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## One-step synthesis of mesoporous Pt-Nb<sub>2</sub>O<sub>5</sub> nanocomposites with enhanced photocatalytic hydrogen production activity<sup>†</sup>

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Mesoporous  $Pt-Nb_2O_5$  photocatalysts with high photocatalytic hydrogen production activity were synthesized by a one-step method. The mesoporous structure of the as-made samples was characterized by X-ray diffraction, N<sub>2</sub> adsorption-desorption isotherms and transmission electron microscopy.  $Pt-Nb_2O_5$  exhibited higher hydrogen production activity than pure  $Nb_2O_5$  and 0.8-Pt-D-M-Nb exhibited the best photocatalytic activity. In addition,  $Pt-Nb_2O_5$  synthesized by a one-step method exhibited higher photocatalytic hydrogen production activity than that prepared by an incipient wetness impregnation method; 0.8-Pt-D-M-Nb exhibits a H<sub>2</sub> evolution rate of 9.79 mmol h<sup>-1</sup> g<sup>-1</sup>, while  $0.8-Pt-I-M-Nb_2O_5$  exhibits a H<sub>2</sub> evolution rate of 7.73 mmol h<sup>-1</sup> g<sup>-1</sup>. The enhanced photocatalytic activity of  $Pt-Nb_2O_5$  was predominantly attributed to the efficient separation of photoinduced electrons and holes.

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### 1. Introduction

After Honda and Fujishima's discovery of photocatalytic  $H_2$  evolution over a TiO<sub>2</sub> electrode in 1972,<sup>1</sup> heterogeneous semiconductor photocatalysis as a promising environmentally friendly technology for the conversion of solar energy into chemical energy has attracted augmenting attention. In the past 40 years, tremendous efforts have been devoted to investigate various inorganic and organic systems as photocatalysts for water splitting.<sup>2</sup> Some semiconductor materials such as Nb<sub>2</sub>O<sub>5</sub>, ZnO,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, and ZnS have been applied to photocatalytic H<sub>2</sub> production in aqueous solution.<sup>3,4</sup>

Among these semiconductor materials, niobium oxide as an n-type photocatalyst with a wide band gap (3.1–3.5 eV) has become widely prevalent because of its unique physical properties such as a high refractive index, good chemical and thermal stability and good photocatalytic characteristics.<sup>5</sup> But the high recombination rate of photo-induced hole–electron pairs hampers the photocatalytic efficiency. Many efforts have been made to improve the photocatalytic activity of niobium oxide by controlling the morphology, surface structure and surface modification.

Meanwhile, constructing mesoporous semiconductors is one of the effective methods to prompt the separation of photoinduced electron–hole pairs, which ultimately leads to excellent photocatalytic activity. Mesoporous materials have tunable structures, a tailored framework, high surface areas and alternative pore shapes, which shorten the transfer path of photogenerated carriers from the bulk to the surface of the photocatalyst, and therefore decrease the electron–hole combination rate.<sup>6-8</sup> It has been reported that the photocatalytic activity of mesoporous Nb<sub>2</sub>O<sub>5</sub> was 20 times higher than that of the unstructured one.<sup>4</sup>

Another method to improve the photocatalytic activity is loading the semiconductor with metal particles. Among the many tested metals, Pt has the highest work function and the smallest  $H_2$  evolution over-potential and is quite suitable for loading onto the semiconductor to enhance the photocatalytic  $H_2$  production capacity.<sup>9</sup> Platinum nanoparticles loaded onto TiO<sub>2</sub> surfaces have been demonstrated to enhance the quantum efficiency of the photochemical reaction process.<sup>10,11</sup> It is suggested that the Pt serves as a trapping centre for electrons generated in light activated TiO<sub>2</sub>. There are also some reports about Pt doped Nb<sub>2</sub>O<sub>5</sub>. Some groups loaded Pt particles onto mesoporous Nb<sub>2</sub>O<sub>5</sub> by photo-deposition to study the photochemical hydrogen production. The results show that after loading with Pt particles, the photocatalytic activity of Nb<sub>2</sub>O<sub>5</sub> was greatly improved.<sup>5,12</sup>

However, many methods for loading Pt on semiconductors mostly involve a multi-step synthesis, such as thermal impregnation and chemical and photo-deposition reduction methods.<sup>13-16</sup> These methods can load Pt onto semiconductor surfaces well but have some shortcomings. The thermal impregnation method is simple, convenient, and easily

