



Physical Chemistry Chemical Physics

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: H. Bahruji, N. Abdullah, S. Rogers, P. Wells, C. R. A. Catlow and M. Bowker, *Phys. Chem. Chem. Phys.*, 2019, DOI: 10.1039/C9CP00826H.



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 Information for Authors.

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 <u>Ethical guidelines</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.





# ARTICLE

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

DOI: 10.1039/x0xx00000x

# Pd local structure and size correlations on the activity of Pd/ TiO<sub>2</sub> for photocatalytic reforming of methanol

Norli Abdullah,<sup>a,b,c</sup> Hasliza Bahruji,<sup>*d*\*</sup> Scott M. Rogers,<sup>a,b</sup> Peter P. Wells,<sup>f,g</sup> Richard A. Catlow<sup>a,b,e</sup> and Michael Bowker,<sup>*a*,e</sup>

The interaction between Pd and  $TiO_2$  for promoting photocatalytic activity was investigated by tailoring the size of Pd nanoparticles and monitoring the photocatalytic activity of methanol photo-reforming reaction for hydrogen gas production. We show that at 0.6 % wt. Pd loading, catalyst with highly dispersed nanoparticles obtained at 1 °C temperature exhibits superior photocatalytic activity for hydrogen gas production. At different weight of Pd loading, tailoring two sets of catalysts with different structural properties provide correlation between the changes of Pd local structures with the rate of hydrogen production. The impact of controlling the structural properties of metal nanoparticles in influencing H<sub>2</sub> production outweighs the effect of metal loading variation. The differences of Pd/TiO<sub>2</sub> activity at the variation of metal loading were correlated with the changes in Pd local structure consequently affecting electronic transfer and photocatalytic efficiency.

#### Introduction

Photocatalytic hydrogen production offers a green sustainable route for clean and renewable energy.<sup>1,2</sup> The performance of TiO<sub>2</sub> is greatly enhanced by the deposition of metal nanoparticles; Pt/TiO<sub>2</sub>, Au/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> catalysts have been widely investigated and are shown to promote hydrogen generation with UV light.<sup>3-8</sup> The enhanced activity is associated with the ability of the photo-induced electron in the conduction band of TiO<sub>2</sub> to be transferred to the metal cocatalysts.9,10 Such transfer occurs at the metal island and the periphery of the TiO<sub>2</sub> interface, which promotes electron-hole separation and consequently extends the lifetime of the energy carriers.<sup>11</sup> The work function differences between metal and TiO<sub>2</sub> semiconductor creates Schottky barrier that allow spontaneous injection of photo-generated electrons from the conduction band of TiO<sub>2</sub> into the metal. <sup>12</sup> The interfacial charge transfer between TiO<sub>2</sub> to metal is a single electron transfer process, although hydrogen generation from water and methanol photo-reforming reaction requires a multi-electron transfer reaction.<sup>13</sup> In order to improve the

the efficiency relies strongly on the interfacial atomic geometry of metal nanoparticles and TiO2.14 Understanding the geometric strain in metal/TiO<sub>2</sub> is important for designing active catalyst. Au nanoparticles deposited on TiO<sub>2</sub> within 3-30 nm size produced hydrogen gas from ethanol, but within 3-12 nm size, the effect on size variation was less significant.<sup>15</sup> We proposed in our previous studies that the catalytic activity is significantly correlated to the Pd loading, with high activity achieved at very low Pd.<sup>11</sup> Model studies by Bloh et.al found that the optimal metal to TiO<sub>2</sub> ratio ~ 2.4 doping atoms per nanometer of particle size was required for ideal catalytic improvement.<sup>16</sup> Exceeding this ratio causes the metal to act as a recombination centre. The decrease in activity at high loading is due to the shadowing effect of metal nanoparticles that reduced the light penetration onto TiO<sub>2</sub><sup>17</sup> The presence of excess metal nanoparticles on TiO<sub>2</sub> is also suggested to become electron and hole trapping sites.<sup>18,19</sup>

electronic transfer between metal-TiO<sub>2</sub> interface, we must note that

Pd is a precious noble metal with large work function to trap electron for efficient electron hole separations. We have previously investigated the activity of Pd/TiO<sub>2</sub> for photocatalytic reforming of alcohols with the mechanism of hydrogen production involved dehydrogenation of alcohol on Pd surface and water reduction occurs on the Pd-TiO<sub>2</sub> interface.<sup>20-23</sup> The efficiency of Pd to promote electron transfer from the conduction band of semiconductor is not only limited to TiO<sub>2</sub>, but studies on visible light driven photocatalytic performance for hydrogen production.<sup>24-26</sup> Alteration of Pd morphology into nanocube improved hydrogen production from Pd/2D-C<sub>3</sub>N<sub>4</sub> composites due to efficient separation of

