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# Room temperature synthesis of reduced $\text{TiO}_2$ and its application as a support for catalytic hydrogenation†

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Reduced  $\text{TiO}_2$  ( $\text{TiO}_{2-x}$ ) materials have attracted increasing attention due to their large solar absorption and high photo-activity. However, their synthesis procedures usually involve harsh conditions, such as high temperature and/or high pressure. Herein, a facile solid ball-milling method for the synthesis of  $\text{TiO}_{2-x}$  under ambient conditions was developed. By using finely dispersed Na/NaCl powders as the reducing agent and  $\text{TiO}_2$  (P25, Degussa) as the precursor, a series of  $\text{TiO}_{2-x}$  of 20–30 nm with a controllable reduction degree can be successfully synthesized through adjusting the reaction conditions. The surface area of  $\text{TiO}_{2-x}$  is much larger than that of pristine  $\text{TiO}_2$ , showing its great potential as a catalyst support in chemical reactions. Our experimental results show that uniform Ru particles with particle size less than 1 nm can be well dispersed on the surface of the  $\text{TiO}_{2-x}$  due to the enhanced surface area and plenty of oxygen vacancies in  $\text{TiO}_{2-x}$ . As a result, Ru/ $\text{TiO}_{2-x}$  exhibited superior activity upon catalytic hydrogenation of *N*-methylpyrrole in comparison with Ru/ $\text{TiO}_2$ .

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## Introduction

Since Honda and Fujishima discovered hydrogen generation from water by using titanium dioxide ( $\text{TiO}_2$ ) as a photo-electrode,<sup>1</sup>  $\text{TiO}_2$  has drawn much attention for its applications in pigments,<sup>2</sup> sunscreens<sup>3</sup> and photocatalysis.<sup>4,5</sup> Apart from the applications in photo-catalysis,  $\text{TiO}_2$  is also a unique material widely employed as a catalyst support for selective catalytic hydrogenation,<sup>6–8</sup> oxidation<sup>9,10</sup> and electrochemical<sup>11,12</sup> reactions.

In 2011, Mao *et al.* found that the reduction of  $\text{TiO}_2$  nanoparticles through hydrogenation was an effective strategy to improve visible light absorption and photo-activity of  $\text{TiO}_2$ .<sup>13</sup> Since then, many studies have been devoted to the synthesis of reduced  $\text{TiO}_2$  (denoted as  $\text{TiO}_{2-x}$ ) that has abundant oxygen vacancies and  $\text{Ti}^{3+}$  species. Annealing  $\text{TiO}_2$  precursors in a reducing gas atmosphere ( $\text{H}_2$  or  $\text{H}_2$  plasma) under high temperature and/or high pressure is a common synthetic route for the preparation of  $\text{TiO}_{2-x}$ .<sup>13,14</sup> Other promising chemical methods including Al vapor,<sup>11</sup>  $\text{CaH}_2$  (ref. 15) and  $\text{NaBH}_4$  (ref. 16)

reduction *etc.*, can also produce  $\text{TiO}_{2-x}$ , where high reaction temperatures were required. Furthermore, electrons,  $\text{Ar}^+$  or other high energy particle bombardments have also been employed to produce  $\text{TiO}_{2-x}$  materials.<sup>17</sup> Despite those significant advances in the synthesis of  $\text{TiO}_{2-x}$ , it is still highly desirable to develop facile and effective synthetic strategies for the scalable synthesis of  $\text{TiO}_{2-x}$  under mild conditions.

As a  $\text{TiO}_2$  derived material with unique electronic properties,  $\text{TiO}_{2-x}$  may show promises as a new kind of catalyst support, however, only limited investigations have been published so far. A model study of Au on a reduced titanium oxide ordered film has demonstrated that the strength of the interaction between over-layer Au and the support comprised of strong bonding between Au and Ti, yielding an electron-rich Au and exhibiting an exceptional high activity for CO oxidation.<sup>18</sup> Very recently, the hydrogen treated  $\text{TiO}_2$  nanotube arrays with more oxygen vacancies and hydroxyl groups was synthesized which served as highly ordered nanostructured electrode supports and were able to significantly improve the electrochemical performance and durability of fuel cells.<sup>11</sup> The unique properties of the  $\text{TiO}_{2-x}$  supported catalysts may be derived from (1) the encapsulation of metal particles in  $\text{TiO}_{2-x}$ , presumably because of the so-called strong metal support interaction (SMSI)<sup>19</sup> between metal and  $\text{TiO}_{2-x}$ , (2) the strong bonding between the metal atoms at the interface with surface defects (reduced Ti site) or (3) the electrons transfer between metal particles and  $\text{TiO}_{2-x}$ .<sup>20</sup> It is, therefore, very interesting to investigate the performance of  $\text{TiO}_{2-x}$  supported catalysts in related chemical reactions.

