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## PAPER

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Hydrogen generation from toxic formaldehyde catalyzed by low-cost Pd–Sn alloys driven by visible light<sup>+</sup>

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Noble metal co-catalysts are efficient for photocatalytic hydrogen generation from formaldehyde, but their high cost and low abundance limit their scale-up applications. Alloying a second metal with noble metals offers an available way to decrease their usage and consumption and enhances their catalytic activity. Among the potential candidates, Sn is a high abundance element in the earth. In this work, a new highly active low-cost Pd–Sn/RGO catalyst has been developed. Under optimized conditions, the hydrogen evolution rate reached up to 530.07  $\mu$ mol h<sup>-1</sup> driven by visible light. By taking advantage of the optimized adsorption nature of the active sites on the alloy cocatalyst, effective separation and transfer of photogenerated charges have been achieved; at the same time, the photo-generated electrons have a longer lifetime. More interestingly, it has been found that trace amounts of oxygen are helpful in catalytic hydrogen production from HCHO.

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## 1. Introduction

Formaldehyde (HCHO) is one of the main by-products in many bio-mass gasification processes and chemical reactions, and is also regarded as an environmental contaminant that causes severe pollution to both the atmosphere and water resources.1-3 Long-term exposure to air containing even a few ppm formaldehyde may lead to many health problems.<sup>4,5</sup> Many methods have been carried out to reduce the harm of formaldehyde, such as by physical adsorption,<sup>6</sup> plasma treatment<sup>7</sup> and catalytic oxidation.8-12 Comparatively, catalytic conversion of formaldehyde to clean energy, such as H<sub>2</sub>, will be an attractive and benign route since it can remove toxic formaldehyde while producing clean energy carrier - hydrogen simultaneously.13-17 Although thermocatalytic methods are effective for conversion of formaldehyde to hydrogen,<sup>15–17</sup> photocatalytic formaldehyde conversion has many advantages,18 for instance the mild operating conditions and the probability to scale-up because the formed hydrogen can be separated from the liquid reaction system easily.19

The noble metals Pt and Pd are very active catalysts in catalytic hydrogen generation from HCHO, but their high-cost

and low-abundance limit their scale-up applications.<sup>20,21</sup> Alloying a second metal with platinum group metals offers an available way to decrease usage and consumption of noble metals and enhances their catalytic activity.<sup>22–26</sup> Among the potential alloying metals, Sn is a high abundance element in the earth. Alloying Sn with Pt can give even higher catalytic activity in some catalytic reactions.<sup>20,27,28</sup> Meanwhile, alloying Sn and Pt or Pd can tune the nature of hydrogen activation sites over the catalyst, on which hydrogen generation takes place.

Herein, we report a new active catalyst, the Pd–Sn alloy catalyst, for catalytic hydrogen evolution from a HCHO–H<sub>2</sub>O mixture driven by visible light at room temperature. The Pd–Sn alloy catalyst exhibited 2 times higher activity for the HER than the Pd catalyst under the same reaction conditions. The activity of alloy Pd–Sn can be enhanced further by loading the Pd–Sn alloy on RGO. A significantly prolonged lifetime of photogenerated electrons and better charge separation efficiency have been achieved. Based on the analysis of HCHO, H<sub>2</sub>O and O<sub>2</sub> adsorption energies, we found that trace amounts of oxygen adsorbed on the Pd–Sn alloy might affect hydrogen adsorption and activation on the Pd–Sn alloy, and as a result, hydrogen and oxygen reverse recombination (HOR,  $2H_2 + O_2 \rightarrow 2H_2O$ )<sup>29,30</sup> could be inhibited and the forward hydrogen generation reaction could be enhanced.

## 2. Experimental

#### 2.1. Preparation method of graphene oxide (GO)

GO was prepared by using a modified Hummers' method<sup>31</sup> and reduced graphene oxide (RGO) dispersions were achieved by reducing graphene oxide using NaBH<sub>4</sub>.<sup>32</sup>

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#### 2.2. Method to prepare the Pd-Sn alloy catalysts

Pd–Sn alloy catalysts were reduced by NaBH<sub>4</sub> using the solution chemistry method.<sup>33</sup> The detailed experimental scheme is as follows: under ultrasonic treatment, an appropriate amount of RGO was dispersed in 50 mL of water. Then, under continuous stirring, a certain amount of trisodium citrate solution was added to the RGO dispersion. A K<sub>2</sub>PdCl<sub>4</sub> and SnCl<sub>4</sub>·2H<sub>2</sub>O (in 0.4 M HCl) solution with different ratios was added into the mixture. Then, the pH of the reaction was adjusted to 9–10. Next, the NaBH<sub>4</sub> solution (0.01 M) prepared freshly was transferred to the dispersion, and Pd–Sn/RGO samples with different Pd–Sn ratios were prepared.

## 3. Results and discussion

#### 3.1. DFT results

As shown in Fig. 1, DFT was used to calculate the adsorption energy of the  $H_2O$  molecule on the Pd–Sn alloy catalyst<sup>34–36</sup> and the calculation models are shown in Fig. S1 and S2 (in the ESI†). On some metal surfaces (shown in Fig. 2), formaldehyde may



Fig. 1 The calculation configuration of the  $Pd_3Sn_1$ ,  $Pd_1Sn_1$ ,  $Pd_1Sn_3$  and Pd catalyst surface.



Fig. 2 Configurations of formaldehyde on different metals.

 $\label{eq:table1} \begin{array}{l} \mbox{Table 1} & \mbox{The formal dehyde and water adsorption energies on different catalysts} \end{array}$ 

$E_{\rm ads}$ HCHO	$E_{\rm ads}$ H <sub>2</sub> O
(0)	(0 )
-0.70	-0.10
-0.72	-0.19
-0.68	-0.23
-0.57	-0.27
	$E_{ads} HCHO (eV)$ $-0.70 -0.72 -0.68 -0.57$

adsorb in an  $\eta^1$ -configuration,<sup>37</sup> and on other metals formaldehyde is adsorbed in an  $\eta^2$ -configuration.<sup>38,39</sup> Both of the two possible configurations were considered and the corresponding data were calculated. As shown in Table 1, the adsorption energy of formaldehyde on the Pd sample surfaces is -0.70 eV, -0.72 eV on the Pd<sub>3</sub>Sn<sub>1</sub> alloy catalyst surface, -0.68 eV on the Pd<sub>1</sub>Sn<sub>1</sub> alloy catalyst surface and -0.57 eV on the Pd<sub>1</sub>Sn<sub>3</sub> sample surface. Table 1 shows that the H<sub>2</sub>O adsorption energy on the Pd catalyst is -0.10 eV, while it is -0.18 eV on the Pd<sub>3</sub>Sn<sub>1</sub> alloy catalyst surface, -0.23 eV on the Pd<sub>1</sub>Sn<sub>1</sub> alloy catalyst surface and -0.27 eV on the Pd<sub>1</sub>Sn<sub>3</sub> alloy catalyst surface. Therefore, by adjusting the Pd-Sn ratio in alloy catalysts, the hydrogen production activity is probably modulated. According to the DFT analysis, we synthesized the Pd catalyst, Pd<sub>3</sub>Sn<sub>1</sub> catalyst, Pd<sub>1</sub>Sn<sub>1</sub> catalyst and Pd<sub>1</sub>Sn<sub>3</sub> catalyst via alloying Pd with Sn to verify the above speculations.

#### 3.2. XRD results

The XRD patterns of the synthesized Pd/RGO,  $Pd_3Sn_1/RGO$ ,  $Pd_1Sn_1/RGO$  and  $Pd_1Sn_3/RGO$  alloy catalysts are shown in

Fig. 3a and b. The peaks in the Pd/RGO samples could be attributed to metallic Pd (111), (200), (220), and (311) (JCPDS no. 050681).<sup>40</sup> With decreased Pd/Sn, the Pd–Sn/RGO alloy catalysts exhibit a stepwise slight shift and broadening. This is because Sn with a large atomic radius is inserted into the Pd lattice, and the diffraction peak moves to a low angle; the lattice expansion can also indicate that a Pd–Sn alloy is formed in the system.<sup>33,41,42</sup> The Pd–Sn/RGO catalyst has an alloy phase composition consistent with the initial feed ratio, so the bimetallic alloy phases Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO were formed through accurate wet chemical processes.

#### 3.3. XPS results

Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO catalysts were investigated using the XPS technology. As shown in Fig. 4a, the C 1s spectra of RGO indicate that there are oxygen-containing functional groups on the surface of RGO. The peak located near 284.9 eV represents the C=C bond, while peaks at 287.2 eV can be assigned to the C=O bond, peaks near 285.8 eV to C-C/C-H, and peaks near 288.1 eV to O-C=O species.<sup>43</sup> In Fig. 4b, peaks of O 1s spectra can be assigned to the oxygen-containing functional groups.<sup>44,45</sup>

As shown in Fig. 4c, the peaks at 335.9 and 341.20 eV were ascribed to Pd  $3d_{3/2}$  and Pd  $3d_{5/2}$  in the metallic state.<sup>46</sup> In different Pd–Sn alloy catalysts, the XPS results indicated that the binding energy of Pd 3d shifted compared with that of metallic Pd, which was due to the synergistic effect of the Pd–Sn alloy.<sup>47</sup> The two peaks at 337.1 and 342.7 fitted well with those of PdO  $3d_{3/2}$  and  $3d_{5/2}$ ,<sup>48</sup> respectively. The binding energies of Sn were



Fig. 3 (a) XRD patterns of Pd-Sn/RGO samples prepared with different Pd/Sn ratios. (b) The (111) patterns of the Pd-Sn/RGO samples.



Fig. 4 XPS results of Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO samples. C 1s of Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO samples (a); O 1s of Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO samples (b); Pd 3d of Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO samples (c); and Sn 3d of the Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO samples (d).

also examined. As shown in Fig. 4d, the two peaks at 485.6 and 494.1 were ascribed to Sn  $3d_{5/2}$  and Sn  $3d_{3/2}$  of metallic Sn, and the binding energies of Sn  $3d_{5/2}$  (487.2 eV) and Sn  $3d_{3/2}$  (495.6 eV) indicated that some Sn was in the +4 of SnO<sub>2</sub>. The presence of PdO and SnO<sub>2</sub> is due to the oxidation of the trace amount of metallic Pd and Sn during heat treatment.<sup>33</sup>

#### 3.4. Morphological analysis

In Fig. 5, the transmission electron microscopy images in Fig. 5a, c and e, show that the  $Pd_3Sn_1$ ,  $Pd_1Sn_3$ , and Pd nanoparticles were adhered on the surface of graphene. In the Pd–Sn/RGO catalyst's HRTEM images, the *d*-spacing of 0.230 nm corresponds to the (111)  $Pd_1Sn_3$  alloy catalyst, and the *d*-spacing of 0.227 and 0.225 nm could be attributed to the (111)  $Pd_3Sn_1$  alloy catalyst and Pd catalyst. Consistent with the XRD patterns, this experimental result proves that the lattice strain effect occurs during the formation of the alloy catalysts. The TEM image and HRTEM image of the  $Pd_1Sn_1$  alloy was dispersed on the

RGO sheet (see Fig. 6a), in which the HRTEM image *d*-spacing of 0.235 nm (see Fig. 6b) is the (111)  $Pd_1Sn_1$  alloy catalyst. The EDX spectrum (see Fig. 6d) implies the presence of C and O elements and not Pd and Sn elements on the  $Pd_1Sn_1/RGO$  catalyst. The HAADF-STEM (see Fig. 6e) image shows that Pd and Sn are uniformly dispersed.

#### 3.5. Catalytic activity performance

From Fig. 7a, it can be seen that as the amount of Pd increased, the photocatalytic activity increased first and then decreased. Among all the catalysts, the  $Pd_1Sn_1/RGO$  sample is the best catalyst, whose photocatalytic activity is nearly 32 times that of the Pt/TiO<sub>2</sub> photocatalyst.<sup>49,50</sup> Further increasing the amount of Pd will reduce the hydrogen production activity, indicating that the catalytic activity can be optimized.

Fig. 7b shows the effect of different formaldehyde concentrations on the hydrogen evolution rate driven by visible light. The activity of hydrogen production is closely related to the concentration of formaldehyde. If the formaldehyde



Fig. 5 The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of Pd/RGO,  $Pd_3Sn_1/RGO$ , and  $Pd_1Sn_3/RGO$  samples, (a and b)  $Pd_1Sn_3/RGO$ ; (c and d)  $Pd_3Sn_1/RGO$ ; and (e and f) Pd/RGO.

concentration is too high or too low, the hydrogen evolution rate would reduce and the optimal concentration of HCHO was  $1.0 \text{ mol } \text{L}^{-1}$ .

The pH of the reaction system has a significant influence on the activity of the catalyst and basic conditions are very necessary for hydrogen evolution from formaldehyde. So we investigated the different sodium hydroxide concentration effects on the Pd<sub>1</sub>Sn<sub>1</sub>/RGO catalyst for the hydrogen generation rate. As shown in Fig. 7c, when the concentration of sodium hydroxide was 1.0 mol  $L^{-1}$ , the hydrogen evolution rate was the highest. This is because the protonation of formaldehyde molecules leads to a decrease in the free formaldehyde molecule concentrations in the system, at lower sodium hydroxide concentrations.<sup>51</sup> However, when the sodium hydroxide concentration was too high, it was difficult for the EY molecules to adsorb on the catalyst surface.<sup>52,53</sup> And if the sodium hydroxide concentration is too high, the Cannizzaro reaction will occur, which will also lead to a decrease in hydrogen production activity.54,55

The cycling stability of the catalyst is an important parameter to evaluate the performance of the catalyst; multi-cycle experiments were used to investigate the stability of catalysts. As shown in Fig. 7d, in the first round, for Pd<sub>1</sub>Sn<sub>1</sub>/RGO, the HER rate was 530.07  $\mu$ mol h<sup>-1</sup>, and it was 431.75  $\mu$ mol h<sup>-1</sup> in the second round. The Pd<sub>1</sub>Sn<sub>1</sub>/RGO sample's HER rate presented almost 81.45% of the first round activity. The slight decrease in the catalytic activity in the following run can be attributed to the catalyst loss during catalyst centrifugation. In order to confirm our deduction, we quantified catalyst losses after four cycling rounds and added the corresponding amount of the catalyst into the system; then the HER activity recovered to the initial level.

We also weighed the remaining Pd/RGO,  $Pd_3Sn_1/RGO$  and  $Pd_1Sn_3/RGO$  catalysts after three cycle stability tests and found that 1.8 mg, 1.0 mg and 1.7 mg of the catalysts were lost, respectively. The corresponding amounts of the catalysts were added into the system in the fourth round and the hydrogen evolution rate also recovered to the initial level. This experiment



Fig. 6 The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) of the  $Pd_1Sn_1/RGO$  sample; (a) TEM image of the  $Pd_1Sn_1/RGO$  sample; (b) HRTEM image of the  $Pd_1Sn_1/RGO$  sample; (c and e) HAADF-STEM image of the  $Pd_1Sn_1/RGO$  sample; and (d) the EDX spectrum of the  $Pd_1Sn_1/RGO$  alloy catalyst.

proves that the Pd/RGO,  $Pd_3Sn_1/RGO$ ,  $Pd_1Sn_1/RGO$  and  $Pd_1Sn_3/RGO$  samples exhibited good stability in the HER.

#### 3.6. Photo-electrochemical performance

The charge formation and transfer over Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/ RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO catalysts were compared; several electrodes using Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO samples were developed. As shown in Fig. 8, the photocurrent curves of catalysts Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO on ITO were examined. As shown in Fig. 8a, the Pd<sub>1</sub>Sn<sub>1</sub>/RGO catalyst shows highest photocurrent among all the catalysts, implying that over the EY sensitized  $Pd_1Sn_1/RGO$  catalyst the electron transfer is fastest. This can be attributed to the high electron transfer rate caused by the coordination effect of the alloy catalyst and the reduced recombination rate of photo-generated carriers.<sup>56</sup>

The linear sweep voltammetry method was used to investigate electrochemical H<sub>2</sub> generation activities of Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO electrodes. As shown in Fig. 8, among all the alloy catalysts the Pd<sub>1</sub>Sn<sub>1</sub>/RGO catalyst shows a lower overpotential of -0.223 V, as we all know that the overpotential of the HER has an effect on the HER activity, and the lower overpotential could attributed to the



Fig. 7 (a)  $H_2$  generation from Sn/RGO, Pd<sub>1</sub>Sn<sub>3</sub>/RGO Pd<sub>1</sub>Sn<sub>1</sub>/RGO, and Pd<sub>3</sub>Sn<sub>1</sub>/RGO catalysts driven by visible light, (b) the effect of different NaOH concentrations on the HER rate, (c) the effect of different HCHO concentrations on the HER rate, and (d) the stability of Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>3</sub>/RGO catalysts.



**Fig. 8** (a) Photocurrent curves, (b) linear sweep voltammograms, (c) cyclic voltammograms (CV), (d) electrochemical impedance spectroscopy (EIS) Nyquist plots, (e) UV-Vis spectra, and (f) PL spectra of EY-sensitized Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO, and Pd<sub>1</sub>Sn<sub>3</sub>/RGO catalysts.

faster electron transfer from the active species surface to the H<sub>2</sub>O molecule.<sup>57</sup> So the Pd<sub>1</sub>Sn<sub>1</sub>/RGO catalyst shows the best activity for the HER compared with other alloy catalysts.

Fig. 8c illustrates the cyclic voltammograms obtained from different catalysts. As can be seen from the voltammograms, all the catalysts display similar CVs and the peaks of all the

Table 2	Fluorescence lifetimes	of Pd/RGO	Pd-Sn/RGO	Pd <sub>4</sub> Sn <sub>4</sub> /R	GO and Pd <sub>4</sub> Sn	-/RGO samples
	I WOI ESCENCE MEMBES	or Fundo,	, ruzsn <u>i</u> /nao,	Fujjij/K		3/INGO samples

System	Lifetime (ns)	Pre-exponential factors B	Average lifetime (ns)	$\chi^2$
EY	au = 1.179	$B_1 = 1$	1.179	1.014
EY-RGO	$\tau_1 = 0.366,  \tau_2 = 1.259$	$B_1 = 0.2361, B_2 = 0.7639$	1.185	1.002
EY-Pd/RGO	$\tau_1 = 0.049,  \tau_2 = 1.266$	$B_1 = 0.5967, B_2 = 0.4033$	1.199	1.003
EY-Pd <sub>3</sub> Sn <sub>1</sub> /RGO	$\tau_1 = 0.501,  \tau_2 = 1.342$	$B_1 = 0.3196, B_2 = 0.6804$	1.216	1.012
EY-Pd <sub>1</sub> Sn <sub>1</sub> /RGO	$ au_1 = 0.797,  au_2 = 1.529$	$B_1 = 0.5507, B_2 = 0.4493$	1.248	1.010
EY-Pd <sub>1</sub> Sn <sub>3</sub> /RGO	$ au_1 = 0.512,   au_2 = 1.346$	$B_1 = 0.3324, B_2 = 0.6676$	1.213	1.000

Table 3 Adsorption energy and dissociation barrier of oxygen on different alloy catalyst surfaces

Catalyst	Pd catalyst	Pd <sub>3</sub> Sn <sub>1</sub> catalyst	Pd <sub>1</sub> Sn <sub>1</sub> catalyst	Pd <sub>1</sub> Sn <sub>3</sub> catalyst
$E_{\rm ads} O_2 (eV)$	-0.48	-0.46	-0.44	-0.38
$E_{\rm a}~({\rm eV})$	1.23	4.04	3.96	3.00

catalysts located near 0.60 eV were peaks of desorption of the oxygenated adsorbates. Compared with that on the Pd/RGO catalyst, the oxygenated adsorbates' voltammetric peak potential on the Pd-Sn/RGO catalyst is larger, which indicates that the oxygenated species desorption from the catalyst takes place more easily than that on the Pd/RGO catalyst, which is consistent with the adsorption energy data of O<sub>2</sub>, *i.e.*, Pd shows higher adsorption energy and lower dissociation energy compared with the Pd-Sn/RGO catalyst (Table 3).58 The Pd/RGO catalysts are more favorable for O<sub>2</sub> to dissociate into two oxygen atoms, which may lead to serious hydrogen-oxygen recombination,59 and is detrimental to the hydrogen production system. In addition, the peaks located near 0.20 eV were peaks of desorption of hydrogen. The hydrogen adsorption peak for Pd-Sn/RGO samples shifts to the positive side compared with those for Pd/ RGO samples, which is due to the better charge transfer.<sup>42</sup> A low hydrogen adsorption energy leads to higher activity for the HER.60

Fig. 8d displays the Nyquist plots in a 0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> solution. In the Nyquist plots, the Pd–Sn/RGO composite diameter decreased significantly compared with that of Pd/RGO, and the Pd<sub>1</sub>Sn<sub>1</sub>/RGO catalyst showed the smallest semicircle among all the catalysts, implying an effective charge transfer over the Pd<sub>1</sub>Sn<sub>1</sub>/RGO catalyst.<sup>61,62</sup> As shown in Fig. 8e, the dye-sensitized catalyst has the highest absorption peak at 518 nm, which is the characteristic absorption peak of the dye

molecule EY,<sup>49</sup> indicating that the sensitized RGO, Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>3</sub>/RGO catalysts can absorb visible light.

Fig. 8f exhibits the PL spectra of Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO catalysts at room temperature. In the EY solution, the PL spectrum exhibits a distinct emission peak at 536 nm, which is due to the fast photogenerated carrier recombination. However, the emissions of Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/ RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/RGO catalysts were quenched. The results demonstrate the ligand effect of Pd and Sn, which is helpful to the photogenerated electron separation and transfer, eventually resulting in the higher hydrogen evolution rate. The quenching efficiency of Pd<sub>1</sub>Sn<sub>1</sub>/RGO is remarkably higher than that of the other catalysts, indicating the excellent photocatalytic performance of the Pd<sub>1</sub>Sn<sub>1</sub>/RGO catalyst.<sup>63,64</sup> The fluorescence lifetime measurement results are given in Table 2. The lifetimes of Pd/RGO, Pd<sub>3</sub>Sn<sub>1</sub>/RGO, Pd<sub>1</sub>Sn<sub>1</sub>/RGO and Pd<sub>1</sub>Sn<sub>3</sub>/ RGO catalysts are 1.199, 1.216, 1.248 and 1.213 ns respectively. Among all the catalysts, Pd<sub>1</sub>Sn<sub>1</sub>/RGO shows the longest lifetime, indicating that charge transfer and separation are most efficient over the Pd<sub>1</sub>Sn<sub>1</sub>/RGO catalyst.<sup>43</sup>

#### 3.7. The oxygen role in the hydrogen evolution reaction

Interestingly, the trace amount of existing oxygen can promote conversion of formaldehyde into hydrogen. Fig. 9a shows the effects of oxygen concentration on the HER driven by visible



Fig. 9 (a)  $O_2$  effect on the HER rate driven by visible light, (b) proposed mechanism of hydrogen evolution from HCHO; (c) the GC-MS spectra of gas products over the  $Pd_1Sn_1/RGO$  catalyst driven by visible light; and (d) difference in the reaction mechanism with and without oxygen.

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light. The HER rate keeps ascending as  $O_2$  increases continuously up to 0.5 mmol. The hydrogen evolution rate was 241.95  $\mu$ mol h<sup>-1</sup> when the amount of  $O_2$  was 0.5 mmol.

According to the report of Robert Czochara *et al.*,<sup>65</sup> formaldehyde could react with sodium hydroxide and hydrogen peroxide to generate hydrogen. As shown in Fig. 9b, the process could be described as shown in eqn (1), in which the bis-(hydroxymethyl)peroxide dianion ( $P^{2-}$ ) is the intermediate that generates hydrogen as shown in eqn (2). In order to verify this hydrogen production mechanism (shown in the ESI Fig. S1†), we measured the reaction order using the chemical kinetics method and found that the experimental results were consistent with the mechanism. Based on the reaction mechanism of hydrogen production from HCHO, we speculate that the oxygen species  $O_2^{2-}$  derived from molecular  $O_2$  reduction on the Pd–Sn alloy catalyst surface might be involved in the reaction as follows.<sup>66,67</sup>

In order to verify the mechanism of the hydrogen evolution reaction further, the gases in the system are tested by the GC-MS method. In Fig. 9c<sub>1</sub>, m/z 2 could be attributed to H<sub>2</sub>, m/z 32 to O<sub>2</sub>, m/z 40 to Ar and m/z 44 to the CO<sub>2</sub> in water. In Fig. 9c<sub>2</sub>, m/z 2 and m/z 4 were present in the D<sub>2</sub>O dispersion. The m/z signal of 2 could be attributed to H<sub>2</sub> and 4 could be attributed to D<sub>2</sub>. These experimental results indicated that H<sub>2</sub> evolved from HCHO and H<sub>2</sub>O. Compared with our previous research results,<sup>68</sup> the current catalyst shows much better activity in the presence of oxygen. This might be because oxygen molecules mainly adsorb at the hcp site of the metal atoms and interact with three metal atoms, while the water molecules mainly adsorb at the top site of the metal catalyst and interact with only one metal atom. The interaction between oxygen molecules and metal atoms is greater than that of water molecules according to theoretical calculations. So HCHO reacts with the oxygen molecules rather than with the water molecules, in the presence  $O_2$  (Fig. 9d).

The ideal catalyst will easily generate hydrogen from the HCHO solution while it will be less active in the dissociation of O2.69-71 Considering the geometric structures of IS, TS and FS of O<sub>2</sub> dissociation on the Pd catalyst, Pd<sub>3</sub>Sn<sub>1</sub>, Pd<sub>1</sub>Sn<sub>1</sub> and Pd<sub>1</sub>Sn<sub>3</sub> catalysts should exhibit different characteristics (shown in Table S1 in the ESI<sup>†</sup> and the corresponding adsorption energy and activation barriers are summarized in Fig. 10). For the process of the O<sub>2</sub> dissociation, the Pd atoms are surrounded by O2, serving as the catalytic center. The Sn atoms are "spectators" for O<sub>2</sub> dissociation, or they act as the "modulator" for the charge transfer and stabilize the Pd atoms.72-74 According to the results shown in Fig. 10 and Table 3, the Pd catalyst shows the highest adsorption energy (-0.48 eV) for oxygen compared with the Pd-Sn alloy catalyst and the activation barrier for O2 dissociation on the Pd catalyst surface is 1.23 eV, while it is 4.04 eV on the Pd<sub>3</sub>Sn<sub>1</sub> alloy catalyst surface, 3.96 eV on the Pd<sub>1</sub>Sn<sub>1</sub> alloy catalyst surface and 3.00 eV on the Pd1Sn3 alloy catalyst surface respectively. Pd shows higher adsorption energy compared with the Pd-Sn/RGO catalyst. There is a significant increase in the activation barriers for the O2 dissociation on the Pd-Sn alloy



Fig. 10 The reaction steps for O<sub>2</sub> dissociation and the corresponding activation energies.



Scheme 1 The mechanism for hydrogen generation from HCHO using the EY-Pd1Sn1/RGO alloy catalyst.

catalysts compared with those on the Pd catalyst, indicating that the oxygen role is more pronounced on the Pd–Sn alloy catalysts than on the Pd catalyst. There is no doubt that the activity of Pd–Sn alloy samples for catalyzing the hydrogen production from formaldehyde is determined by the dissociation energy of  $O_2$  molecules on the alloy catalyst.

As for the hydrogen formation process, it is believed that the hydrogen evolution from HCHO and  $H_2O$  over the sensitized catalysts occurs *via* the following mechanism (shown in Scheme 1). Driven by visible light,  $EY^{1*}$  was formed because the EY absorbed the input photons, and the lowest-lying triplet state  $EY^{3*}$  was produced *via* an intersystem crossing. Next, the  $EY^{-*}$  species was formed due to the quenched HCHO. And the excited electron was formed. The excited electron was then injected into the surface of RGO with strong conductivity and transferred to the Pd<sub>1</sub>Sn<sub>1</sub> catalyst surface. The hydrogen was formed by reducing the protons on the Pd<sub>1</sub>Sn<sub>1</sub> alloy surface. In the meantime, driven by visible light, O<sub>2</sub> absorbs excited photons to form O<sub>2</sub><sup>--</sup>,<sup>67</sup> and two O<sub>2</sub><sup>--</sup> will form O<sub>2</sub><sup>2-</sup>; O<sub>2</sub><sup>2-</sup> will react with HCHO on the Pd–Sn alloy catalyst surface.

## 4. Conclusion

In summary, a new low-cost PdSn alloy cocatalyst for the HER from a formaldehyde solution driven by visible light has been prepared. The developed  $Pd_1Sn_1/RGO$  catalyst showed high activity for hydrogen evolution. Under optimized conditions, the hydrogen evolution rate reached up to 530.07 µmol h<sup>-1</sup>. Moreover, the performance could be optimized by tuning the surface nature of the Pd–Sn alloy in the catalyst. The DFT results show that the adsorption energies of formaldehyde, water and oxygen are key parameters in the design of active sites for hydrogen evolution from formaldehyde.

## Conflicts of interest

There are no conflicts to declare.

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