 <sup>&</sup>lt;sup>a.</sup> The UK Catalysis Hub, Research Complex at Harwell, Harwell, Oxon, OX11 0FA, UK
 <sup>b.</sup> Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

<sup>&</sup>lt;sup>c</sup> Department of Chemistry, Centre for Foundation Defence Studies, National Defence University of Malaysia, 57000, Malaysia

<sup>&</sup>lt;sup>d.</sup>Centre of Advance Material and Energy Sciences, Universiti Brunei Darussalam, Jalan Tungku Link, BE 1410, Brunei

e. Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, CF10 AT, Cardiff, UK

 <sup>&</sup>lt;sup>f.</sup> University of Southampton, University Road, Southampton SO17 1BJ.UK
 <sup>g.</sup> Diamond Light Source Ltd. Harwell Science and Innovation Campus, Chilton,

Didcot OX11 ODE, UK

#### ARTICLE

photogenerated energy carriers.<sup>27</sup> Understanding the role of the metal nanoparticles in promoting catalytic activity of TiO<sub>2</sub> is often hampered by morphology alterations, particularly at high metal loading.<sup>15</sup> The aims of the work are to improve Pd/TiO<sub>2</sub> photocatalytic activity and to gain fundamental understanding of structural changes of Pd upon variation of metal loading. In these studies, tailored Pd metal nanoparticles were prepared using controlled kinetic growth of Pd colloids via synthesis temperature variations to obtain Pd nanoparticles of different, but controlled nanoparticles size. Systematic Pd/TiO<sub>2</sub> catalysts design manage to differentiate the promotional effect caused by the size of Pd nanoparticles and the amount of metal loading, allowing us to gain an understanding of the effect of the Pd-TiO<sub>2</sub> interaction on promoting hydrogen production from photo-reforming of methanol:

 $CH_{3}OH ~+~ H_{2}O ~+~ h\nu ~\rightarrow~ 3H_{2} ~+~ CO_{2}$ 

#### Results

Published on 25 June 2019. Downloaded on 6/26/2019 1:29:03 AM

To enhance the activity of Pd/TiO<sub>2</sub> catalysts, the particle size of Pd were tailored by controlling the synthesis temperature of Pd colloid at a fixed loading of 0.6 % wt. The EXAFS is a useful technique that allows study of nanoparticle and provides local structural information of palladium. The local coordination of the Pd was obtained by ex situ Pd K-edge EXAFS spectra of catalysts after drying at ambient temperature (Fig 1). Ex-situ Pd K-edge EXAFS spectra were recorded on 0.6 Pd wt% TiO<sub>2</sub> catalysts when the temperature of Pd synthesis were carried out at 1 °C, 25 °C, 50 °C and 75°C. The Pd K-edge XANES of 0.6 % Pd/TiO<sub>2</sub> prepared at 1°C shows the Pd environment of the samples corresponded to Pd metal with Pd-Pd distance of 2.78 Å.<sup>28</sup> The sample also illustrates the peak associated with the Pd-O first shell with the distance of 2.00 Å.<sup>29</sup> The absence of a second shell of Pd-(O)-Pd at 3.3 Å evidence that the Pd particles may exist as subnanometer Pd cluster.<sup>30</sup> As the synthesis temperature increased to 25 °C, the Pd-O first shell peak height with the distance of 1.99 Å decreased and accompanied by an increase of Pd-Pd peak with the radius distance of 2.74 Å, suggesting the growth of Pd<sup>o</sup> nanoparticles. The amplitude of Pd-O first shell decreased with the temperature which correlates well with the increasing intensity of Pd-Pd peak at 2.74 Å. This signifies the enlargement of Pd metal nanoparticles as the temperature of colloidal Pd solution were increased up to 75 °C.<sup>31</sup> The EXAFS fitting parameter in Table 1 also revealed the coordination number of Pd-Pd and Pd-O first shell. It is clear that the Pd-O first shell coordination number reduced from 2.8 for catalyst obtained at 1 °C to 0.7 as the temperature increased to 75 °C. In contrast, the Pd-Pd coordination numbers increased from 2.8 to 8.4. The variation of coordination number is associated with the structural and morphological changes which in this case is due to the enlargement of Pd nanoparticles as the temperature of colloidal Pd solution increased.<sup>32</sup> We can conclude that there are no large PdO crystallites and rather the PdO component originates from the surface oxide, due to there is an absence of the Pd-Pd scattering at 3.00 Å which would be present in such crystallites. For the catalyst obtained at 1 °C, the Pd-O and Pd-Pd coordination numbers of 2.8 signifies that the Pd nanoparticles for this sample are significantly smaller in comparison to the catalys Poblained Cat Poligher temperatures of synthesis.