In this paper, a solid ball-milling reduction process for the synthesis of nanosized  $\text{TiO}_{2-x}$  from crystalline  $\text{TiO}_2$  (P25,

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Degussa) at room temperature was developed. The reductant is Na that has been well dispersed in NaCl powders. A series of  $\text{TiO}_{2-x}$  samples with color changing from white to dark blue manifesting the increase in the reduction degree can be facilely prepared. The  $\text{TiO}_{2-x}$  possesses much higher surface area and visible light absorption than those of the pristine  $\text{TiO}_2$ . Highly dispersed Ru particles supported on  $\text{TiO}_{2-x}$  were prepared and tested as catalyst for the hydrogenation of *N*-methylpyrrole, which obviously outperformed that of Ru particles supported on pristine  $\text{TiO}_2$ , evidencing stronger promoting effect of  $\text{TiO}_{2-x}$  on Ru.

## Experimental section

### Chemicals and materials

$\text{TiO}_2$  were purchased from Degussa. Na,  $\text{NaBH}_4$ , NaCl, and NaOH were purchased and used directly without further purification. Tetrahydrofuran (THF) was purchased from Merck, and dried by molecular sieve before usage.

### Preparation of Na/NaCl fine powders

Due to the soft and ductile nature of Na metal, NaCl powders were used to disperse Na metal by ball milling.<sup>21</sup> In a typical experiment, Na metal and NaCl powders with a weight ratio of 1/10 were mechanically milled under argon atmosphere using a Retsch PM400 planetary ball milling. All the manipulations were conducted inside a glove box filled with purified argon. The ball milling was carried out at a milling rate of 150 rpm for 4 h at room temperature, and then black Na/NaCl fine powders can be obtained.

### Synthesis of $\text{TiO}_{2-x}$

The Na/NaCl fine powder, composed of small Na particles dispersed by NaCl, is expected to be an effective reducing agent for the reduction of crystalline  $\text{TiO}_2$  to  $\text{TiO}_{2-x}$  (Scheme 1). In a typical experiment, crystalline  $\text{TiO}_2$  was milled with Na/NaCl fine powders with a weight ratio of 1/*n* (*n* = 1–4) under argon atmosphere using a Retsch PM400 planetary ball milling, which was carried out at a series of milling rates, such as 80, 120, 150

and 180 rpm at room temperature. The samples milled for 0.25 to 4 hours were collected and washed with deionized water for several times to remove the Na and NaCl. Finally, the obtained  $\text{TiO}_{2-x}$  products were dispersed in a small amount of deionized water and then vacuum-dried at room temperature to get  $\text{TiO}_{2-x}$  powders. The synthesized  $\text{TiO}_{2-x}$  samples are marked as  $\text{TiO}_{2-x}$ -*n-v-t*, where *n*, *t* and *v* stand for weight ratio between Na/NaCl and  $\text{TiO}_2$ , ball milling rate and reaction time, respectively. For example,  $\text{TiO}_{2-x}$ -4-80-1 means that the obtained  $\text{TiO}_{2-x}$  was synthesized at a milling rate of 80 rpm for 1 h, and the weight ratio of Na/NaCl fine powders to P25 is 4.

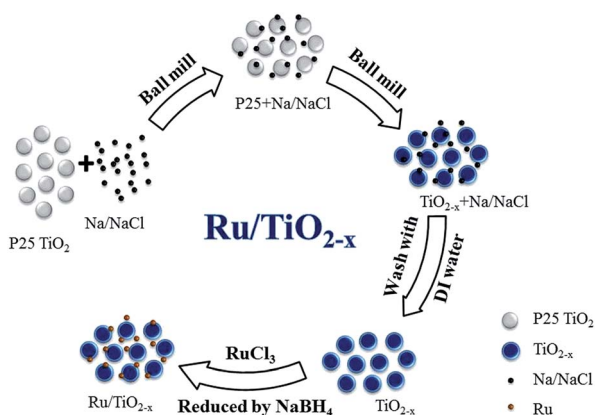
### Preparations of catalysts and characterizations

5% Ru/ $\text{TiO}_2$  and 5% Ru/ $\text{TiO}_{2-x}$  catalysts were both prepared by a deposition method using  $\text{NaBH}_4$  as the reducing agent (Scheme 1). The support  $\text{TiO}_2$  or  $\text{TiO}_{2-x}$  was added to a certain concentration of  $\text{RuCl}_3$  aqueous solutions and stirred for 6 h. Then a  $\text{NaBH}_4$  solution was added slowly to reduce the  $\text{Ru}^{3+}$  cations with intensive stirring. Finally the powders were filtered, washed with deionized water and dried under vacuum overnight.

Powder X-ray diffraction (XRD) patterns were recorded on an X'Pert Pro (PANalytical) diffractometer with Cu K $\alpha$  radiation at 40 kV and 40 mA. Raman spectra were recorded with a Renishaw Raman spectrometer equipped with a He/Ne laser with a wavelength of 514 nm. Transmission electron microscopy (TEM) images were obtained on a JEOL 2000EX electronic microscope operating at 120 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected on a JEM-2100F instrument equipped with STEM dark-field (DF) detector operating at 200 kV. The specific surface area was measured on Autosorb-1 system (Quantachrome, USA) by  $\text{N}_2$  adsorption isotherm through BET method. The X-ray photoelectron spectroscopy (XPS) measurements were performed using an Escalab 250 Xi X-ray photoelectron spectrometer (Thermo Scientific) with non monochromatic Al K $\alpha$  radiation (photon energy, 1486.6 eV). Due to the overlapped signal of C 1s and Ru 3d, all the samples were mixed with a certain amount of silicon that is used for calibration (Si 2p at 98.4 eV).<sup>22</sup> The UV-Vis absorption spectra were measured on a Shimadzu UV 2600 UV/Vis spectrophotometer. The Ru loadings of the catalysts were determined by inductively coupled plasma spectrometry (ICP-OES, optima 7300DV, Perkin-Elmer, USA).

### Hydrogenation of *N*-methylpyrrole

5% Ru/ $\text{TiO}_2$  and 5% Ru/ $\text{TiO}_{2-x}$  catalysts were employed for catalytic hydrogenation of *N*-methylpyrrole ( $\text{C}_5\text{H}_7\text{N}$ ), which is a commercial chemical with large annual global production. The reactions were carried out in the autoclave reactor (PARR®5500 series compact reactor). 100 mg catalyst (Ru/ $\text{TiO}_2$  or Ru/ $\text{TiO}_{2-x}$ ), 425  $\mu\text{L}$  *N*-methylpyrrole and 30 mL THF (as the solvent) were put into the autoclave filled with Ar. The temperature programmer began to heat the reactor with stirring speed of 500 rpm. When the temperature of the reactor was stable at the value we set, 30 atm hydrogen was filled into the



Scheme 1 The route for preparation of Ru/ $\text{TiO}_{2-x}$ .



reactor. At this time, the reaction started and the pressure of the reactor was recorded to monitor the hydrogenation progress. The final products were analysed by the gas chromatography (Agilent 7890-B).

## Results and discussion

A highly efficient and economic viable reducing agent is needed to synthesize scalable  $\text{TiO}_{2-x}$  under mild condition. Previous study reported that  $\text{TiO}_2$  could be reduced by Al vapor at high temperatures,<sup>23</sup> showing the strong reducing potential of metals. To perform the reduction of  $\text{TiO}_2$  at room temperature, a more powerful reductant and a better contact between  $\text{TiO}_2$  and reductant are needed. Recently, Na metal dispersed in inert medium (for instance NaCl) has received attention for its use as a very strong reducing agent in the synthesis of  $\text{NaB}_3\text{H}_8$ .<sup>21</sup> The well dispersed Na metal in Na/NaCl may function as a promising reductant for the reduction of  $\text{TiO}_2$ . Thus, we chose a commercially available crystalline  $\text{TiO}_2$  (P25, Degussa), consisting of mixed phases of anatase and rutile, as precursor for the synthesis of  $\text{TiO}_{2-x}$ . Ball milling of P25 with Na/NaCl fine powders at room temperature and different mechano-chemical conditions led to reduction of P25 into  $\text{TiO}_{2-x}$  of different oxygen vacancies content as evidenced by the visible color changes after reduction reaction (Fig. 1). The degree of reduction can be facily controlled by varying the reaction conditions, *i.e.*, weight ratio of P25 nanocrystals to Na/NaCl fine powders, milling rate and reaction time. The synthesized  $\text{TiO}_{2-x}$  samples are marked as  $\text{TiO}-n-v-t$ , where  $n$ ,  $t$  and  $v$  stand for weight ratio between Na/NaCl and  $\text{TiO}_2$ , ball milling rate and reaction time, respectively. The color of post-reduced P25 samples ranges from white to light blue and finally to dark blue with the increase of ball milling speed, reaction time and weight

ratio of Na/NaCl and P25 (Scheme 1). The corresponding UV-Vis diffuse reflectance spectra clearly show the intensity of the absorption in the visible light region (400–800 nm) gradually increases with the increases of reduction degree, which is consistent with the color changes of the  $\text{TiO}_{2-x}$  samples (Fig. S1†).

TEM images (Fig. 2) were collected to show the morphology and particle size of the P25 and  $\text{TiO}-4-180-4$ . The particle size of  $\text{TiO}-4-180-4$  sample is similar to that of P25 nanocrystals (20–30 nm), which indicates that such a solid reduction treatment has little influence on the particle size of the reduced  $\text{TiO}_2$  samples. Different from that of the pristine P25, disordered layer can be observed on the surface of  $\text{TiO}-4-180-4$  particles, which is probably resulted from ball-milling treatment and/or surface reaction between  $\text{TiO}_2$  and Na. As a consequence, a remarkable increase of BET surface area was obtained, *i.e.*, the  $\text{TiO}-4-180-4$  ( $113 \text{ m}^2 \text{ g}^{-1}$ ) has a BET surface area that is *ca.* 2.5 times of the pristine P25 ( $45 \text{ m}^2 \text{ g}^{-1}$ ).

The crystal structure of  $\text{TiO}_{2-x}$  is characterized by XRD and compared with that of P25 nanocrystals. As shown in Fig. S2,† a mild reduction treatment with ball milling speed of 80 rpm has little influence on the crystallinity of  $\text{TiO}_{2-x}$ . However, obvious changes occurred under harsh solid ball milling conditions (longer ball milling time with high Na/ $\text{TiO}_2$  ratio or at a high ball milling speed, Fig. 3). Compared with that of the pristine  $\text{TiO}_2$ , there is no obvious change in the intensities of diffraction peaks corresponding to the rutile phase in the  $\text{TiO}_{2-x}$  samples treated with different ball milling speeds. However, the intensities of peaks corresponding to the anatase phase significantly weaken with the increase of ball milling speed. The maintenance of rutile phase in the synthesized  $\text{TiO}_{2-x}$  may be due to its chemical stability compared with that of anatase.

As shown in Fig. 4, P25 nanocrystals display the typical anatase Raman active modes with frequencies at 144, 197, 399, 515, 519 (superimposed with the  $515 \text{ cm}^{-1}$  band), and  $639 \text{ cm}^{-1}$  together with modes at 447 and  $612 \text{ (should peak) cm}^{-1}$  corresponding to the rutile phase.<sup>24</sup> The relatively low intensity of rutile mode may originate from the low Raman response and low content of rutile in the P25.<sup>25</sup> For  $\text{TiO}_{2-x}$  samples, intensities of peaks corresponding to the rutile phase did not show any obvious change. However, intensities of the peaks corresponding to the anatase phase decreased obviously (Fig. 4e). More

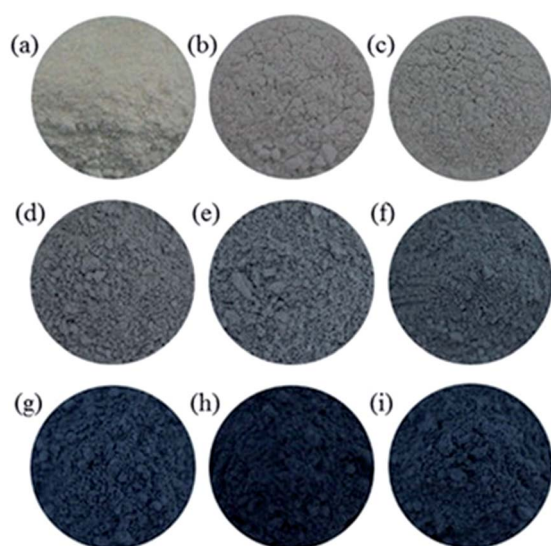


Fig. 1 Photographs of P25 nanocrystals and  $\text{TiO}_{2-x}$ . (a) P25 nanocrystals; (b)  $\text{TiO}-1-80-0.5$ ; (c)  $\text{TiO}-1-80-1$ ; (d)  $\text{TiO}-1-120-4$ ; (e)  $\text{TiO}-1-150-4$ ; (f)  $\text{TiO}-1-180-4$ ; (g)  $\text{TiO}-2-180-4$ ; (h)  $\text{TiO}-3-180-4$  and (i)  $\text{TiO}-4-180-4$ .

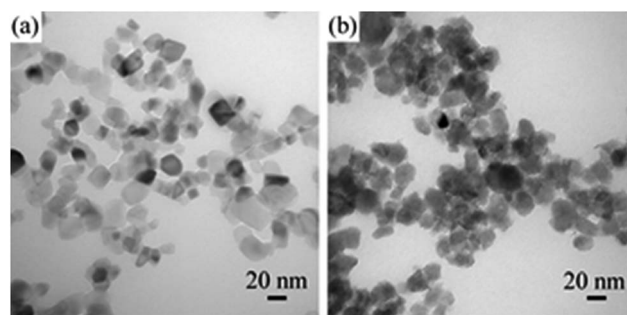


Fig. 2 TEM images of (a) P25 nanocrystals and (b)  $\text{TiO}-4-180-4$ .





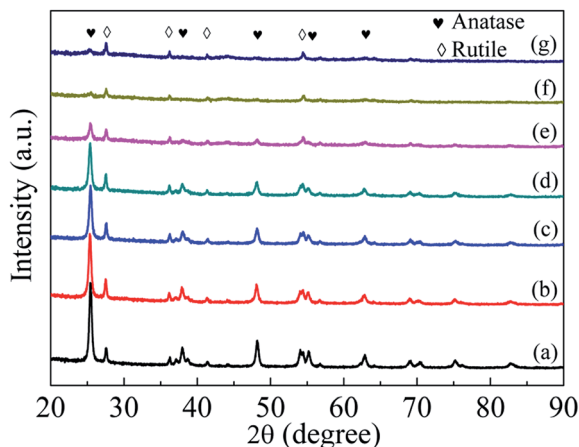


Fig. 3 XRD patterns of P25 nanocrystals and  $\text{TiO}_{2-x}$  (a) P25 nanocrystals; (b) TiO-1-120-4; (c) TiO-1-150-4; (d) TiO-1-180-4; (e) TiO-2-180-4; (f) TiO-3-180-4 and (g) TiO-4-180-4.

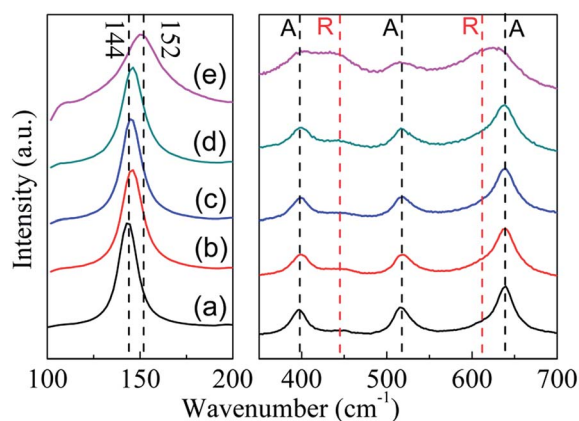


Fig. 4 Raman spectra of P25 nanocrystals and  $\text{TiO}_{2-x}$  (a) P25 nanocrystals; (b) TiO-1-120-4; (c) TiO-1-150-4; (d) TiO-1-180-4; (e) TiO-4-180-4. A: anatase, R: rutile.

importantly, a blue shift of the strongest  $E_g$  mode at  $144\text{ cm}^{-1}$  for anatase can be detected. As reported in previous research, this peak shift was mainly caused by the stoichiometry defects in  $\text{TiO}_2$ .<sup>26</sup> Therefore, the shift in the present study suggests the formation of oxygen vacancies in  $\text{TiO}_{2-x}$  during solid reduction treatment. Since the anatase was detected by Raman technique, the disappearance of anatase phase in XRD should be attributed to its amorphous state. Noting that the reduction of  $\text{TiO}_2$  could mainly occur on its surface or near surface, the synthesized  $\text{TiO}_{2-x}$  here may have a core-shell structure with reduced shell and unchanged core, which is similar to the results reported in literature.<sup>13</sup>

XPS was also applied to characterize the chemical state of surface elements in TiO-4-180-4. The full XPS survey (Fig. S3†) reveals that no elements other than C, O, Ti can be detected on the surface of P25 and TiO-4-180-4. The C 1s at approximate  $284.5\text{ eV}$  may arise from adventitious carbon on the surface of samples.<sup>27</sup> For P25, the Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  peaks center at binding energies of  $458.6$  and  $464.4\text{ eV}$ , respectively, which are

characteristics of the  $\text{Ti}^{4+}\text{-O}$  bonds in  $\text{TiO}_2$ . However, these two peaks shift to lower binding energies of  $458.2$  and  $464.0\text{ eV}$  for TiO-4-180-4 (Fig. 5a), which can be an indication of the existence of  $\text{Ti}^{3+}$  in the TiO-4-180-4. The binding energy of O 1s of TiO-4-180-4 shows a slight decrease compared with that of P25 (Fig. 5b). It has been reported that the shift of binding energies to lower region can be observed in the hydrogen reduced  $\text{TiO}_2$  nanotube,<sup>11</sup> which is similar to our result. Consistent with Raman result, the XPS data also evidence that the formation of oxygen vacancies in TiO-4-180-4.

$\text{TiO}_2$  has been widely used as a support for various metal catalysts for selective catalytic hydrogenation,<sup>6-8</sup> oxidation<sup>9,10</sup> and electrochemical<sup>11,12</sup> reactions. There is a SMSI between  $\text{TiO}_2$  and metal particles that induces unique catalytic performance. However, the SMSI was usually observed at high temperatures under reducing atmosphere, where  $\text{TiO}_2$  was highly likely to be reduced.<sup>28</sup> Moreover, the specific surface area of  $\text{TiO}_{2-x}$  (TiO-4-180-4) is about 2.5 times as large as pristine P25. Therefore, it is very interesting to investigate the prepared  $\text{TiO}_{2-x}$  as catalyst support. There are growing research activities in employing hydrocarbons and N-heterocycles as liquid organic hydrogen carriers (LOHCs) in recent years because of their compatibility with existing gasoline infrastructure facilitating the switch to hydrogen energy system.<sup>29-31</sup> Catalyst development for the hydrogenation and dehydrogenation of those LOHCs are of practical importance. In the context, the  $\text{TiO}_{2-x}$  supported Ru catalyst is prepared and tested for the hydrogenation of *N*-methylpyrrole, a commercially available LOHC with large annual global production.

As shown in Fig. 6a, uniformly distributed Ru on the pristine  $\text{TiO}_2$  has a mean particle size of about  $1.1\text{ nm}$  (Fig. S4†). The Ru supported on  $\text{TiO}_{2-x}$ , on the other hand, is hardly distinguishable by TEM (Fig. S5†), indicating even smaller particle size of Ru on  $\text{TiO}_{2-x}$ . Fortunately, the HAADF-STEM image evidences the presence of Ru particles (particle size  $< 1\text{ nm}$ , Fig. 6b), but the specific particle size is difficult to be calculated because of the ambiguous boundary of those particles. