 423.
- 15 Marcinkowski, M. D.; Liu, J.-L.; Murphy, C. J.; Liriano, M. L.; Wasio, N. A.; Lucci, F. R.; Flytzani-Stephanopoulos, M. and Sykes, E. C. H. ACS Catal., 2017, 7, 413.
- 16 Zhang, X. Y.; Shang, N. Z.; Zhou, X.; Feng, C.; Gao, S. T.; Wu, Q. H.; Wang, Z.; and Wang, C. New J. Chem., 2017, 41, 3443.
- 17 Boukha, Z.; Ayastuy, J. L.; González-Velasco, J. R. and Gutiérrez-Ortiz, M. A. Applied Catalysis B: Environmental, 2017, 201, 189.
- 18 Zhu, Q. L.; Tsumori, N. and Xu, Q. J. Am. Chem. Soc., 2015, 137, 11743.
- Majeed, I.; Manzoor, U.; Kanodarwala, F. K.; Nadeem, M. A.; Hussain, E.; Ali, H.; Badshah, A.; Stride, J. A. and Nadeem M. A. *Catal. Sci. Technol.*, 2018, 8, 1183.
- 20 Shao, X. Z. AIChE, 2016, 62, 2410.
- 21 Lee, H. J.; Ryu, J.; Kim, J. Y.; Nam, S.-W.; Han, J. H.; Lim, T.-H.; Gautam, S.; Chae, K. H. and Yoon, C. W. J. Mater. Chem. A, 2014, 2, 9490.
- 22 Cheng, S. S.; Meng, X. F.; Shang, N. Z.; Gao, S. T.; Feng, C.; Wang, C. and Wang, Z. *New J. Chem.*, 2018, **42**, 1771
- 23 Oh, T. H. Energy, 2016, **112**, 679.
- 24 Deng, Q.-F.; Zhang, Z.-F.; Cui, J.-F. and Jia, L.-H. International journal of Hydrogen Energy, 2017, 42, 14865.
- 25 Wu, Y. M.; Wen, M. C.; Navlani-Garcia, M.; Kuwahara, Y.; Mori, K. and Yamashita, H. *Chem. Asian J.*, 2017, **12**, 860.
- 26 Xu, L. X.; Zhang, J.; Cheng, D.-G.; Chen, F. Q.; An, Y.; Cui, P. and Wan, C. RSC Adv., 2016, 6, 46908.
- 27 Vilé, G.; Albani, D.; Nachtegaal, M.; Chen, Z.; Dontsova, D.; Antonietti, M.; López, N. and Pérez-Ramírez, J. Angew. Chem. Int. Ed., 2015, 54, 11265.
- 28 Quan, J. M.; Kondo, T.; Wang, G. C. and Nakamura, J. Angew. Chem. Int. Ed., 2017, 56, 3496.
- 29 He, F.; Li, K.; Yin, C.; Wang, Y.; Jiao, M. G.; Tang, H. and Wu, Z. J. Applied Surface Science, 2016, 387, 221.
- 30 Wang, P.; Steinmann, S. N.; Fu, G.; Michel, C. and Sautet, P. ACS Catal. 2017, 7, 1955.
- Shi, Y. K.; Hu, X. J.; Zhao, J. T.; Zhou, X. J.; Zhu, B. L.; Zhang, S. M. and Huang, W. P. New J. Chem, 2015, 39, 6642.
- Jiang, L. B.; Yuan, X. Z.; Pan, Y.; Liang, J.; Zeng, G. M.; Wu, Z.
 B. and Wang, H. *Applied Catalysis B: Environmental*, 2017, 217, 388.
- 33 An, H. Q.; Zhu, B. L.; Li, J. X.; Zhou, J.; Wang, S. R.; Zhang, S. M.; Wu, S. H. and Huang, W. P. J. Phys. Chem. C, 2008, 112, 18772.

6 | J. Name., 2012, 00, 1-3

This journal is © The Royal Society of Chemistry 20xx

Journal Name

- 34 Prakash, N.; Lee, M.; Yoon, S. and Jung, K.-D. *Catalysis Today*, 2017, **293**, 33.
- 35 Yan, S. C.; Li, Z. S. and Zou, Z. G. Langmuir, 2009, 25, 10397.
- 36 Wang, X. C.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K. and Antonietti, M. Nature Materials, 2009, 8, 76.
- 37 Papailias, I.; Giannakopoulou, T.; Todorova, N.; De-motikali, D.; Vaimakis, T. and Trapalis, C. *Applied Surface Science*, 2015, **358**, 278.
- 38 Tura J.M.; Regull P.; Victori L. and Dolors de Castellar M. Surf. Interface Anal. 1988, **11**, 447.
- 39 Ding, Y. J.; Sun, W. Z.; Yang, W. Y. and Li, Q. *Applied Catalysis* B: Environmental, 2017, **203**, 372.





Text: $Pd/g-C_3N_4$ of d- π interaction between Pd NPs and g- C_3N_4 with π -conjugated system shows high catalytic activity in dehydrogenation of FA.