XANES linear combination analysis (LCA) of the 1<sup>st</sup> derivatives, using PdO and Pd foil as reference standard, was performed to calculate the ratio between Pd<sup>2+</sup> and Pd<sup>0</sup> as summarised in Table 1. Small Pd nanoparticles form an oxidic surface layer at room temperature. Since smaller particles have a higher surface contribution to the XAFS compared with larger particles, the relative size of the Pd nanoparticles can be inferred from the ratio of Pd<sup>2+</sup>/Pd<sup>0</sup>. Analysis data given in Table 1 showed that the influence of synthesis temperature on the Pd<sup>2+</sup>/Pd<sup>0</sup> ratio is evident by a higher percentage of Pd<sup>2+</sup> for the catalyst prepared at 1°C (69% Pd<sup>2+</sup>), in comparison to that prepared at 75°C (22% Pd<sup>2+</sup>). The ratio of Pd<sup>2+</sup>/Pd<sup>0</sup> for catalyst synthesised at 1° C is 2.2, significantly higher than the rest of the catalyst. The calculated Pd<sup>2+</sup>/Pd<sup>0</sup> ratios for 0.6 % Pd/TiO<sub>2</sub> decreases with the increasing of synthesis temperatures.

The variation of the Pd nanoparticle size distribution from 0.6 wt % Pd/TiO<sub>2</sub> catalyst was further confirmed by the TEM analysis given in fig 2. The Pd size was measured based on the average diameter of 100 Pd particles observed from TEM images. Controlling the temperature at 1°C produced Pd nanoparticles with an average particle size of 2.3 nm. Increasing the synthesis temperature to 25 °C, shows relatively larger particles with average of 3.0 nm. The Pd nanoparticles size continue to grow with average diameter of 3.8 nm for 50 °C synthesis, and 5.2 nm for 75 °C. In general by increasing the synthesis temperature on 0.6 % Pd/TiO<sub>2</sub> catalysts, the Pd-O (at 2.00 Å) coordination increases meanwhile the Pd-Pd (~ 2.78 Å) coordination decreases, with decreasing average Pd particle size.



Fig 1: *K3* weighted Fourier transform (magnitude) EXAFS data for the 0.6 % wt. Pd/TiO<sub>2</sub> catalysts prepared at 1 °C, 25 °C, 50 °C and 75 °C.

The resulting 0.6 % Pd/TiO<sub>2</sub> catalysts were subsequently used in photocatalytic hydrogen generation from photoreforming of methanol. Fig 3 shows the plot of hydrogen gas production analysed for every 30 minutes during 3h reaction. 0.6 % Pd/TiO<sub>2</sub> catalyst obtained from colloidal sol that was prepared at 1 °C, produced ~676 µmol of H<sub>2</sub> in 3h of reaction. The value is significantly higher than the rest of the catalysts at similar weight loading.

Published on 25 June 2019. Downloaded on 6/26/2019 1:29:03 AM.

# ARTICLE

**Table 1.** EXAFS fitting parameters derived from the k2 weighted Fourier transform for the Pd K edge EXAFS data and the average Pd nanoparticle diameter evaluated from TEM analysis.

Catalysts	Pd size,	Abs Sc	Ν	R/Å	2 / A	E <sub>f</sub> /eV	R factor	Reference standards (%)			
	nm						_	Pd <sup>2+</sup>	Pd <sup>0</sup>	Rfactor	Pd <sup>2</sup> / Pd <sup>0</sup>
0.6 %Pd/TiO <sub>2</sub>	2.3±0.6	Pd-Pd	2.8(3)	2.78(1)	0.008	4(1)	0.02	69	31	0.063	2.22
1 °C		Pd-O	2.8(2)	2.00(1)	0.003						
0.6 %Pd/TiO <sub>2</sub>	3.0±0.4	Pd-Pd	5.4(3)	2.738(7)	0.008	7(1)	0.02	46	54	0.025	0.85
25 °C		Pd-O	1.8(2)	1.99(1)	0.003						
0.6 %Pd/TiO <sub>2</sub>	3.8±0.3	Pd-Pd	7.2(2)	2.743(3)	0.008	8(0)	0.003	30	70	0.038	0.43
50 °C		Pd-O	1.1(1)	1.98(1)	0.003						
0.6 %Pd/TiO <sub>2</sub>	5.2±0.8	Pd-Pd	8.4(2)	2.750(3)	0.008	8(0)	0.003	22	78	0.026	0.28
75 °C		Pd-O	0.7(1)	1.98(1)	0.003						
1%Pd/TiO <sub>2</sub>	2.6±0.4	Pd-Pd	4.2(4)	2.75(1)	0.008	5(1)	0.019	57	43	0.099	1.32
1 °C		Pd-O	1.7(4)	2.00(0)	0.006						
1%Pd/TiO <sub>2</sub>	3.3±0.7	Pd-Pd	7.7(3)	2.744(4)	0.008	5(1)	0.007	33	67	0.048	0.49
50 °C		Pd-O	1.1(2)	1.99(1)	0.006						
2%Pd/TiO <sub>2</sub>	3.5±0.8	Pd-Pd	6.6(3)	2.739(5)	0.008	5(1)	0.009	35	65	0.198	0.53
1 °C		Pd-O	1.7(2)	2.00(1)	0.006						
4%Pd/TiO <sub>2</sub>	3.8±0.8	Pd-Pd	8.3(4)	2.735(5)	0.008	6(1)	0.013	33	67	0.494	0.49
<u> </u>		Pd-O	0.5(3)	1.97(5)	0.006						

As the temperature of the colloidal sol increases, the 0.6 % Pd/TiO<sub>2</sub> catalysts showed that the hydrogen generation is significantly affected with the total hydrogen volume reduced to give ~ 434 µmol for catalyst produced at 25 °C, 230 µmol for 50 °C and only 186 µmol when the synthesis temperature was raised to 75 °C. The increased activity of 0.6% Pd/TiO<sub>2</sub> catalysts produced at 1 °C was compared with our previous finding in which the rate of hydrogen production showed twofold enhancement in comparison with Pd/TiO<sub>2</sub> produced via impregnation method.<sup>10,20</sup>



Fig 2: TEM images and Pd size distribution histograms of 0.6 % wt. Pd TiO<sub>2</sub> synthesised at; a. 1 °C condition, b. 25 °C condition, c. 50 °C condition and d. 75 °C condition.

As the impact of controlling the size of metal nanoparticles on increasing  $H_2$  productivity is dramatic, we therefore increased the Pd metal loading to study its effect on photocatalytic performance. The Pd loadings were varied at 0.6 % wt, 1 % wt, 2 % wt and 4 % wt. Two

sets of catalysts were prepared at different weight loading, with first set of catalysts were produced at 1 °C to ensure narrow Pd nanoparticles distribution were achieved. The second set of catalysts were prepared by varying the synthesis temperature in order to obtain Pd nanoparticles with similar particle sizes. TEM analysis data in table 1 showed the particle size of Pd on TiO<sub>2</sub> in the first set of catalysts were increased with the amount of metal loading, despite the undertaking of the synthesis at 1°C. Fig **4** shows the TEM images of 1%, 2% and 4% Pd/TiO<sub>2</sub> and particle size distribution histogram produced from sol immobilisation method carried out at 1 °C. Pd at 1% loading shows Pd diameter of 2.6 nm meanwhile at 2% loading the average diameter was measured at 3.5 nm. As the Pd loading increases, so the size increases to 3.8 nm for 4% loading.



Fig 3. Photocatalytic hydrogen production from methanol on 0.6% wt.  $Pd/TiO_2$  prepared at different synthesis temperature

#### ARTICLE

Published on 25 June 2019. Downloaded on 6/26/2019 1:29:03 AM

Table 1 also summarised XAFS analysis data of the Pd/TiO<sub>2</sub> catalysts at different weight loading. The value of Pd-Pd coordination numbers increased with the amount of Pd loading implying larger Pd particles were produced at higher Pd loading. Similar occurrences on the Pd<sup>2+</sup>/Pd<sup>0</sup> ratios derived from XANES analysis that revealed the ratio decreases with the amount of Pd loading, from 1.32 in 1% Pd, to 0.53 in 2% Pd and 0.49 in 4% Pd loading. In general, for the first set of catalysts obtained at 1 °C while the amount of Pd loading were varied at 0.6 % – 4 % wt loading, produced the catalysts with average Pd nanoparticles size between 2 - 4 nm, with the Pd<sup>2+</sup>/Pd<sup>0</sup> ratios in the range of 2.2 - 0.49. The catalysts were subsequently used for photocatalytic hydrogen production from photoreforming of methanol. The plot of hydrogen production against reaction time when using the first set of catalysts were shown in fig 5a. The catalysts showed high volume of hydrogen within 3h of reaction at low Pd loading, with ~ 636  $\mu$ mol of hydrogen for 0.6 % of Pd loading. The volume were significantly reduced to 512 µmol for 1 % Pd/TiO<sub>2</sub>. As the Pd loading were increased, the photocatalytic activity of the catalysts were significantly reduced with only ~181  $\mu$ mol of hydrogen was produced at 4 % Pd loading.