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operated but the particle size of Pt is non-uniform and the activity of the catalyst needs to be improved. The chemical reduction method often needs chemical agents in the reduction process, such as formaldehyde and hydrazine or sodium borohydride, which are not environmentally friendly. Photodeposition is an efficient and environmentally friendly method for preparing Pt co-catalysts,<sup>17</sup> but the distribution of Pt nanoparticles on the surface of the semiconductors is non-uniform.<sup>18</sup> Recently, Pt has been loaded onto TiO<sub>2</sub> with uniform size and good distribution by a single-step method and Pt/TiO<sub>2</sub> exhibits higher photocatalytic activity than that prepared by an incipient wetness impregnation method (IWI) and PCD methods.<sup>16</sup>

In this work, Pt was loaded onto mesoporous Nb<sub>2</sub>O<sub>5</sub> by a onestep method. Compared with the traditional method, this method was simple, convenient and it was easier to obtain a uniform size and high distribution of Pt on mesoporous Nb<sub>2</sub>O<sub>5</sub>. Pt–Nb<sub>2</sub>O<sub>5</sub> exhibited higher photocatalytic H<sub>2</sub> evolution activity than pure Nb<sub>2</sub>O<sub>5</sub>. In addition, Pt–Nb<sub>2</sub>O<sub>5</sub> also exhibited much higher photocatalytic activity than that prepared by an incipient wetness impregnation method (IWI). Finally, a possible mechanism for enhancement of the photocatalytic activity in Pt–Nb<sub>2</sub>O<sub>5</sub> was also discussed.

### 2. Experimental

#### 2.1. Materials

Pluronic P-123, supplied by Aladdin, was used as a template. Anhydrous niobium chloride supplied by Alfa Aesar was used as the metal source. Anhydrous ethanol, used as the solvent, was obtained from the Nanjing Chemical Reagent Company. Chloroplatinic acid was purchased from Aladdin. It was prepared as a solution with a Pt content of 7.53 g L<sup>-1</sup>. DMPO is an abbreviation of 5,5-dimethyl-1-pyrroline-*N*-oxide, supplied by Aladdin, and was used as the trapping agent.

#### 2.2. Synthesis of the mesoporous photo-catalysts

Mesoporous Nb<sub>2</sub>O<sub>5</sub> was synthesized by versatile evaporation induced self-assembly (EISA).<sup>19</sup> 0.6 g of Pluronic P-123 was dissolved in 20 ml anhydrous ethanol followed by addition of 2.3 mmol NbCl<sub>5</sub> under vigorous stirring. The as-prepared sol was kept at 40 °C for 2 days and then a gel was obtained. Subsequently, the gel was calcined firstly at 350 °C for 6 h and then at 450 °C for 6 h. The as-prepared white powder was named M–Nb.

The mesoporous  $Nb_2O_5$  loaded with Pt nanoparticles was synthesized by two different methods.

(1) One-step method. 0.6 g of Pluronic P-123 was dissolved in anhydrous ethanol followed by addition of 2.3 mmol NbCl<sub>5</sub> under continuous stirring. Then the HPtCl<sub>6</sub> solution was added drop wise to the above solution. The as-prepared sol was kept at 40 °C for 2 days and then a gel was obtained. Subsequently, the gel was calcined firstly at 350 °C for 6 h and then at 450 °C for 6 h. Thereby, a series of Nb<sub>2</sub>O<sub>5</sub> compounds loaded with different Pt contents were prepared by adjusting the amount of HPtCl<sub>6</sub>. The prepared samples were denoted as *x*-Pt-D-M-Nb, where *x*  refers to the controlled volume ratio of Pt (x = 0.1%, 0.3%, 0.50%, 0.80%, 1.0%, 1.5%), which would also be abbreviated to 0.1-Pt-D-M-Nb, 0.3-Pt-D-M-Nb, 0.5-Pt-D-M-Nb, 0.8-Pt-D-M-Nb, 1.0-Pt-D-M-Nb, and 1.5-Pt-D-M-Nb.

