

## RESEARCH ARTICLE

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# Boosted charge transfer in Pt cluster anchored TiO<sub>2</sub> microspheres with rich oxygen vacancies for solar driven H<sub>2</sub> production from lignocellulosic biomass†

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Solar driven lignocellulosic biomass-to-H<sub>2</sub> conversion through photocatalysis is an economical and clean approach to generate hydrogen fuel. However, the photocatalytic lignocellulosic biomass-to-H<sub>2</sub> conversion efficiency is still very low owing to the lack of a highly reactive photocatalyst. Herein, we reported the construction of Pt nanocluster chemically anchored porous TiO<sub>2</sub> microspheres with abundant oxygen vacancies as a highly efficient photocatalyst for solar driven lignocellulosic biomass-to-H<sub>2</sub> conversion. The oxygen vacancies on the TiO<sub>2</sub> surface not only boost electron transfer across the Pt–TiO<sub>2</sub> interface, but also benefit the formation of <sup>•</sup>OH which acts as a key intermediate for the oxidation of lignocellulose. The Pt/TiO<sub>2</sub> photocatalysts show high photocatalytic performance with the highest H<sub>2</sub> generation rate of 494 μmol g<sup>−1</sup> h<sup>−1</sup> and an apparent quantum yield of 3.21% at 380 nm in α-cellulose aqueous solution. Furthermore, photocatalytic H<sub>2</sub> production from lignocellulosic biomass has been successfully achieved, and the H<sub>2</sub> generation rate of the optimal Pt/TiO<sub>2</sub> photocatalyst in rice straw, wheat straw, polar wood chip, bamboo, rice hull and corncob aqueous solution was 2, 3, 23, 32, 11 and 6 μmol g<sup>−1</sup> h<sup>−1</sup>, respectively. This study provides an opportunity for encouraging more research on solar driven lignocellulosic biomass-to-H<sub>2</sub> conversion.

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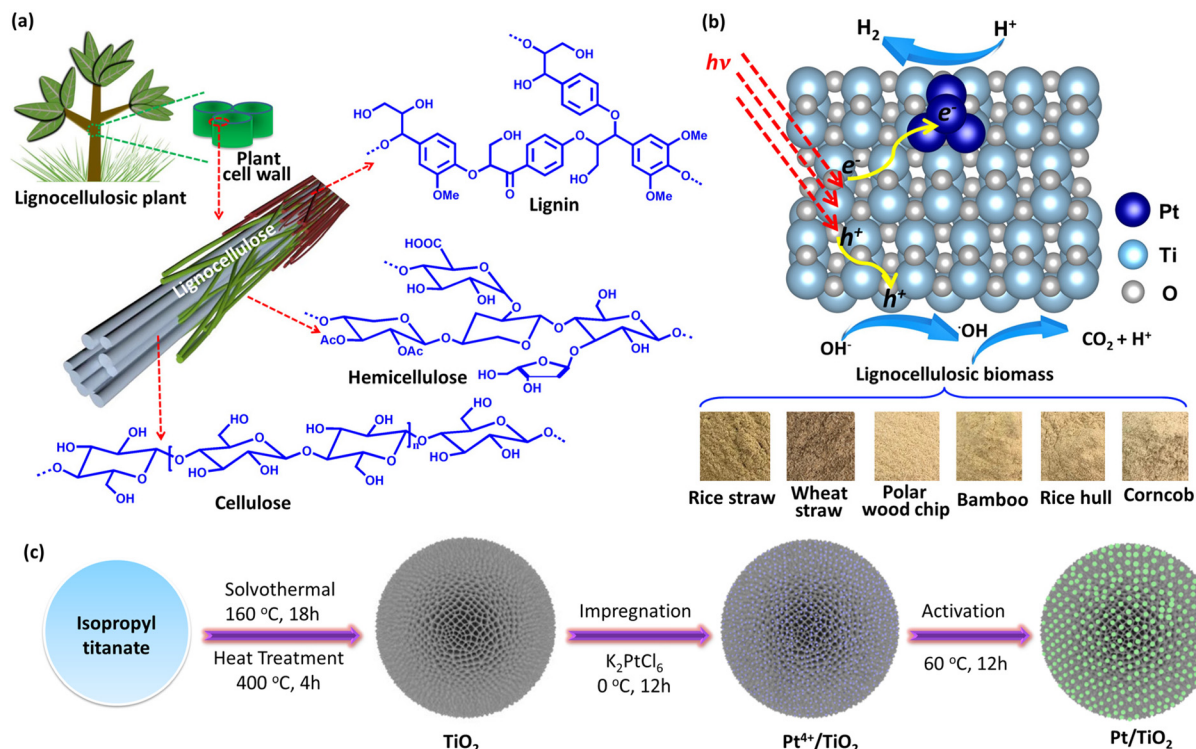
## 1. Introduction

Photocatalytic H<sub>2</sub> production from lignocellulosic biomass using solar energy to drive the reaction of lignocelluloses with water into H<sub>2</sub> and CO<sub>2</sub> over a semiconductor photocatalyst provides a “green” way to achieve the conversion of lignocellulosic biomass to H<sub>2</sub> fuel, which has recently attracted a lot of research attention due to its unique advantages of simplicity,

low cost, *etc.*<sup>1–8</sup> Different from these classical enzymatic fermentation and thermocatalytic technologies,<sup>9–11</sup> the H<sub>2</sub> generated from photocatalytic systems can be easily separated and collected for utilization. Since lignocellulose has a complex and highly robust structure with staggered cellulose, hemicellulose and lignin (Fig. 1a), the oxidation and decomposition of lignocellulose are difficult kinetically. Currently, visible-responsive photocatalysts used for photocatalytic H<sub>2</sub> production from lignocellulose are limited to a few specific materials. For example, some studies have shown that CdO<sub>x</sub> modified CdS (CdO<sub>x</sub>/CdS) and cyanamide-functionalized carbon nitride (<sup>NCN</sup>g-C<sub>3</sub>N<sub>4</sub>) photocatalysts are capable of transferring holes to lignocellulose through the cyanamide group and CdO<sub>x</sub> acted as the hole-transfer bridge,<sup>12,13</sup> resulting in the oxidation of lignocellulose and H<sub>2</sub> production. Apart from these photocatalysts with a specific group or species, the <sup>•</sup>OH radical with high reactivity generated by reaction of photogenerated holes in the valence band (VB) of photocatalysts with OH<sup>−</sup> was recognized as the critical intermediate for the decomposition of lignocelluloses.<sup>14,15</sup> Because of the harsh thermodynamic requirements for <sup>•</sup>OH generation, only some wide-gap semiconductors were demonstrated to be active photocatalysts for photocatalytic lignocellulosic biomass-to-H<sub>2</sub>

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**Fig. 1** (a) Chemical composition and structure of lignocellulosic biomass. (b) Photocatalytic H<sub>2</sub> production from lignocellulosic biomass over Pt nanocluster anchored porous TiO<sub>2</sub> microspheres photocatalysts. (c) Schematic illustration for the synthesis of Pt/TiO<sub>2</sub> photocatalysts.

conversion. Very recently, we reported the use of (001) facet exposed ultrathin anatase TiO<sub>2</sub> nanosheets as a highly active photocatalyst for photocatalytic H<sub>2</sub> production from lignocellulose. Owing to the low energy barrier for <sup>•</sup>OH generation over the (001) facet and the rapid charge separation resulting from the ultrathin structure, the ultrathin TiO<sub>2</sub> nanosheets showed a relatively high photocatalytic H<sub>2</sub> production activity with a H<sub>2</sub> generation rate of 275 μmol h<sup>-1</sup> g<sup>-1</sup> and an apparent yield of 1.89% at 380 nm in the presence of Pt nanoparticles as a cocatalyst.<sup>16</sup> Although some progress has been made by using the (001) facet exposed ultrathin TiO<sub>2</sub> nanosheets as the photocatalyst, the photocatalytic H<sub>2</sub> production performance is still low. And thus, the development of highly efficient photocatalysts remains the biggest challenge for photocatalytic H<sub>2</sub> production from lignocellulosic biomass.