Fig 4. TEM images and Pd size distribution histograms of a. 1% Pd/TiO<sub>2</sub> synthesis at 1 °C, b. 1% Pd/TiO<sub>2</sub> synthesis at 50 °C, c. 2% Pd/TiO<sub>2</sub> prepared at 1°C and d. 4% Pd/TiO<sub>2</sub> prepared at 1°C



Fig 5a. Photocatalytic hydrogen production from methanol on  $Pd/TiO_2$  prepared at 1 °C at different weight loading with average diameter of between 2 - 4 nm; b. Photocatalytic hydrogen production from methanol on  $Pd/TiO_2$  prepared at different weight loading with average diameter of 3.5 nm.

The decrease of  $TiO_2$  activity at high metal loading if often related to the shadowing effect of metal that reduce  $TiO_2$  photosensitivity.<sup>17</sup> To gain further understanding of the factor influencing catalytic activity at high metal loading, second set of catalysts were used for

#### **Journal Name**

evaluation on photocatalytic performance. The catalysts obtained by varying the synthesis temperature for 0.6 % Wel 1% WE 2% WP and 4% wt of Pd in order to produce catalysts with approximately similar Pd nanoparticles intrinsic structural properties. For 0.6 % Pd/TiO<sub>2</sub> and 1% Pd/TiO<sub>2</sub> catalysts, the synthesis temperature was set at 50 °C, meanwhile for 2 % and 4% Pd/TiO<sub>2</sub> catalysts, the temperatures were set at 1°C to give Pd diameter ~ 3.5 nm. The list of particle sizes of Pd nanoparticles analysed using TEM and the local structure of Pd from XAFS analysis are summarised in Table 1. Apart from similar Pd diameter within 3.3 nm - 3.8 nm, the catalysts also consisted of palladium nanoparticles with approximately similar Pd<sup>2+</sup>/Pd<sup>0</sup> ratios ~ 0.43-0.53 (Table 1). Photocatalytic performance of the catalysts for hydrogen gas production were illustrated in Fig 5b. The catalysts produced similar rates of hydrogen production with the volume of hydrogen production are ~ 180 to 230  $\mu$ mol in 3h of reaction. In comparison to the first set of catalysts that were produced at 1 °C, controlling the size of Pd nanoparticles to be around 3.5 nm appears to reduce the differences in catalytic performance of Pd/TiO<sub>2</sub> catalysts despite different weight of metal loading deposited on TiO<sub>2</sub>.

#### Discussion

We tailored the size of Pd nanoparticles deposited on TiO<sub>2</sub> by controlling the kinetic growth of Pd in the sol solutions. The correlation between the catalytic performance, the size and the local structure of Pd for 0.6% Pd obtained at different temperature were shown in Fig. 6. The catalyst obtained from colloids prepared at 1 °C with the average Pd diameter of 2.3 nm shows superior activity for hydrogen production. The photocatalytic performance is appreciably reduced with increasing the size of Pd particles. Fig 6 also shows a clear relationship between the extent of Pd<sup>2+</sup> and the Pd particle diameter by TEM. The presence of Pd<sup>2+</sup> from an oxidic surface layer of Pd is associated with the surface contribution of Pd to form interfacial interaction with TiO<sub>2</sub> It is important for Pd to be in Pd<sup>0</sup> oxidation states in order to catalyse hydrogen production steps.<sup>8</sup> PdO on the TiO<sub>2</sub> is reduced to Pd<sup>0</sup> in the presence of methanol under UV irradiation prior to sustainable hydrogen production from methanol.<sup>10</sup> The susceptibility of Pd<sup>2+</sup> to accept electron increased the efficiency of photogenerated electron trapping that occurs at the Pd-TiO<sub>2</sub> interface. Small Pd nanoparticles on TiO<sub>2</sub> enhanced the interfacial interaction between TiO<sub>2</sub> and palladium, subsequently promote efficient electronic transfer between the conduction bands of TiO<sub>2</sub> to the Pd metal. Clearly, at similar metal loading, the catalytic activity in promoting hydrogen generation is significantly influenced by the particle size of Pd, which we relate to the surface  $Pd-TiO_2$ interaction. Since all the catalysts were pre-treated under similar conditions i.e. drying at room temperature prior to the reaction, the strong metal support interaction that often occurs via high temperature annealing is not applicable in this case. However, generating small Pd nanoparticles produced a higher degree of interfacial interaction between TiO<sub>2</sub> and palladium. The increase in the oxide-metal interface area promotes the Schottky effect for electron excitation and subsequently enhances the electronic transfer between the conduction bands of TiO<sub>2</sub> and the Pd.

Published on 25 June 2019. Downloaded on 6/26/2019 1:29:03 AM

#### Journal Name

Understanding the fundamental aspect of the effect of particle size and metal weight loading is a challenging task due to the agglomeration of nanoparticles at high metal loading. Controlling the particle size of Pd while increasing the weight of metal deposited on TiO<sub>2</sub> allows understanding on the geometric influence of Pd nanoparticles on photocatalytic performance. Fig 7a shows the hydrogen production rate dependence on Pd loading and the normalised H<sub>2</sub> rate over Pd loading for the first set of catalysts with average Pd size of 2-4 nm. The rate of hydrogen evolution is significantly reduced as the Pd loading increased to 4%. When the activity is normalised to the amount of Pd loading, the differences in catalytic activity are even more significant. Varying the amount of metal loading is often associated with agglomeration of nanoparticles particularly at high metal loading, thus altering the local structure of the metal. This proved the reduction of Pd/TiO<sub>2</sub> activity at high metal loading is due to the differences of Pd local structure that affected the efficiency of electronic transfer between Pd-TiO<sub>2</sub> interfaces.



Fig 6. Comparison of the catalysts performance on the hydrogen production plotted against the size of tailored 0.6 % Pd made by temperature controlled colloidal synthesis. Percentage of Pd oxidation states derived from normalized XANES spectra were also plotted against the particle size of Pd derived using TEM analysis.

On the other hand, the second set of Pd/TiO<sub>2</sub> catalysts prepared by varying the synthesis temperature showed a near invariant rate of hydrogen evolution of ~ 80 µl/h regardless of the amount of Pd loading. When the rate of hydrogen production is normalised to the amount of Pd content, there is only a slight decrease in the hydrogen production rate at higher Pd loading (fig 7b). A linear relationship was observed between the rate of hydrogen and the amount of Pd loading implying similar Pd local structure of the catalysts. We can deduce that the catalytic activity is affected by Pd structural properties, and varies little with the amount loading. The results showed that the impact of controlling the amount of surface

palladium interacting with  $TiO_2$  in increasing  $H_{2/ieW}$  Article Unity outweighs the effect of metal weight loading OI: 10.1039/C9CP00826H

250 400 350 200 300 -4-150 150 250 200 H<sub>2</sub> rate/ 150 100 = 50 50 \$ п Π ..... 0.5 1.0 2.0 4.0 Pd loading, wt % 100 <mark>- b.</mark> 500 5 80 400 👼 H<sub>2</sub> rate/ µmol.h<sup>-1</sup> 60 300 ₹ 200 40 100 2 20 0 0 0.5 1.0 2.0 4.0 Pd loading, wt %

Fig 7. Photocatalytic hydrogen generation on  $Pd/TiO_2$  at various Pd loadings. a) Plot of hydrogen generation rate; ---- and normalised hydrogen rate ---- against Pd weight loading on the catalyst with a variation of Pd diameter in the range of 2 - 4 nm. b) Plot of hydrogen generation rate; --- and normalised hydrogen rate --- against Pd weight loading on the catalyst with controlled Pd diameter of 3.5 nm.

# Experimental Catalysts preparation

To synthesis the Pd colloidal sol, PVA was used as stabiliser ligand with NaBH<sub>4</sub> as reducing agent. The size of Pd nanoparticles were controlled by controlling the temperature of Pd nucleation, in which the kinetic growth was altered by variation of the temperature from 1 – 75 °C. This method was previously reported on Au that is reliable for synthesis of small Au nanoparticles.<sup>33</sup> An aqueous solution of K<sub>2</sub>PdCl<sub>4</sub> (Alfa Aesar, 99.9 % metal basis) of the desired concentration was prepared. Polyvinylalcohol (PVA) (1wt% solution, Aldrich, Mw = 10000, 80% hydrolysed) was added (PVA/Pd = 0.65 weight ratio). A 0.1 M freshly prepared solution of NaBH<sub>4</sub> (>96% Aldrich, NaBH<sub>4</sub>/Pd=5 molar ratio) was then added to form a dark-brown sol. After 30 min of sol generation, the colloid was immobilised by adding TiO<sub>2</sub> (acidified at pH 1 by sulphuric acid) under vigorous stirring conditions. After 2h the slurry was filtered and washed with deionised water before drying in air at ambient temperature for 16 hours. Palladium loading was varied at 0.6 wt%, 1 wt% and 2 wt% and 4 wt % on TiO<sub>2</sub> P25 support. Detail experimental procedures and characterisation data are available in supplementary documents.

This journal is C The Royal Society of Chemistry 20xx

### Journal Name

#### ARTICLE

#### Photocatalytic measurement

Photocatalytic activity was determined in gas phase photoreforming of methanol under UV region (280-380 nm). 50 mg of catalyst was mixed with water to form a paste and was dispersed on a glass slide with the irradiated area of the film is ~ 7.5 cm<sup>2</sup>. The catalyst was left to dry at ambient condition. The glass slide was then placed on the three neck flask containing 15 ml of water and 100  $\mu$ l of methanol. The system was purged with Ar for 30 minutes and sealed with rubber stopper. The catalyst was irradiated using Oriel Xe lamp with 150 watt from the side of the flask. Gas sample was analysed at every 30 mins for 3 hours using Perkin Elmer Clarus GC with TCD detector.

# Conclusions

Published on 25 June 2019. Downloaded on 6/26/2019 1:29:03 AM

Temperature controlled immobilisation of Pd on TiO<sub>2</sub> is a reliable method to produce tailored Pd nanoparticles with control size and local structures. In correlation with the TEM and XAFS analysis, it is clear that reducing the size of Pd nanoparticles while maintaining the amount of metal weight loading is significantly enhanced the photocatalytic activity of  $Pd/TiO_2$  for hydrogen gas production. Tailoring two sets of catalysts when increasing the Pd loading allow understanding on the geometrical effect of metal nanoparticles in enhancing photocatalytic performance of TiO<sub>2</sub> in UV region. The first set of catalysts revealed that increasing the Pd weight loading also affects the Pd intrinsic structure which consequently produced large Pd particles and reduced the efficiency of electronic transfer between Pd and  $TiO_2$  interface. However, in the second set of catalysts in which the particle diameter and structural properties of Pd were tailored to be approximately similar, showed negligible differences in the rate of hydrogen generation. The presence of surface  $Pd^{2+}$  to accept electron from the conduction band of TiO<sub>2</sub> increased the efficiency of photogenerated electron trapping that occurs at the Pd-TiO<sub>2</sub> interface. This shows the dominant effect of Pd size and local structure in influencing photocatalytic activity of Pd/TiO<sub>2</sub> catalyst for hydrogen production from photoreforming of methanol

# **Conflicts of interest**

There are no conflicts to declare.

# Acknowledgements

The authors would like to acknowledge UK Catalysis Hub and EPSRC for research funding to H. Bahruji through grant EP/ I038748/1. The Ministry of Education, Malaysia (MOE) is thanks for financial support for a Post-doctoral award to N. Abdullah

# Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter

under discussion, limited experimental and spectral data, and crystallographic data. DOI: 10.1039/C9CP00826H

§§ etc.

1

2

3.

4

5

6

8

- C. Acar, I. Dincer, G. F. Naterer, International Journal of Energy Research **2016**, 40, 1449-1473
- A. A. Ismail, D. W. Bahnemann, Solar Energy Materials and Solar Cells **2014**, 128, 85-101
- A. L. Luna, D. Dragoe, K. Wang, P. Beaunier, E. Kowalska, B. Ohtani, D. Bahena Uribe, M. A. Valenzuela, H. Remita, C. Colbeau-Justin, *The Journal of Physical Chemistry C* **2017**, *121*, 14302-14311
- Z. H. N. Al-Azri, W.-T. Chen, A. Chan, V. Jovic, T. Ina, H. Idriss, G. I. N. Waterhouse, *Journal of Catalysis* **2015**, *329*, 355-367
- J.-J. Zou, H. He, L. Cui, H.-Y. Du, International Journal of Hydrogen Energy **2007**, 32, 1762-1770
- G. M. Haselmann, D. Eder, ACS Catalysis 2017, 7, 4668-4675
- J. B. Priebe, J. Radnik, A. J. J. Lennox, M.-M. Pohl, M. Karnahl, D. Hollmann, K. Grabow, U. Bentrup, H. Junge, M. Beller, A. Brückner, *ACS Catalysis* **2015**, *5*, 2137-2148
- H. Bahruji, M. Bowker, P. Davies, D. A. Morgan, C. A. Morton, T. Egerton, J. Kennedy, W. Jones, *Topic in Catalysis* **2014**, 2-3, 70-76.
- M. Ni, M. K. H. Leung, D. Y. C. Leung, K. Sumathy, Renewable and Sustainable Energy Reviews **2007**, 11, 401-425
- 10 H. Bahruji, M. Bowker, P. R. Davies, J. Kennedy, D. J. Morgan, *International Journal of Hydrogen Energy* **2015**, 40, 1465-1471.
- 11 A. Dickinson, D. James, N. Perkins, T. Cassidy, M. Bowker, Journal of Molecular Catalysis A: Chemical **1999**, 146, 211-221
- M. R. Khan, T. W. Chuan, A. Yousuf, M. N. K. Chowdhury, C. K. Cheng, *Catalysis Science & Technology* 2015, 5, 2522-2531
- 13 H. Park, H.-i. Kim, G.-h. Moon, W. Choi, *Energy & Environmental Science* **2016**, 9, 411-433.
- 14 H. Chen, P. Li, N. Umezawa, H. Abe, J. Ye, K. Shiraishi, A. Ohta, S. Miyazaki, *The Journal of Physical Chemistry C* **2016**, *120*, 5549-5556
- 15 M. Murdoch, G. I. N. Waterhouse, M. A. Nadeem, J. B. Metson, M. A. Keane, R. F. Howe, J. Llorca, H. Idriss, *Nat Chem* **2011**, *3*, 489-492.
- 16 J. Z. Bloh, R. Dillert, D. W. Bahnemann, *The Journal of Physical Chemistry C* **2012**, *116*, 25558-25562
- 17 J. B. Zhong *et al.*, *Journal of Hazardous Materials* **2009**, 168, 1632-1635
- 18 O. Ola, M. M. Maroto-Valer, Applied Catalysis A: General
  2015, 502, 114-121
- K. Bhattacharyya, S. Varma, A. K. Tripathi, S. R. Bharadwaj,
  A. K. Tyagi, *Journal of Physical Chemistry C* 2008, 112, 19102-19112
- 20 J. Kennedy, H. Bahruji, M. Bowker, P. R. Davies, E. Bouleghlimat, and S. Issarapanacheewin, Journal of Photochemistry and Photobiology A: Chemistry 2018, 356, 451-456.
- 21 H. Bahruji, M. Bowker, P. R. Davies, F. Pedrono, *Applied Catalysis B: Environmental* **2011**, 107, 205-209.
- 22 H. Bahruji, M. Bowker, P. R. Davies, L. S. Al-Mazroai, A. Dickinson, J. Greaves, D. James, L. Millard, F. Pedrono,

Physical Chemistry Chemical Physics Accepted Manuscript

View Article Online DOI: 10.1039/C9CP00826H

Journal of Photochemistry and Photobiology A: Chemistry 2010,216, 115-118.

- 23 H. Bahruji, M. Bowker, P. R. Davies, Journal of Chemical Sciences 2019, 131, 33.
- 24 Wang, S.; Chen, D.; Niu, F.; Zhang, N.; Qin, L.; Huang, Y., Applied Physics A 2016, 122, 867.
- 25 Wang, S.; Chen, D.; Niu, F.; Zhang, N.; Qin, L.; Huang, Y., RSC Advances 2016, 6, 34574-34587.
- 26 Li, Z.; Zhang, F.; Han, J.; Zhu, J.; Li, M.; Zhang, B.; Fan, W.; Lu, J.; Li, C., Catalysis Letters 2018, 148, 933-939.
- 27 Mo, Z.; Xu, H.; She, X.; Song, Y.; Yan, P.; Yi, J.; Zhu, X.; Lei, Y.; Yuan, S.; Li, H., Applied Surface Science 2019, 467-468, 151-157.
- 28 E. K. Dann, E. K. Gibson, R. A. Catlow, P. Collier, T. E. Eralp, D. Gianolio, et al. Molecular Precursors. Chemistry of Materials 2017, 29(17), 177515-7523
- 29 K. Okumura, R. Yoshimoto, T. Uruga, H. Tanida, K. Kato, S. Yokota, et al. The Journal of Physical Chemistry B. 2004, 108, 6250-6255
- 30 E. J. Peterson, A. T. DeLaRiva, S. Lin, R. S. Johnson, H. Guo, J. T. Miller, J. Hun Kwak, C. H. F. Peden, B. Kiefer, L. F. Allard, F. H. Ribeiro, A. K. Datye, Nature Communications 2014, 5, 4885
- 31 A. M. Beale, B. M. Weckhuysen, Physical Chemistry Chemical Physics 2010, 12(21), 5562-74.
- 32 M. A. Newton, C. Belver-Coldeira, A. Martinez-Arias, M. Fernandez-Garcia, Nat Mater 200, 6, 528-532.
- 33 S. M. Rogers, C. R. A. Catlow, C. E. Chan-Thaw, D. Gianolio, E. K. Gibson, A. L. Gould, N. Jian, A. J. Logsdail, R. E. Palmer, L. Prati, N. Dimitratos, A. Villa, P. P. Wells, ACS Catalysis 2015, 5, 4377-4384.

View Article Online DOI: 10.1039/C9CP00826H

Published on 25 June 2019. Downloaded on 6/26/2019 1:29:03 AM.