(2) Incipient we tness impregnation method. 0.4 g of mesoporous  $\rm Nb_2O_5$  and 20 ml ethanol was added into a special vase. Then the HPtCl6 solution was added and the Pt content was 0.8% wt relative to the mesoporous  $\rm Nb_2O_5$ . After ultrasonication for 30 min, the ethanol was removed by a rotary evaporation method. The obtained buff solid was firstly calcined at 350 °C for 6 h and then at 450 °C for 6 h. The Pt nanoparticle loading was denoted as 0.8-Pt–I–M–Nb.

#### 2.3. Sample characterization

The samples were characterized by XRD recorded on a Bruker D8 Advance X-ray diffractometer equipped with a Cu Ka X-ray source ( $\lambda = 1.5406$  Å). The nitrogen adsorption-desorption isotherms were measured on a Micromeritics apparatus model ASAP 2020 using the Brunauer-Emmett-Teller (BET) method at 77 K after the sample had been degassed in a flow of N2 at 160 °C for 4 h. The BET surface area was calculated from the linear part of the BET plot ( $P/P_0 = 0.05-0.30$ ). The average pore size and the pore size distribution plots were estimated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula. Transmission electron microscopy (TEM) and HRTEM images were obtained on a JEOL model JEM 2010 EX microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy was carried out on an ESCALAB 250 XPS system with a mono-chromatized Al Ka X-ray source (15 kV, 200 W, 500 mm, pass energy = 20 eV). All binding energies were referenced to the C 1s peak at 284.58 eV of surface adventitious carbon. Photo-luminescence (PL) measurements were obtained on an Edinburgh Analytical Instrument PLS920 FL spectrophotometer and a 320 nm He-Cd laser was used as an excitation light source.

#### 2.4. Photocatalytic activity measurements

The photocatalytic methanol reforming reactions to generate H<sub>2</sub> were carried out in a closed gas circulation system. The reaction cell was equipped with an inner irradiation quartz reaction vessel and a cooling water jacket to keep the temperature at 10 °C. A scheme of the photo-reactor is shown in Fig. S1.<sup>†</sup> 0.1 g of photocatalyst powder was suspended in 165 ml distilled H<sub>2</sub>O in the inner quartz cell (Fig. S1<sup>†</sup>) and stirred at a speed of 550 rpm. Then 5 ml methanol was added to the suspension as an oxidizable reducing reagent. A 165 W highpressure mercury lamp was used to provide a UV light source. The electronic spectrum of the lamp is shown in Fig. S2.<sup>†</sup> Prior to irradiation, the reaction system was evacuated using a mechanical pump and then filled with 101 kPa of high-purity Ar (>99.99%). This process was repeated three times in order to remove O<sub>2</sub> from the system. At given irradiation time intervals, the generated H<sub>2</sub> was circulated using a micro diaphragm gas pump in the system and its amount was determined using an online gas chromatograph (GC112A, Shanghai Precision Scientific Instrument Co, Ltd, TCD, Ar carrier).

## 3. Results and discussion

#### 3.1. Sample characterization

XRD analysis was carried out to investigate the mesoporous structure and phase structures of the catalysts. In the wideangle XRD patterns (Fig. 1b), two broad peaks were observed at 25 and 55° which can be indexed to the orthorhombic crystallized phase (*Pbam* 55, JCPDS no. #71-0336), indicating that the three samples were in a low crystalline phase because of the low calcination temperatures. No platinum species were detected for 0.8-Pt–D–M–Nb and 0.8-Pt–I–M–Nb owing to the small content of Pt.

#### 3.2. Pore structure

The pore structures of these materials were analysed by smallangle XRD, nitrogen adsorption-desorption isotherms, TEM and HRTEM. In Fig. 1a, the low-angle XRD patterns of M-Nb and 0.8-Pt-D-M-Nb samples showed well-resolved peaks at  $1.2^{\circ}$ and  $2.0^{\circ}$ , indicating an ordered 2D-hexagonal mesoporous structure (space group *P6mm*). The obvious low-angle X-ray diffraction of 0.8-Pt-D-M-Nb showed that loading of platinum on Nb<sub>2</sub>O<sub>5</sub> by the one-step method did not break the mesoporous structure. However, the low-angle XRD patterns of 0.8-Pt-I-M-Nb have lower peaks at  $1.2^{\circ}$  and  $2.0^{\circ}$ . This indicated that the mesoporous structure may have been damaged a little by platinum during the impregnation process. In Fig. 1b, we can see the M-Nb, 0.8-Pt-D-M-Nb and 0.8-Pt-I-M-Nb wide-angle XRD patterns. All of them have two similar, extremely broad peaks at 25° and 55°, which is in accordance with Lin and Chen's report.<sup>4,12</sup> Those broad peaks indicate an amorphous phase by a lack of long-range order.

Fig. 2 shows nitrogen adsorption-desorption isotherms and BJH pore size distribution plots of M–Nb, 0.8-Pt–D–M–Nb and 0.8-Pt–I–M–Nb. From the N<sub>2</sub> adsorption-desorption isotherms, the samples (M–Nb, 0.8-Pt–D–M–Nb and 0.8-Pt–I– M–Nb) showed the characteristics of mesoporous materials. But their size distributions did exhibit some differences, where the most probable aperture distribution of M–Nb was at 5.37 nm and that of 0.8-Pt–D–M–Nb was at 6.22 nm. However, the samples of 0.8-Pt–I–M–Nb possess an average pore diameter of *ca.* 7.55 nm. In addition, the pore size distribution of 0.8-Pt–I–M–Nb was wider than those of M–Nb and 0.8 Pt–D–M– Nb. These results indicated that loading of Pt onto mesoporous Nb<sub>2</sub>O<sub>5</sub> by the incipient wetness impregnation method more seriously damaged the mesoporous structure of Nb<sub>2</sub>O<sub>5</sub> than by the one-step method.

More structural information about Nb<sub>2</sub>O<sub>5</sub>, Pt–D–M–Nb and Pt–D–M–Nb was provided by TEM analysis. The TEM image in Fig. 3a reveals that Nb<sub>2</sub>O<sub>5</sub> showed wormhole-like mesoporous structures with a diameter of 4–6 nm in the pore channels and the pores were well-ordered hexagonal arrays of mesoporous symmetry. The TEM images in Fig. 3b of 0.8-Pt–D–M–Nb also revealed well ordered two-dimensional pores. Compared with M–Nb, the structure of 0.8-Pt–D–M–Nb has little changed.

However, the TEM of 0.8-Pt-I-M-Nb in Fig. 3c showed that the wormhole-like mesoporous structures were damaged to



Fig. 1 The small-angle XRD (a) and wide-angle XRD patterns (b) of M–Nb and the 0.8-Pt–D–M–Nb and 0.8-Pt–I–M–Nb samples.



Fig. 2 The  $N_2$  adsorption–desorption isotherm (a) and Barret–Joy-ner–Halenda (BJH) pore size distribution plots (b) of (red)  $M-Nb_2O_5$ , (black) 0.8-Pt-D-M-Nb, and (blue) Pt-I-M-Nb.



Fig. 3 TEM images obtained of M–Nb (a), 0.8-Pt–D–M–Nb (b), and 0.8-Pt–I–M–Nb<sub>2</sub>O<sub>5</sub> (c) and HRTEM images of 0.8-Pt–D–M–Nb (d).

some extent. From Fig. 3d, HRTEM analysis of 0.8-Pt–D–M–Nb showed that there are many black spots that were distributed uniformly on Nb<sub>2</sub>O<sub>5</sub>. Their lattice space is 0.22 nm which is well matched with the (111) lattice spacing of the face-centre Pt cubic phase,<sup>20</sup> indicating that the Pt nanoparticles were deposited uniformly on the Nb<sub>2</sub>O<sub>5</sub>. However, the size of the Pt particles was larger than that of those in Pt–D–M–Nb and the distribution of Pt was non-uniform as shown in Fig. S3.<sup>†</sup> These results suggest that the Pt particle loading on Nb<sub>2</sub>O<sub>5</sub> by the one-step method has little influence on the mesoporous structure of Nb<sub>2</sub>O<sub>5</sub> and the Pt particle loading on Nb<sub>2</sub>O<sub>5</sub> by the impregnation method to a certain extent damaged the mesoporous structure of Nb<sub>2</sub>O<sub>5</sub>.

#### 3.3. Photocatalytic activity

The photocatalytic activities of M–Nb and Pt–D–M–Nb were examined by the photocatalytic hydrogen production upon UVlight irradiation as shown in Fig. 4. As can be seen, M–Nb exhibits little photocatalytic activity for hydrogen production.



Fig. 4 The rates of  $H_2$  production of mesoporous Pt-D-M-Nb with different Pt contents of 0, 0.1, 0.3, 0.5, 0.8, 1.5, and 2.0 wt%.

After loading a small amount (0.1%) of Pt, the activity for hydrogen production is greatly increased. In addition, with the increase in the content of Pt, the hydrogen production activity also gradually improved. After reaching a maximum, the production activity declined with the increase in the content of Pt. This phenomenon was similar to Sreethawong's work,<sup>16</sup> which reported that there is a certain optimum content of Pt for each synthesis method. In this work, the optimum amount of Pt loading is 0.8% wt, which exhibits the H<sub>2</sub> evolution rate 9.79 mmol h<sup>-1</sup> g<sup>-1</sup>.

According to previous suggestions,<sup>16,21</sup> with the initial increase in the content of Pt, a mesoporous wall of Nb<sub>2</sub>O<sub>5</sub> may carry more Pt nanoclusters that facilitate the separation of photo-generated electron-hole pairs, and lead to an increase in the photocatalytic activity. However, excess metal particles loaded on the semiconductor may form a recombination centre for electron-hole pairs. Despite the activities, the stability of the photo-catalyst plays an important role in its practical application. Thus, a stability test of 0.8-Pt-D-M-Nb for H<sub>2</sub> evolution under UV light irradiation was carried out 5 times in recycle experiments. As shown in Fig. S4,† the hydrogen evolution rate is linear as a function of time and remains almost unchanged after 5 cycles of UV irradiation, indicating the sufficient stability of 0.8-Pt-D-M-Nb for photocatalytic hydrogen evolution.

In addition to the content of Pt, the same Pt loading content on Nb<sub>2</sub>O<sub>5</sub> prepared by different methods also exhibited different photocatalytic activity. As shown in Fig. 5, 0.8-Pt-D-M-Nb exhibits a H<sub>2</sub> evolution rate of 9.79 mmol h<sup>-1</sup>  $g^{-1}$ , while 0.8-Pt-I-M-Nb<sub>2</sub>O<sub>5</sub> exhibits a H<sub>2</sub> evolution rate of 7.73 mmol h<sup>-1</sup>  $g^{-1}$ . The preparation methods have great effects on the surface distribution, size of the Pt particles and the chemical states of the Pt particles, which may influence the photocatalytic activity of Pt modified catalysts. As reported, Pt particles loaded on TiO<sub>2</sub> by a Pt-citrate sol are very finely dispersed and exhibit higher photocatalytic activity, but those that are prepared by an irradiation deposition method agglomerated into large particles and show lower photocatalytic activity.<sup>22</sup> They suggested that Pt particles that used a one step method may deposit on the surface of TiO<sub>2</sub>



Fig. 5 The rates of  $H_2$  production of mesoporous 0.8-Pt–D–M–Nb and 0.8-Pt–I–M–Nb.

through the mesoporous network instead of on the outer and near the outer surface of the  $TiO_2$  supporter.<sup>16</sup> In this case, the Pt particles prepared by the one step method were obviously embedded in the network instead of on the outer and near the surface of the Nb<sub>2</sub>O<sub>5</sub> aggregates (TEM images (b and d)). However, compared with the one-step method, the Pt nanoparticles prepared by the impregnation method precipitated on the Nb<sub>2</sub>O<sub>5</sub> surface, and the sizes were larger than those prepared by the one step method (from the TEM images).

3.3.1. XPS analysis of the different catalyst loading methods. To further characterize the differences in Pt-D-M-Nb and Pt-I-M-Nb, the chemical states of Pt-D-M-Nb and Pt-L-M-Nb were investigated by XPS analysis. As shown in Fig. S5,† only C, Nb, O and Pt were detected in the samples of Pt-D-M-Nb and Pt-I-M-Nb. The C 1s peak at around 285.0 eV is ascribed to the carbon signal from within the instrument and was used for calibration. The O 1s in Fig. 6a at around 531.39-531.55 eV is characteristic of O-Nb in all samples, and the O 1s peak at 529.82-530.06 eV is due to the surface hydroxyl groups (O-H) on the samples.<sup>23</sup> The Nb 3d<sub>5/2</sub> and Nb 3d<sub>3/2</sub> XPS in Fig. 6b show two peaks at 207.01 and 209.74 eV, respectively, which is in good agreement with those of Nb<sub>2</sub>O<sub>5</sub>.<sup>24</sup> No additional diffusive electronic states were observed from the spectra of the Nb elements of the M-Nb sample. But the binding energies of Nb reveal small chemical shifts due to the addition of the Pt element. The binding energy of Nb on Pt-D-M-Nb shifts from 207.01 eV to 206.81 eV and that of Pt-I-M-Nb shifts from 207.01 eV to 206.66 eV. These shifts were ascribed to the interaction of the Nb species with Pt particles and the size of Pt particles. The larger the Pt particles, the more the binding energy of Nb decreases.

The Pt 4f XPS spectrum of 0.8-Pt-D-M-Nb and 0.8-Pt-I-M-Nb is shown in Fig. 6c. It showed that both the Pt spectra of 0.8-Pt-D-M-Nb and 0.8-Pt-I-M-Nb exhibit three chemical states. The peaks at 70.0 eV and 71.3 eV can be attributed to Pt<sup>0</sup>. The peak at 73.1 eV was particular to Pt<sup>2+</sup> and the peak at 74.8 eV was due to Pt4+.25 However, compared to 0.8-Pt-I-M-Nb, the number of oxidized states of Pt<sup>2+</sup> and Pt<sup>4+</sup> in 0.8-Pt-D-M-Nb is fewer than in 0.8-Pt-I-M-Nb. Generally, Pt<sup>0</sup> is beneficial to the separation of electron-hole pairs but too many oxidized states of Pt<sup>2+</sup> and Pt<sup>4+</sup> may form recombination centres of electron-hole pairs, which reduces the generation of radicals. According to the photocatalytic hydrogen production of M-Nb, 0.8-Pt-D-M-Nb and 0.8-Pt-I-M-Nb (Fig. 5), 0.8-Pt-D-M-Nb may exhibit a higher separation rate of electron-hole pairs than that of 0.8-Pt-I-M-Nb and M-Nb. Here, the fluorescence spectra of M-Nb, 0.8-Pt-D-M-Nb and 0.8-Pt-I-M-Nb were further tested. Fluorescence spectra are a helpful method to disclose the efficiency of charge carrier trapping, migration and transfer in semiconductors.<sup>29</sup> As shown in Fig. 7, all the spectra revealed two emission bands located at  ${\sim}400$  and  ${\sim}475$ nm. The two signals are attributed to the surface irradiative recombination and bulk irradiative recombination below the conductive band and free holes at the valance band edge.<sup>30</sup> However, the intensity of both the emission bands in 0.8-Pt-D-M-Nb and 0.8-Pt-I-M-Nb was much lower than that in



Fig. 6 X-ray photoelectron spectra (XPS) of (a) O 1s and (b) Nb 3d of M–Nb, 0.8-Pt–D–M–Nb and 0.8-Pt–I–M–Nb; (c) Pt 4f spectrum of 0.8-Pt–D–M–Nb and 0.8-Pt–I–M–Nb. The orange peak is assigned to Pt<sup>0</sup>, the blue peak to Pt<sup>2+</sup>, and the pink peak to Pt<sup>4+</sup>.

 $Nb_2O_5$ , indicating a quenching of PL emissions due to the incorporation of Pt on the  $Nb_2O_5$  surface. In addition, their photoluminescence (PL) spectrum intensity decreases in the order 0.8-Pt-D-M-Nb < 0.8-Pt-I-M-Nb < M-Nb, indicating the highest separation of photo-induced electron-hole pairs in the case of 0.8-Pt-D-M-Nb.

**3.3.2.** ESR analysis of the different catalyst loading methods. According to previously-reported work, the photocatalytic  $H_2$  production reaction process is a complex process. The process involves several elemental steps such as separation and interfacial transfer of photogenerated carriers, electron-reduction, hole-oxidization, and sequential radical reactions, in



Fig. 7 Fluorescence spectra of M–Nb, 0.8-Pt–D–M–Nb and 0.8-Pt– I-M-Nb.

which the generation of radicals such as 'OH and 'O<sup>2-</sup> has a very significant task in the photocatalytic process.<sup>26</sup> Analysis of these radicals will help us to better understand the co-catalyst effect of Pt in mesoporous Nb<sub>2</sub>O<sub>5</sub>. Thus, we compared the generation capability of 'O<sub>2</sub><sup>-</sup> and 'OH radicals of 0.8-Pt–D–M– Nb and 0.8-Pt–I–M–Nb in the dark and under UV light irradiation by the DMPO spin-trapping EPR technique. There were no signals in the dark, confirming that the radicals were generated by catalyst irradiation under UV light (not shown here). This



**Fig. 8** (A) EPR signals of the DMPO- $^{-}$ CH<sub>2</sub>OH and  $^{-}O_{2}^{-}$  spin adducts in the sample–methanol suspension; (B) EPR signals of the DMPO –  $^{-}$ OH spin adducts in the sample – water suspension.

observation is highly consistent with the results reported by Jie  $Xu^{27}$ . Fig. 8a shows the EPR signal of 'O<sub>2</sub><sup>-</sup> and CH<sub>2</sub>OH' in the suspension of 0.8-Pt-D-M-Nb, 0.8-Pt-I-M-Nb and -M-Nb in a DMPO/methanol system. Two sets of lines were assigned unambiguously to the DMPO-'O2- and DMPO-CH2OH' adducts, respectively.25 The EPR signal intensity of both the DMPO-'O<sub>2</sub><sup>-</sup> and DMPO-CH<sub>2</sub>OH adducts decreases in the order of 0.8-Pt-D-M-Nb > 0.8-Pt-I-M-Nb > M-Nb, which indicates the greater abilities for generating 'O<sub>2</sub><sup>-</sup> radicals of 0.8-Pt-D-M-Nb than those of 0.8-Pt-I-M-Nb and Nb<sub>2</sub>O<sub>5</sub>. The EPR signal of the DMPO-'OH adducts in the irradiated catalyst/DMPO/water system is shown in Fig. 8b. The four characteristic peaks with intensity of 1:2:2:1 were assigned to DMPO-'OH. It can be seen that the EPR signal intensity of the DMPO-'OH adducts decreases in the order of 0.8-Pt-D-M-Nb > 0.8-Pt-I-M-Nb > M-Nb. In Gu's report,<sup>26</sup> the intensity of 'OH reflects the hole transfer rate of a photocatalyst and the signal of DMPO-'O<sub>2</sub><sup>-</sup> could judge the electron transfer rate. The nano-particles of Pt on the support will capture the photo-generated electrons of the photocatalyst and decrease the recombination of the photoexited electron-hole pairs.10 The above results indicate that the interfacial transfer rate has been improved by Pt NPs and that the Pt NPs prepared by the one step method exhibit a higher interfacial transfer rate than that prepared by the impregnation method.

**3.3.3. Possible mechanism.** According to the photocatalytic activity and analysis of the ESR and PL, a possible mechanism for photocatalytic hydrogen evolution was proposed as illustrated in Scheme 1. When under UV light irradiation, the mesoporous Nb<sub>2</sub>O<sub>5</sub> generates photo-excited electrons and holes. Electrons and holes may experience two major processes. On the one hand, the electrons and holes migrate to the surface of the photocatalyst and then recombine. On the other hand, the photo-electrons are captured by the Pt particles and the photo-generated holes oxidize CH<sub>3</sub>OH to CO<sub>2</sub>. The latter process prompts the separation of the photocatalytic activity. Pt has the highest work function and the smallest H<sub>2</sub> evolution over-potential which is beneficial to H<sub>2</sub> production.<sup>20,28</sup>



Scheme 1 Schematic of photocatalytic hydrogen evolution over  $\mbox{Pt-Nb}_2\mbox{O}_5$  under UV light irradiation.

## 4. Conclusions

Mesoporous Nb<sub>2</sub>O<sub>5</sub> with a uniform and narrow pore size distribution was prepared. The loading of platinum onto the mesoporous Nb<sub>2</sub>O<sub>5</sub> greatly improved the photocatalytic H<sub>2</sub> evolution activity. Pt–Nb<sub>2</sub>O<sub>5</sub> prepared by a one step method provided superior and more stable photocatalytic activity than that prepared by an impregnation method. The main reason may be ascribed to the fact that the Pt particles loaded onto Nb<sub>2</sub>O<sub>5</sub> by the one step method are more uniform and smaller in size, which was beneficial to interfacial transfer and produced more radicals.

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