There are three main factors that efficiently affect the photocatalytic activity of TiO<sub>2</sub> for H<sub>2</sub> production from lignocellulose, including the active sites of the photocatalyst for <sup>•</sup>OH generation, the active sites of the cocatalyst for H<sub>2</sub> generation and the carrier separation efficiency of the photocatalyst. It is highly desirable that the construction of photocatalysts with abundant active sites for both <sup>•</sup>OH and H<sub>2</sub> generation reactions as well as rapid charge separation efficiency would be the most effective way to improve the photocatalytic lignocellulose-to-H<sub>2</sub> conversion performance of TiO<sub>2</sub> photocatalysts. Herein, we reported the construction of Pt nanocluster anchored porous TiO<sub>2</sub> microsphere (Pt/TiO<sub>2</sub>) photocatalysts with abundant oxygen vacancies for photocatalytic ligno-

cellulosic biomass-to-H<sub>2</sub> conversion (Fig. 1b). The oxygen vacancies on the TiO<sub>2</sub> surface benefit both the charge transfer across the Pt/TiO<sub>2</sub> interface and the formation of <sup>•</sup>OH and the small size of Pt benefits the H<sub>2</sub> evolution reaction. As a result, the Pt/TiO<sub>2</sub> catalyst was demonstrated to be an efficient photocatalyst for photocatalytic H<sub>2</sub> production from α-cellulose as well as lignocellulosic biomass such as rice straw, wheat straw, polar wood chip, bamboo, rice hull and corncob. The highest H<sub>2</sub> generation rate of Pt/TiO<sub>2</sub> photocatalysts from α-cellulose aqueous solution was 494 μmol g<sup>-1</sup> h<sup>-1</sup> with an apparent quantum yield of 3.21% at 380 nm.

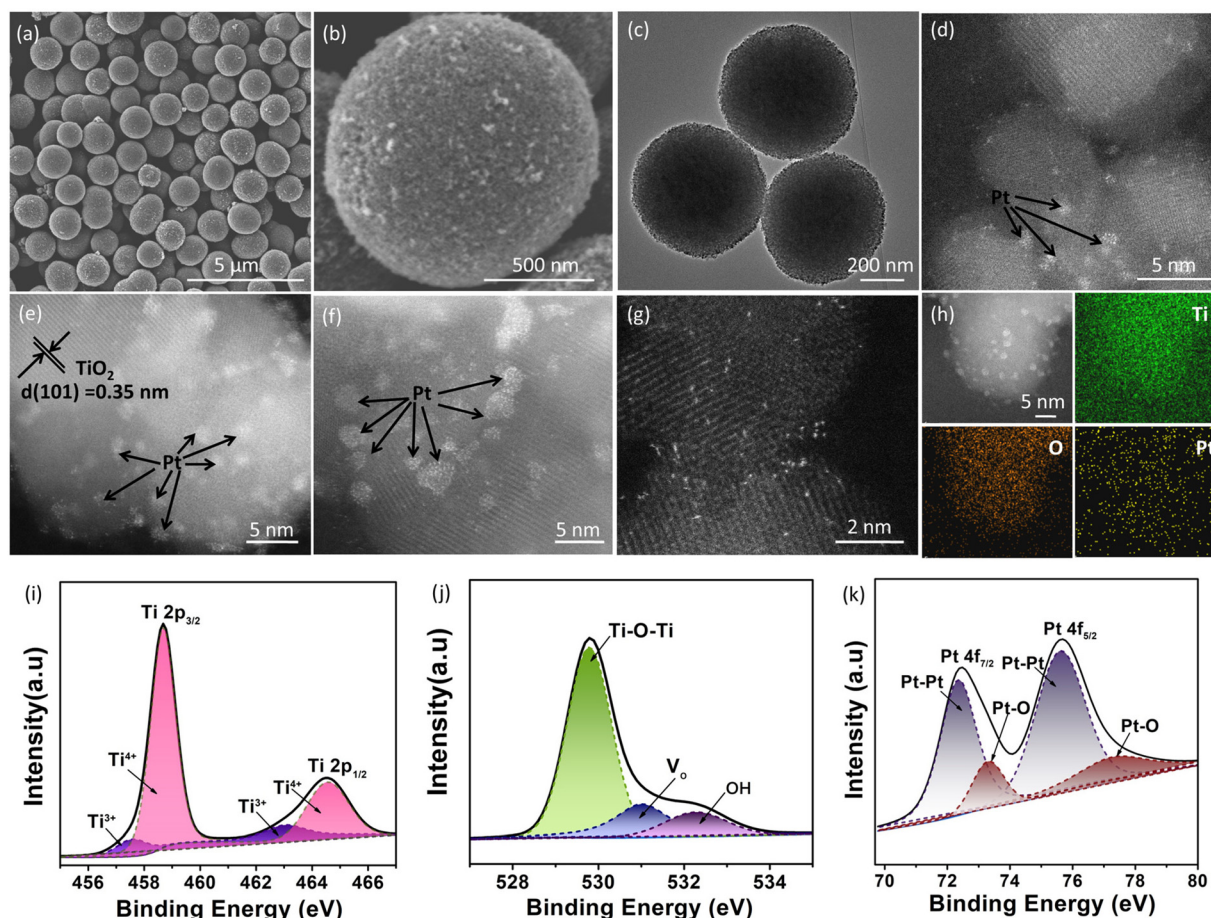
## 2. Results and discussion

### 2.1 Preparation and characterization

Fig. 1c shows the rapid synthetic method for Pt/TiO<sub>2</sub> photocatalysts. The preliminary porous TiO<sub>2</sub> microspheres were prepared from titanium isopropyl in acetone solution by a solvothermal method, and the preliminary product was then heated at 400 °C under air to remove the adsorbed organics. During the solvothermal process, the condensation hydrolysis of acetone results in the generation of H<sub>2</sub>O, which provides the oxygen source for the growth of TiO<sub>2</sub> microspheres,<sup>17</sup> but TiO<sub>2</sub> microspheres cannot be prepared from an acetone–water solution by using H<sub>2</sub>O as the oxygen source. To grow the Pt nanoclusters on porous TiO<sub>2</sub> microspheres, tetravalent Pt species was firstly bonded to porous TiO<sub>2</sub> microspheres by stirring the

mixed aqueous solution of  $\text{TiO}_2$  and  $\text{K}_2\text{PtCl}_6$  in an ice bath in a dark environment, and then the tetravalent Pt species with relatively strong oxidability was reduced to Pt on porous  $\text{TiO}_2$  microspheres at 60 °C, resulting in the formation of a Pt nanocluster anchored  $\text{TiO}_2$  microsphere photocatalyst ( $\text{Pt}/\text{TiO}_2$ ), and the reduction of tetravalent Pt species can produce oxygen vacancies in  $\text{TiO}_2$  in an oxygen-deficient environment.<sup>18</sup> The X-ray diffraction analysis in Fig. S1† confirms that the  $\text{TiO}_2$  microspheres have a crystal structure of the anatase phase (JCPDS No. 21-1272),<sup>19</sup> and the heat treatment does not change the crystal phase. As for these  $\text{Pt}/\text{TiO}_2$  samples, no diffraction peak of Pt was observed in the XRD patterns (Fig. S2†), which could be related to the low content and high dispersion of Pt on  $\text{TiO}_2$ . The  $\text{N}_2$  adsorption-desorption curves of the as-prepared porous  $\text{TiO}_2$  microspheres show a large Brunauer-Emmett-Teller (BET) specific surface area of  $145 \text{ m}^2 \text{ g}^{-1}$  (Fig. S3†) and an average porous size of 9.5 nm (inset in Fig. S3†). And then, the morphology and microstructure of bare  $\text{TiO}_2$  and  $\text{Pt}/\text{TiO}_2$  samples were investigated by SEM and TEM analysis. As shown in Fig. 2a and b, the as-prepared  $\text{TiO}_2$  exhibited the typical microspherical morphology, and the

average diameter of  $\text{TiO}_2$  microspheres was estimated to be  $0.87 \mu\text{m}$  (Fig. S4†). The SEM analysis showed that heat treatment does not change the morphology and size of  $\text{TiO}_2$  (Fig. S5 and S6†), indicating that the morphology of  $\text{TiO}_2$  was formed during the solvothermal process. The TEM image of  $\text{TiO}_2$  microspheres illustrated in Fig. 2c shows that the surface of  $\text{TiO}_2$  microspheres is very rough rather than smooth, confirming the porous structure of  $\text{TiO}_2$ . The rough surface is related to the existence of abundant  $\text{TiO}_2$  nanoparticles on the surface of  $\text{TiO}_2$  microspheres (Fig. S7†). After the growth of Pt nanoclusters, the morphology of  $\text{Pt}/\text{TiO}_2$  microspheres does not change as compared to that of bare  $\text{TiO}_2$  microspheres, as demonstrated by SEM and TEM analysis shown in Fig. S8 and S9.† For  $\text{Pt}/\text{TiO}_2$  samples, the existence of Pt nanoclusters was not observed in the TEM images of the  $\text{Pt}/\text{TiO}_2$  samples (Fig. S9 and S10†), which can be attributed to the low amount and small size of Pt nanoclusters, but the existence of Pt element can be observed in the EDX elemental mapping images of the  $\text{Pt}/\text{TiO}_2$  samples (Fig. S11 and S12†). Spherical aberration-corrected HAADF-STEM was then used to investigate the existence of Pt on  $\text{TiO}_2$  microspheres. As shown in



**Fig. 2** (a and b) SEM and (c) TEM image of bare  $\text{TiO}_2$ . (d–g) Spherical aberration-corrected HAADF-STEM image of 0.2%  $\text{Pt}/\text{TiO}_2$  (d), 0.4%  $\text{Pt}/\text{TiO}_2$  (e and g) and 1.0%  $\text{Pt}/\text{TiO}_2$  (f). (h) HAADF-STEM and elemental mapping images of 0.4%  $\text{Pt}/\text{TiO}_2$ . (i–k) High-resolution Ti 2p, O 1s and Pt 4f XPS spectra of 0.4%  $\text{Pt}/\text{TiO}_2$ .



Fig. 2d–f, obvious Pt nanoclusters can be observed in the spherical aberration-corrected HAADF-STEM images of the Pt/TiO<sub>2</sub> samples with an average diameter of 0.95 nm (Fig. S13†). Meanwhile, clear lattice fringes of 0.35 nm corresponding to the (101) planes of anatase TiO<sub>2</sub> were seen in the spherical aberration-corrected HAADF-STEM image (Fig. 2e).<sup>20</sup> The Pt nanoclusters without any lattice fringe were not strictly nanocrystalline, but were made up of random Pt atoms, and this relatively highly disordered structure of Pt nanoclusters is beneficial for catalyzing the H<sub>2</sub> evolution reaction owing to the increased number of active sites. Meanwhile, the white bright dots corresponding to the single Pt atoms were located on the surface of TiO<sub>2</sub> (Fig. 2g). The TEM analysis shows that the Pt species on the TiO<sub>2</sub> surface was mainly exhibited in the form of nanoclusters rather than single atoms, which could be attributed to the fact that the formation of Pt single atoms requires relatively harsh conditions of abundant coordination-unsaturated anions. In addition, the corresponding EDS elemental mapping images of Ti, O and Pt elements in Fig. 2h confirm the uniform distribution of Pt element in the Pt/TiO<sub>2</sub> photocatalyst.

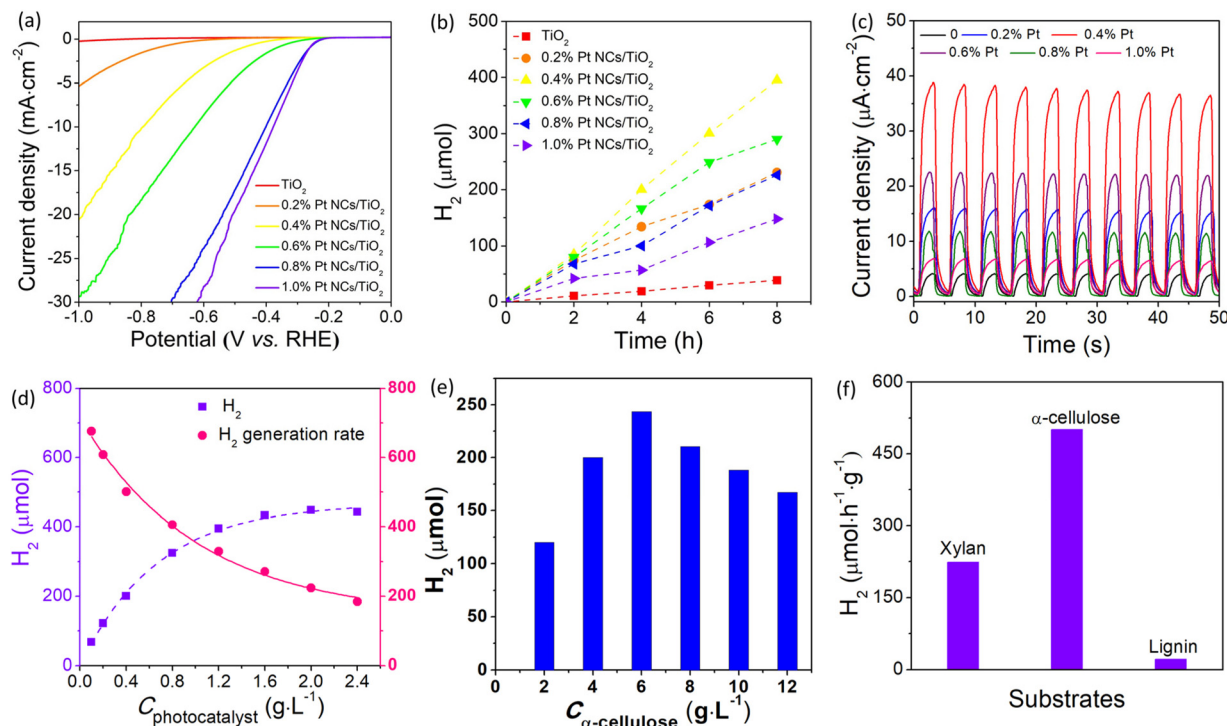
The light-harvesting ability of the as-prepared bare TiO<sub>2</sub> and Pt/TiO<sub>2</sub> investigated by UV-Vis diffuse reflectance spectroscopy shows that the bare TiO<sub>2</sub> only shows a strong absorption peak in the UV region with an absorption edge at 397 nm (Fig. S14†). With the introduction of Pt, the Pt/TiO<sub>2</sub> samples exhibit a strong absorption in the UV region as well as a low weak absorption in the visible region, which is consistent with the color change from white to faint yellow. The visible light-harvesting ability of the Pt/TiO<sub>2</sub> samples can be referred to as an absorption tail caused by defect of oxygen vacancies as well as the light-absorption of Pt.<sup>21,22</sup> Although the Pt/TiO<sub>2</sub> samples exhibit weak visible light absorption, the bandgap of TiO<sub>2</sub> in the Pt/TiO<sub>2</sub> photocatalysts does not show an obvious red-shift as compared to that of bare TiO<sub>2</sub> (Fig. S14†). The electronic states of bare TiO<sub>2</sub> and Pt/TiO<sub>2</sub> photocatalysts were then investigated by X-ray photoelectron spectroscopy (XPS). The survey XPS spectrum for the 0.4% Pt/TiO<sub>2</sub> photocatalyst in Fig. S15† shows strong Ti 2p and O 1s peaks as well as a weak Pt 4f peak. As shown in Fig. 2i, the Ti 2p signals with binding energies at 458.7 and 464.8 eV for Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub>, respectively, were assigned to Ti<sup>4+</sup>.<sup>23</sup> Meanwhile, a relatively weak Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> peak of Ti<sup>3+</sup> was also observed at 457.3 and 463.1 eV, respectively.<sup>24</sup> That is, it is very easy to form trivalent titanium in the formation of V<sub>O</sub>, resulting in a lower binding energy of the Ti 2p peak.<sup>25</sup> Furthermore, the O 1s XPS spectrum in Fig. 2j can be deconvoluted into three peaks at 529.7, 531.4 and 533.3 eV, which can be attributed to the Ti–O–Ti, V<sub>O</sub> and surface oxygen species, respectively.<sup>26</sup> And a stronger peak related to V<sub>O</sub> was observed in the O 1s XPS of the 0.4% Pt/TiO<sub>2</sub> sample as compared to that of bare TiO<sub>2</sub> (Fig. S16†), suggesting more V<sub>O</sub> exhibited in the Pt/TiO<sub>2</sub> sample. As for the high-resolution Pt 4f XPS peak of 0.4% Pt/TiO<sub>2</sub> shown in Fig. 2k, two peaks of 4f<sub>7/2</sub> and 4f<sub>5/2</sub> respectively located at 72.8 and 75.9 eV can be deconvoluted into four sub peaks at 71.6, 72.9, 75.1 and 76.2 eV, in which the peaks at 71.6 and 75.1 eV

can be attributed to the Pt–Pt species in Pt, and the peaks at 72.9 and 76.2 eV can be attributed to the Pt atoms bonded to the O atoms at the interface of TiO<sub>2</sub>.<sup>22</sup> It is obvious that the signal peak of Pt–Pt species was much stronger than that of the Pt–O bond, confirming that Pt<sup>0</sup> exhibited in the form of Pt nanoclusters was the main component of Pt. And then, the existence of oxygen vacancies (V<sub>O</sub>s) in the Pt/TiO<sub>2</sub> sample was confirmed by electron paramagnetic resonance (EPR) analysis. As displayed in Fig. S17,† a very weak peak with a *g* value at 2.003 related to V<sub>O</sub> was observed for the bare TiO<sub>2</sub> sample.<sup>27,28</sup> After the introduction Pt on TiO<sub>2</sub>, the EPR peak of V<sub>O</sub> remarkably strengthens, indicating that a higher V<sub>O</sub> concentration was present in 0.4% Pt/TiO<sub>2</sub> as compared to that of bare TiO<sub>2</sub>.

## 2.2 The effect of Pt on H<sub>2</sub> generation of Pt/TiO<sub>2</sub> catalysts

Generally, an efficient cocatalyst used for photocatalytic H<sub>2</sub> production is usually an excellent H<sub>2</sub> generation reaction electrocatalyst, and thus the electrocatalytic performance can provide important information to identify whether it qualifies as a suitable cocatalyst.<sup>29</sup> From this view, the electrocatalytic H<sub>2</sub> generation performance of various Pt/TiO<sub>2</sub> catalysts was studied in 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution using a typical three cell system. The linear sweep voltammetry (LSV) plots displayed in Fig. 3a show that bare TiO<sub>2</sub> is an ineffective catalyst for electrocatalytic H<sup>+</sup> reduction, but the introduction of Pt can promptly improve the electrocatalytic activity of TiO<sub>2</sub>, which can be attributed to the positive effect of Pt in accelerating hydrogen release. Obviously, owing to the increasing active sites for the H<sub>2</sub> generation reaction, the Pt/TiO<sub>2</sub> catalysts display a higher electrocatalytic activity with the increased amount of Pt. Under a hold potential of −0.3 V vs. RHE, the current density increases quickly from 0.18 to 4.05 mA cm<sup>−2</sup> when the Pt amount increases from 0 to 1.0%. Besides, only −0.38 V was required for 1.0% Pt/TiO<sub>2</sub> to achieve a current density of 10 mA cm<sup>−2</sup>. These results suggest that Pt would be an efficient cocatalyst to enhance photocatalytic H<sub>2</sub> production from lignocellulosic biomass.

The photocatalytic lignocellulosic biomass-to-H<sub>2</sub> conversion performance of the as-prepared Pt/TiO<sub>2</sub> was evaluated by using α-cellulose, rice straw, wheat straw, polar wood chip, bamboo, rice hull and corncob powder as the lignocellulosic biomass in neutral aqueous solution under 300 W Xe irradiation. In view of the fact that the lignocellulosic biomass is mainly composed of cellulose, hemicelluloses and lignin, and the proportion of cellulose is the largest, cellulose was used as the lignocellulosic substrate to optimize the amount of Pt in Pt/TiO<sub>2</sub> for photocatalytic H<sub>2</sub> production. Fig. 3b compares the photocatalytic H<sub>2</sub> production activity of various Pt/TiO<sub>2</sub> photocatalysts as well as bare TiO<sub>2</sub> in cellulose aqueous solution. The bare TiO<sub>2</sub> sample shows a low photocatalytic activity with a H<sub>2</sub> generation rate of 48.3 μmol h<sup>−1</sup> g<sup>−1</sup>. It is notable that the introduction of Pt significantly enhances the photocatalytic H<sub>2</sub> production activity because Pt can improve the photogenerated carrier separation efficiency as well as provide abundant active sites for H<sub>2</sub> generation. The positive effect of Pt in improving photogenerated carrier separation efficiency was verified by



**Fig. 3** (a) LSV plots of bare TiO<sub>2</sub> and various Pt/TiO<sub>2</sub> electrodes. (b) Time course of photocatalytic H<sub>2</sub> production over various Pt/TiO<sub>2</sub> photocatalysts in  $\alpha$ -cellulose aqueous solution. (c) Photocurrent density of bare TiO<sub>2</sub> and various Pt/TiO<sub>2</sub> electrodes. (d) Photocatalytic H<sub>2</sub> yields as a function of photocatalyst concentration in  $\alpha$ -cellulose aqueous solution, irradiation time 4 h. (e) Photocatalytic H<sub>2</sub> yields as a function of  $\alpha$ -cellulose concentration using 0.4% Pt/TiO<sub>2</sub> as a photocatalyst, irradiation time 4 h. (f) Photocatalytic H<sub>2</sub> generation rate of 0.4% Pt/TiO<sub>2</sub> in  $\alpha$ -cellulose, xylan and lignin aqueous solutions. Photocatalytic reaction conditions: 100 mg photocatalyst, 300 W Xe lamp, 1 g substrate, and 250 ml water.

transient photocurrent response measurement. Fig. 3c shows the photocurrent density of various Pt/TiO<sub>2</sub> electrodes modified with different amounts of Pt. The bare TiO<sub>2</sub> electrode shows a low photocurrent density of 4.4  $\mu\text{A cm}^{-2}$ , suggesting a low carrier separation efficiency in bare TiO<sub>2</sub>. After the introduction of Pt on TiO<sub>2</sub>, these Pt/TiO<sub>2</sub> electrodes demonstrate much higher photocurrent density than that of the bare TiO<sub>2</sub> electrode, indicating that Pt can efficiently accelerate photo-generated carrier separation and transfer. The highest photocurrent density of 38.8  $\mu\text{A cm}^{-2}$  was observed for the 0.4% Pt/TiO<sub>2</sub> electrode, which is about 8.8 times higher than that of the bare TiO<sub>2</sub> electrode. The order of photocurrent density for Pt/TiO<sub>2</sub> electrodes is consistent with the photocatalytic H<sub>2</sub> production performance of Pt/TiO<sub>2</sub> photocatalysts, confirming that a suitable amount of Pt plays a key factor in determining their photocatalytic activity for H<sub>2</sub> production. The 0.4% Pt/TiO<sub>2</sub> photocatalyst shows the highest H<sub>2</sub> generation rate of 494  $\mu\text{mol h}^{-1} \text{g}^{-1}$ , which is about 10 times higher than that of bare TiO<sub>2</sub>. The apparent quantum yield at 380 nm of this photocatalytic H<sub>2</sub> production system using 0.4% Pt/TiO<sub>2</sub> as the photocatalyst was 3.21%, which is higher than those reported for TiO<sub>2</sub>-based photocatalysts (Table S1†). In contrast to the electrocatalytic results that the electrocatalytic activity of Pt/TiO<sub>2</sub> catalysts increases with the increasing amount of Pt, the further increase in the amount of Pt nanoclusters leads to a decreased photocatalytic H<sub>2</sub> production activity of the Pt/TiO<sub>2</sub>

photocatalyst when the Pt amount exceeds 0.4%, which could be attributed to the aggregation of Pt as well as the shading effect of Pt.<sup>15</sup> The aggregation of Pt lowered the utilization efficiency of the Pt cocatalyst, while the shading effect of Pt hinders the absorption of light harvested by TiO<sub>2</sub>. A similar phenomenon was also observed in previously reported Pt/TiO<sub>2</sub> systems.<sup>30</sup> In addition, in control experiments in the absence of any component of photocatalyst, substrate or irradiation H<sub>2</sub> was generated, indicating that H<sub>2</sub> was produced from cellulose via a light-catalyzed reaction. Furthermore, although the Pt/TiO<sub>2</sub> photocatalyst can absorb some visible light related to the formation of defect levels (V<sub>O</sub> and Ti<sup>3+</sup>) in TiO<sub>2</sub>,<sup>31</sup> these Pt/TiO<sub>2</sub> samples were inactive photocatalysts for visible light photocatalytic H<sub>2</sub> production, which could be attributed to the fact that the defect level was not negative enough to reduce H<sup>+</sup> to H<sub>2</sub>.<sup>32</sup>

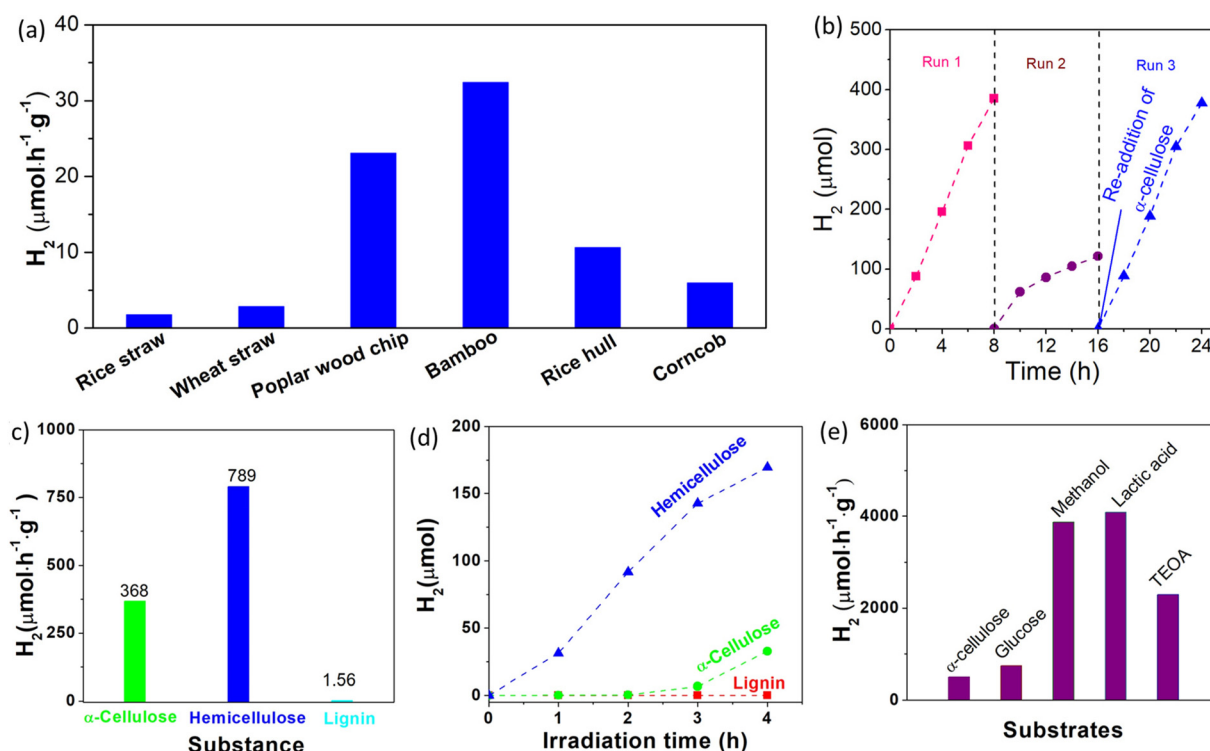
### 2.3 The dependence of photocatalyst and substrate

To investigate the concentration dependence of the photocatalyst and substrate, photocatalytic H<sub>2</sub> production experiments were performed in aqueous solution with different concentrations of the photocatalyst (0.1–2.4 g L<sup>-1</sup>) and substrate (2–12 g L<sup>-1</sup>). As shown in Fig. 3d, the amount of H<sub>2</sub> evolved from the photocatalytic system with a fixed  $C_{\alpha\text{-cellulose}}$  of 4.0 g L<sup>-1</sup> increases with increased  $C_{\text{photocatalyst}}$ . Obviously, the total amount of H<sub>2</sub> evolved from the photocatalytic system increases

with the increased concentration of the photocatalyst, but the  $H_2$  generation rate decreased from  $676 \mu\text{mol h}^{-1} \text{g}^{-1}$  to  $184 \mu\text{mol h}^{-1} \text{g}^{-1}$  when the  $C_{\text{photocatalyst}}$  changed from  $0.1 \text{ g L}^{-1}$  to  $2.4 \text{ g L}^{-1}$ , which can be attributed to the limited quantity of both illuminated photons and  $\alpha$ -cellulose. On the other hand, at a fixed concentration of the photocatalyst ( $0.4 \text{ g L}^{-1}$ ), the  $H_2$  generation rate with respect to the Pt/TiO<sub>2</sub> photocatalyst increases from  $301 \mu\text{mol h}^{-1} \text{g}^{-1}$  at  $C_{\alpha\text{-cellulose}}$  of  $2 \text{ g L}^{-1}$  to  $609 \mu\text{mol h}^{-1} \text{g}^{-1}$  at  $C_{\alpha\text{-cellulose}}$  of  $6 \text{ g L}^{-1}$ , and then reduces to  $417 \mu\text{mol h}^{-1} \text{g}^{-1}$  at  $C_{\alpha\text{-cellulose}}$  of  $12 \text{ g L}^{-1}$  (Fig. 3e). When  $C_{\alpha\text{-cellulose}}$  exceeds  $6 \text{ g L}^{-1}$ , the  $H_2$  amount decreases with the increased  $C_{\alpha\text{-cellulose}}$ , which is related to the shading effect of  $\alpha$ -cellulose, that is  $\alpha$ -cellulose as a solid substance blocks light absorbed by the photocatalyst when there is excess  $\alpha$ -cellulose in the photocatalytic system. These results confirm that the photocatalytic  $H_2$  production activity increases when one component was appraised with an excess of the other component.

Apart from cellulose, lignin and hemicelluloses are the other two main components of lignocelluloses, and it is very necessary to investigate the photocatalytic  $H_2$  production performance from lignin and hemicelluloses. Because hemicellulose is a heterogeneous polymer composed of several different types of monosaccharides, and xylan is the main component of hemicelluloses, it is used instead of hemicellu-

loses. As shown in Fig. 3f, the photocatalytic  $H_2$  generation activity of the 0.4% Pt/TiO<sub>2</sub> photocatalyst in  $\alpha$ -cellulose, lignin and hemicelluloses (xylan from corncob) was observed to be 494, 21.2 and  $765 \mu\text{mol h}^{-1} \text{g}^{-1}$ , respectively. The lowest  $H_2$  generation rate was observed in the lignin system, which could be assigned to its more stable structure. That is, there are some glycosidic bonds in cellulose and xylan, while lignin has a polymerized aromatic group which exhibited a conjugated *para* C-C bond. It has been known that the C-C bond has a bond energy of approximately  $86.2\text{--}104.3 \text{ kcal mol}^{-1}$ ,<sup>33</sup> which is much higher than that of glycosidic bonds with a bond dissociation energy of approximately  $54\text{--}72 \text{ kcal mol}^{-1}$ .<sup>34</sup> And thus, lignin has higher stability and is difficult to be decomposed by the photocatalyst. It has been known that commercial TiO<sub>2</sub> (Degussa P25, Germany) is a highly reactive photocatalyst for  $H_2$  production, and it is used as a reference photocatalyst. As illustrated in Fig. S18,† the photocatalytic  $H_2$  generation rate of the 0.4% Pt/TiO<sub>2</sub> photocatalyst ( $494 \mu\text{mol h}^{-1} \text{g}^{-1}$ ) was much higher than that of the 0.4% Pt/P25 sample ( $302 \mu\text{mol h}^{-1} \text{g}^{-1}$ ), indicating that the TiO<sub>2</sub> microspheres are a more highly efficient photocatalyst, which could be ascribed to their large specific surface area (Fig. S3†). After the optimization of the Pt nanocluster amount, the photocatalytic  $H_2$  production performance of 0.4% Pt/TiO<sub>2</sub> from lignocellulosic biomass



**Fig. 4** (a) Photocatalytic  $H_2$  generation rate of 0.4% Pt/TiO<sub>2</sub> photocatalyst from different biomass under 300 W Xe irradiation. (b) Cyclic photocatalytic  $H_2$  production of 0.4% Pt/TiO<sub>2</sub> in  $\alpha$ -cellulose aqueous solution. (c) Photocatalytic  $H_2$  generation rate over 0.4% Pt/TiO<sub>2</sub> photocatalyst in  $\alpha$ -cellulose, hemicelluloses (xylan from corncob) and lignin aqueous solutions under sunlight. (d) Time course of photocatalytic  $H_2$  production over various 0.4% Pt/TiO<sub>2</sub> under simulated sunlight ( $100 \text{ mW cm}^{-2}$ ) irradiation. (e) Comparison of  $H_2$  generation rate of 0.4% Pt/TiO<sub>2</sub> photocatalyst from  $\alpha$ -cellulose with a commonly used electron donor under 300 W Xe irradiation. Photocatalytic reaction conditions: 100 mg photocatalyst, 1 g substrate, and 250 ml of water.

including rice straw, rice hull, corncob, wheat straw, polar wood chip and bamboo powder was investigated. As shown in Fig. 4a, the  $\text{H}_2$  generation rate with respect to the 0.4% Pt/TiO<sub>2</sub> photocatalyst in rice straw, wheat straw, polar wood chip, bamboo, rice hull and corncob aqueous solution was 2, 3, 23, 32, 11 and 6  $\mu\text{mol h}^{-1} \text{g}^{-1}$ , respectively. As compared to the photocatalytic  $\text{H}_2$  production system in  $\alpha$ -cellulose solution, the photocatalytic activity of the 0.4% Pt/TiO<sub>2</sub> photocatalyst was lower in these lignocellulosic biomass solutions mentioned above, which is related to the larger size of lignocellulosic biomass. Furthermore, relatively higher photocatalytic  $\text{H}_2$  production performance was obtained for the photocatalytic system of polar wood chip and bamboo as compared to that of rice straw, rice hull, corncob, wheat straw and corncob, which could be related to the higher proportion of cellulose in their composition.

To investigate the stability of the Pt/TiO<sub>2</sub> photocatalyst for photocatalytic  $\text{H}_2$  generation in a cellulose aqueous solution, the photocatalytic  $\text{H}_2$  generation experiments were performed for 24 h with intermittent evacuation every 8 h. As shown in Fig. 4b, the  $\text{H}_2$  generation rate does not remarkably decrease during the first run, but the amount of evolved  $\text{H}_2$  levels off during the second run, and the average  $\text{H}_2$  generation rate during the second run is only about 31.5% of that in the first run. The noticeable degradation of photocatalytic  $\text{H}_2$  production performance can be assigned to the inactivation of the Pt/TiO<sub>2</sub> photocatalyst and/or the consumption of cellulose. To reveal the real causes for the noticeable degradation, original amount (1.0 g) of cellulose was re-added into the photocatalytic reaction solution after 16 h of irradiation. The  $\text{H}_2$  generation rate recovers quickly during the third run after the re-addition of 1.0 g cellulose and reached 472  $\mu\text{mol h}^{-1} \text{g}^{-1}$ . These results clearly reveal that the noticeable degradation of the  $\text{H}_2$  generation rate can be due to the consumption of cellulose rather than the inactivation of the Pt/TiO<sub>2</sub> photocatalyst, indicating that the Pt/TiO<sub>2</sub> photocatalyst has high stability for photocatalytic  $\text{H}_2$  production.

## 2.4 Outdoor photocatalytic testing

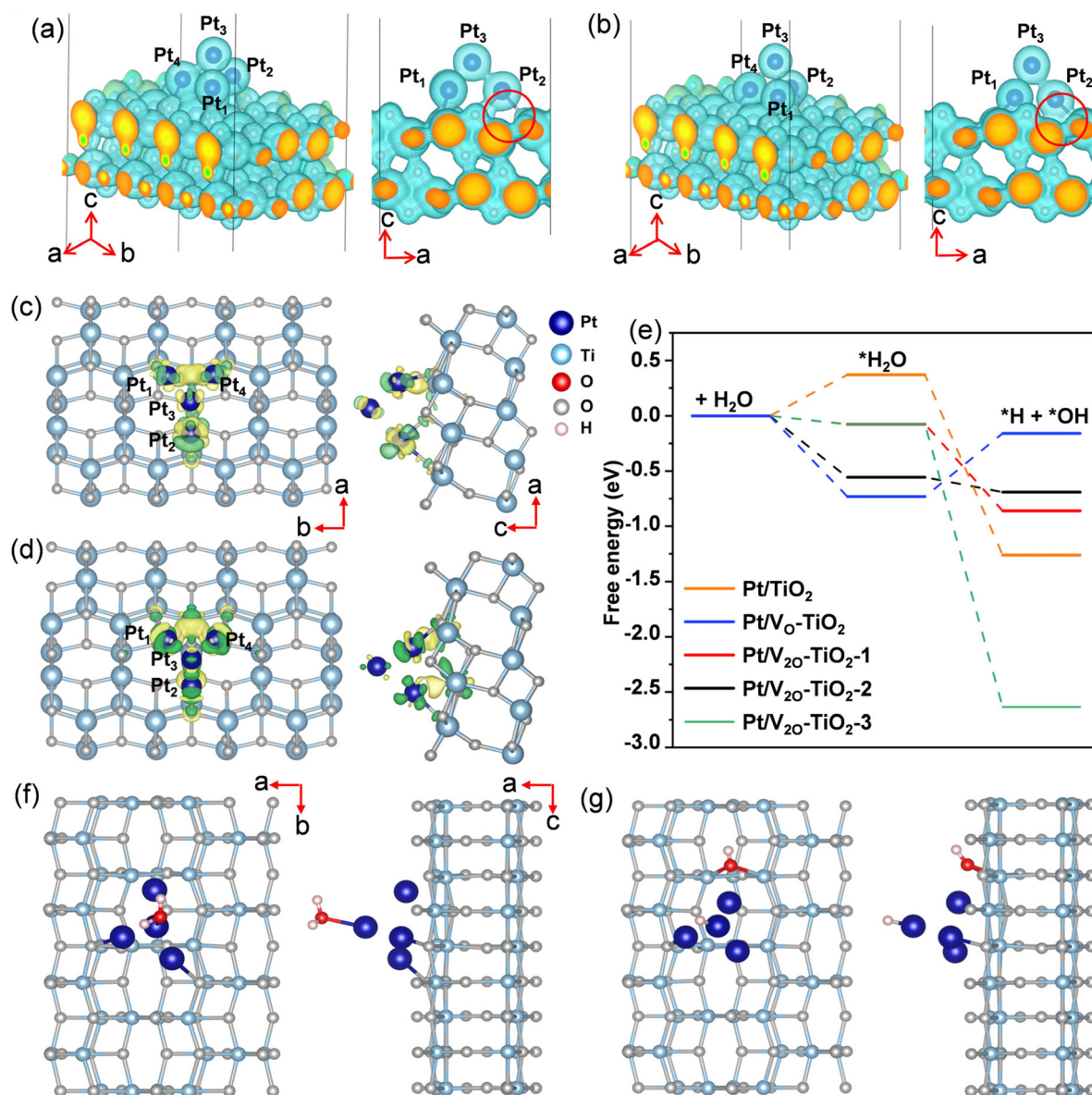
To obtain more insight into the photocatalytic activity of the Pt/TiO<sub>2</sub> photocatalyst under sunlight, photocatalytic  $\text{H}_2$  production experiments were carried out in a sealed glass reaction flask under outdoor sunlight (Fig. S19†). As shown in Fig. 4c,  $\text{H}_2$  gas was continuously produced in  $\alpha$ -cellulose, hemicelluloses (xylan from corncob) and lignin aqueous solutions under direct sunlight outdoors during a 4 h test, and the  $\text{H}_2$  generation rate was estimated to be 368, 789 and 1.56  $\mu\text{mol h}^{-1} \text{g}^{-1}$ , respectively. Under simulated sunlight irradiation with a light power density of 100  $\text{mW cm}^{-2}$ , the  $\text{H}_2$  generation rate with respect to the 0.4% Pt/TiO<sub>2</sub> photocatalyst in  $\alpha$ -cellulose, hemicelluloses (xylan from corncob) and lignin was found to be 82, 424 and 0  $\mu\text{mol h}^{-1} \text{g}^{-1}$ , respectively (Fig. 4d). Although the light intensity of sunlight outdoors (Fig. S20†) was weaker than that of simulated sunlight, the photocatalytic  $\text{H}_2$  activity of the Pt/TiO<sub>2</sub> photocatalyst under sunlight irradiation exceeds that under simulated sunlight irradiation, which can be

assigned to the large irradiation area (Fig. S21†). It has been known that glucose,<sup>35</sup> methanol,<sup>36</sup> lactic acid,<sup>37</sup> and triethanolamine (TEOA)<sup>38</sup> are frequently used as sacrificial reagents in semiconductor-based photocatalytic  $\text{H}_2$  production systems, and they were used as references for comparison. As shown in Fig. 4e, the  $\text{H}_2$  generation rate with respect to the 0.4% Pt/TiO<sub>2</sub> photocatalyst in the presence of only 1 g glucose, methanol, lactic acid and triethanolamine was respectively observed to be 740, 3867, 4085, and 2294  $\mu\text{mol h}^{-1} \text{g}^{-1}$ , demonstrating the excellent photocatalytic activity of the Pt/TiO<sub>2</sub> photocatalysts. As compared to the photocatalytic systems in  $\alpha$ -cellulose and lignocellulosic biomass, a higher photocatalytic  $\text{H}_2$  production performance of the Pt/TiO<sub>2</sub> photocatalyst was observed in glucose, methanol, lactic acid and TEOA solution, which can be ascribed to the following reasons: one is that the  $\alpha$ -cellulose and lignocellulosic biomass were in the solid state, in which it is difficult to react directly with solid photocatalysts owing to the absence of effective molecular collisions. The other reason is the fact that the photogenerated holes cannot directly oxidize lignocellulose but they can directly oxidize glucose, methanol, lactic acid and TEOA owing to their strong reducibility. The Pt/TiO<sub>2</sub> photocatalyst shows a lower photocatalytic  $\text{H}_2$  production performance in the lignocellulose system as compared to that in methanol, lactic acid and TEOA systems under the same reaction conditions, as the oxidation and decomposition of lignocellulose are the most difficult processes, which is thus related to the modest number of surface active sites of TiO<sub>2</sub>. Therefore, the large surface area of porous TiO<sub>2</sub> with abundant active sites for  $\cdot\text{OH}$  generation could be more important for the enhanced photocatalytic activity of Pt/TiO<sub>2</sub> photocatalysts for  $\text{H}_2$  production from lignocellulose.

## 2.5 Effect of O vacancy

DFT calculations were performed to understand the effect of  $\text{V}_\text{O}$  on the electron transfer between Pt nanoclusters and TiO<sub>2</sub>. The electrostatic potential distributions for the Pt nanoclusters consisting of 4 Pt atoms on the pristine TiO<sub>2</sub> surface (Pt/TiO<sub>2</sub>) and the TiO<sub>2</sub> surface with a single  $\text{V}_\text{O}$  (Pt/ $\text{V}_\text{O}$ -TiO<sub>2</sub>) were calculated, and the results are shown in Fig. 5a and b. It is found that as a result of the  $\text{V}_\text{O}$  right below the Pt (the position of the  $\text{V}_\text{O}$  is shown in Fig. S22†), the Pt atoms are bound to the TiO<sub>2</sub> surface more closely in Pt/ $\text{V}_\text{O}$ -TiO<sub>2</sub>. The bond lengths between Pt<sub>1</sub>, Pt<sub>2</sub>, Pt<sub>4</sub> and their neighboring O atoms change from 2.19, 2.29 and 2.17 Å to 2.16, 2.06, and 2.19 Å, respectively. The generally shorter Pt–O bond lengths result in a relatively lower energy barrier for the electron transfer across the interface. For instance, the space near the middle of the Pt<sub>2</sub>–O bond (highlighted by the red circles in the side view) is not wrapped by the isosurface with the electrostatic potential energy of 9 eV in Pt/TiO<sub>2</sub>, indicating a transferring energy barrier higher than 9 eV for the electrons at the Fermi level. In Pt/ $\text{V}_\text{O}$ -TiO<sub>2</sub>, the reverse happens due to the obviously shorter bond length. These results indicate that  $\text{V}_\text{O}$  defects provide a better channel for electron transfer between the TiO<sub>2</sub> surface and Pt nanoclusters. The differential charge density distribution for attach-





**Fig. 5** (a and b) 3D spatial distribution of electrostatic potential energy for Pt/TiO<sub>2</sub> (a) and Pt/V<sub>o</sub>-TiO<sub>2</sub> (b) in both tilted (left) and side (right) views. Electrons in the isosurface bounding regions have electrostatic potential energy lower than 9 eV, where the Fermi level is set as 0 eV. The red circles in the side view are used to highlight the differences between (a) and (b). (c and d) Calculated differential charge density of Pt/TiO<sub>2</sub> (c) and Pt/V<sub>o</sub>-TiO<sub>2</sub> (d), where green and yellow colors of the isosurfaces represent the dissipation and accumulation of electrons. (e) Free energy profiles for the H<sub>2</sub>O decomposition reaction on Pt/TiO<sub>2</sub> with no V<sub>o</sub>, single V<sub>o</sub> and double V<sub>o</sub>s at different positions. (f and g) Structure for \*H<sub>2</sub>O (f) and \*OH/\*H (g) adsorbed on the Pt/V<sub>20</sub>-TiO<sub>2</sub>-2 surface.

ing Pt nanoclusters on the TiO<sub>2</sub> surface were further calculated in both Pt/TiO<sub>2</sub> and Pt/V<sub>o</sub>-TiO<sub>2</sub>, as shown in Fig. 5c and d. It can be seen that there is an obvious electron redistribution when a single V<sub>o</sub> is involved and relatively greater electron dissipation is found in TiO<sub>2</sub> for Pt/V<sub>o</sub>-TiO<sub>2</sub> in comparison to Pt/TiO<sub>2</sub>. The Bader charge analysis shows that the Pt nanoclusters give 0.45 electrons to the TiO<sub>2</sub> surface in Pt/TiO<sub>2</sub> while they gain 0.13 electrons from the TiO<sub>2</sub> surface in Pt/V<sub>o</sub>-TiO<sub>2</sub>. The results indicate that O-vacancies at the interface between Pt nanoclusters and the TiO<sub>2</sub> surface will dramatically affect the

electron distribution and lead to electron-rich Pt nanoclusters, which is favorable for the \*H desorption process.

In order to study the effect of V<sub>o</sub> on the H<sub>2</sub>O decomposition reaction, another V<sub>o</sub> was introduced on the TiO<sub>2</sub> surface at different sites besides the Pt nanoclusters and three double V<sub>o</sub> structures were constructed, namely Pt/V<sub>20</sub>-TiO<sub>2</sub>-1, Pt/V<sub>20</sub>-TiO<sub>2</sub>-2, and Pt/V<sub>20</sub>-TiO<sub>2</sub>-3. The detailed positions of the vacancies in the double O-vacancy structures are shown in Fig. S22.† As is known, the decomposition of H<sub>2</sub>O needs two steps, including the adsorption and cleavage of H<sub>2</sub>O mole-



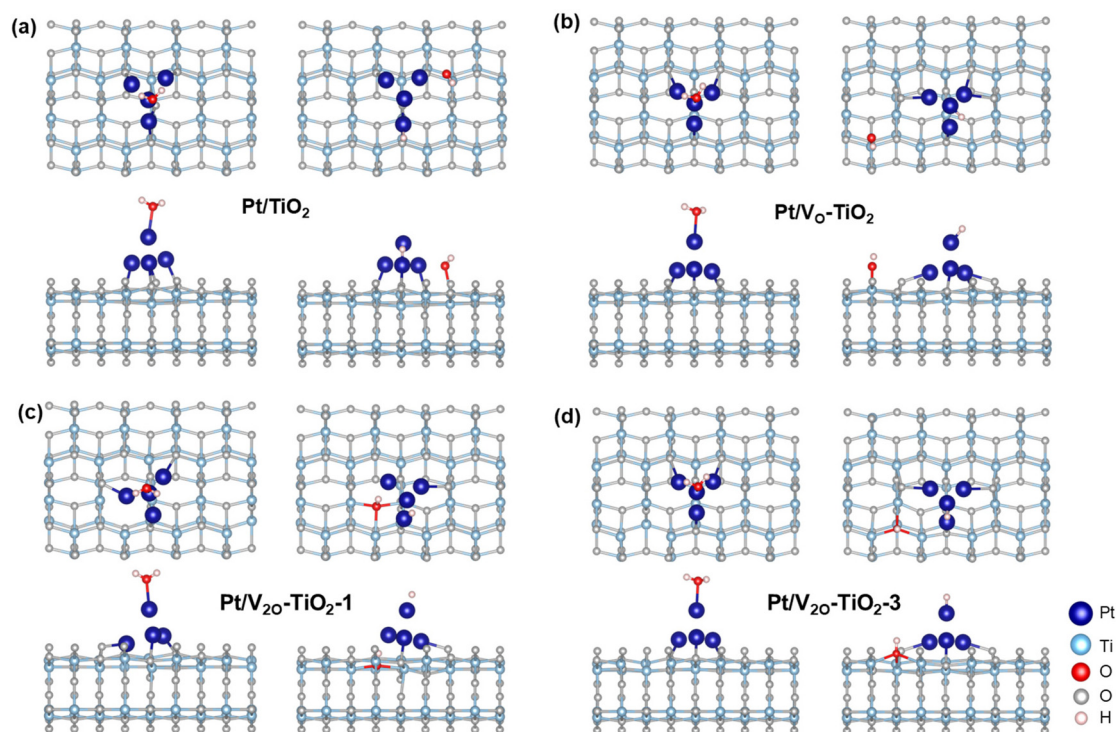


Fig. 6 Structures for \*H<sub>2</sub>O and \*OH/\*H adsorbed on the (a) Pt/TiO<sub>2</sub>, (b) Pt/V<sub>O</sub>-TiO<sub>2</sub>, (c) Pt/V<sub>2O</sub>-TiO<sub>2</sub>-1, (d) Pt/V<sub>2O</sub>-TiO<sub>2</sub>-3 surfaces.

cules. As the typical geometry of the intermediates during the reaction process for Pt/V<sub>2O</sub>-TiO<sub>2</sub>-2 shown in Fig. 5f and g and that for the other systems shown in Fig. 6, \*H<sub>2</sub>O and \*H prefer to be attached on the top of the Pt nanoclusters and \*OH prefers to fill the exposed V<sub>O</sub>. The free energy of all the intermediates for different structures was calculated and the diagram is shown in Fig. 5e. It is found that the adsorption of H<sub>2</sub>O for all the structures with V<sub>O</sub> is exothermic while that for Pt/TiO<sub>2</sub> without V<sub>O</sub> it is endothermic. This is because the electron-rich Pt nanoclusters in the structures with V<sub>O</sub> have an enhanced ability to transfer electrons to the electron-deficient O atom in H<sub>2</sub>O, leading to a stronger adsorption of H<sub>2</sub>O. In addition, when comparing the  $\Delta G$  of the H<sub>2</sub>O cleavage process for the four structures with V<sub>O</sub>, all the structures with a double V<sub>O</sub> exhibit an exothermic process while Pt/V<sub>O</sub>-TiO<sub>2</sub> with a single V<sub>O</sub> exhibits an endothermic process. This is due to the dramatically larger adsorption energy of \*OH filled in the V<sub>O</sub> than that of \*OH attached to a Ti atom on the pristine surface. These results show that the V<sub>O</sub> on the TiO<sub>2</sub> surface benefits both the charge transfer across the Pt-TiO<sub>2</sub> interface and the formation of the intermediates. Finally, Pt/V<sub>2O</sub>-TiO<sub>2</sub>-2 is considered as the best structure for the H<sub>2</sub>O decomposition process due to the appropriate free energy decrease during the reaction path, which will facilitate both the adsorption of H<sub>2</sub>O and the desorption of the formed \*H and \*OH.

## 2.6 Photocatalytic mechanism exploration

To verify that Pt/TiO<sub>2</sub> has the ability to drive both H<sub>2</sub> production and lignocellulose decomposition reactions, the conduction band (CB) and valence band (VB) levels were measured

by a combined method of UV-vis absorption and Mott-Schottky plot analysis.<sup>39,40</sup> Fig. S23† shows the Mott-Schottky plots of TiO<sub>2</sub> electrode with a flat band potential of approximately -0.12 V vs. RHE. Because the flat band potential of TiO<sub>2</sub> as an n-type semiconductor was generally more positive 0.2 eV than its CB level,<sup>41</sup> the CB level of TiO<sub>2</sub> was estimated to be -0.32 V vs. RHE, which is more negative than the reduction potential of H<sup>+</sup>. Meanwhile, the calculated VB level of TiO<sub>2</sub> located at 2.80 V vs. RHE provides sufficient driving force for the oxidation of OH<sup>-</sup> to \*OH [ $E(\text{OH}/\text{OH}^-) = +2.31$  V vs. RHE],<sup>15,42</sup> and the generated \*OH was the critical species to oxidize lignocellulosic biomass.<sup>43</sup> Photoluminescence (PL) analysis utilizing terephthalic acid (TA) as a probe molecule was performed to confirm the formation of \*OH during the photocatalytic reaction since \*OH can react with TA to generate 2-hydroxyl terephthalic acid (TAOH) with a characteristic PL peak at about 430 nm, and the PL peak intensity can provide key information about the concentration of \*OH.<sup>44</sup> Fig. S24† shows an obvious PL peak at 428 nm, confirming the successful generation of \*OH during the photocatalytic reaction. The PL peak intensity increases remarkably with increased irradiation time, indicating an increasing concentration of \*OH. Furthermore, a stronger PL peak was observed for 0.4% Pt/TiO<sub>2</sub> as compared to that of bare TiO<sub>2</sub> under the same irradiation time, indicating that the introduction of Pt on TiO<sub>2</sub> was beneficial for \*OH generation. This phenomenon can be attributed to the positive role of Pt in improving carrier separation efficiency, which provides more holes to oxidize OH<sup>-</sup> to generate \*OH.

To obtain more insight into the oxidation and decomposition of the lignocellulosic biomass, the decomposition product after 8 h of irradiation in  $\alpha$ -cellulose solution was analyzed by high performance liquid chromatography (HPLC). As shown in Fig. S25–S27,<sup>†</sup> mannose, ribose, glucuronic acid, glucose, xylose, arabinose, fucose and lactic acid were detected in the reaction solution, and the total organic carbon (TOC) was measured to be 0.23 mg mL<sup>-1</sup>, indicating that the decomposition ratio of  $\alpha$ -cellulose exceeds 12.9%. Furthermore, Fig. S28<sup>†</sup> shows that CO<sub>2</sub> was also detected in the gas of the reaction system, but the CO<sub>2</sub> to H<sub>2</sub> ratio of 7.2% is far lower than the theoretical value of 50% obtained from the equation  $(C_6H_{10}O_5)_n + 7n H_2O = 12n H_2 + 6n CO_2$ , confirming that the main oxidation products of  $\alpha$ -cellulose were small organic molecules rather than CO<sub>2</sub>. After the photocatalytic reaction, the residual  $\alpha$ -cellulose was separated from the reaction solution which was characterized by FT-IR and SEM. It is obvious that residual  $\alpha$ -cellulose exhibits surface groups of  $\delta$ -C-OH,  $\gamma$ -CO,  $\gamma$ -ring,  $\gamma$ -C-O-C,  $\delta$ -CH,  $\delta$ -CH<sub>2</sub>,  $\gamma$ -CH(sp<sub>3</sub>) and  $\gamma$ -OH (Fig. S29<sup>†</sup>). As compared to that of fresh  $\alpha$ -cellulose, the surface of residual  $\alpha$ -cellulose becomes rough after the photocatalytic reaction (Fig. S30<sup>†</sup>). These results indicate that the surface of  $\alpha$ -cellulose was constantly oxidizing during the photocatalytic reaction. Based on the above experimental observations and calculations, a proposed mechanism for the enhanced photocatalytic H<sub>2</sub> production from lignocellulosic biomass over Pt/TiO<sub>2</sub> is illustrated in Fig. S31.<sup>†</sup> When the photocatalyst was irradiated, the electrons in the VB of TiO<sub>2</sub> were excited to its CB, resulting in the formation of photogenerated electron-hole pairs.<sup>45</sup> Because the oxygen vacancies on the TiO<sub>2</sub> surface benefit the charge transfer across the Pt-TiO<sub>2</sub> interface as confirmed by DFT calculation, the photoexcited electrons in the CB of TiO<sub>2</sub> can rapidly transfer to Pt. The electrons accepted by Pt can reduce H<sup>+</sup> to evolve H<sub>2</sub>, and the holes in the VB of TiO<sub>2</sub> can oxidize H<sub>2</sub>O to  $\cdot$ OH promoted by oxygen vacancies on the TiO<sub>2</sub> surface. The  $\cdot$ OH radical has a strong oxidability to oxidize lignocellulose, resulting in the decomposition of lignocellulose biomass. And thus, the main reasons for the high photocatalytic performance of Pt/TiO<sub>2</sub> photocatalysts include the rapid charge transfer and accelerated  $\cdot$ OH generation rate derived from the oxygen vacancies on TiO<sub>2</sub> surface as well as the abundant active sites related to the large surface area of the porous TiO<sub>2</sub> microspheres and the small size of Pt.

### 3. Conclusions

In conclusion, a simple wet chemical method was developed to prepare Pt nanocluster anchored TiO<sub>2</sub> photocatalysts with abundant oxygen vacancies for light driven H<sub>2</sub> production from lignocellulosic biomass. Owing to the synergistic effect of rapid charge separation and  $\cdot$ OH generation promoted by oxygen vacancies as well as abundant active sites for H<sub>2</sub> generation, the Pt/TiO<sub>2</sub> photocatalysts show excellent photocatalytic performance for H<sub>2</sub> production from lignocellulosic biomass.

The optimized Pt/TiO<sub>2</sub> photocatalyst shows a H<sub>2</sub> generation rate of 494  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup> under 300 W Xe irradiation and an apparent yield of 3.21% at 380 nm in  $\alpha$ -cellulose aqueous solution. Meanwhile, H<sub>2</sub> gas was successfully evolved from lignocellulosic biomass of rice straw, rice hull, corncob, wheat straw, polar wood chip and bamboo.

### Author contributions

Y. J. Yuan and J. Guan designed the experiment and co-wrote the manuscript. F. G. Zhang and Q. Y. Liu performed the preparation and characterization experiments, F. G. Zhang and Q. Cheng performed the electrochemical experiments, F. G. Zhang performed the photocatalytic H<sub>2</sub> production experiments, M. Cheng and J. Guan performed the theoretical calculation. All authors analyzed the data and commented on the manuscript.

### Conflicts of interest

The authors declare no competing interests.

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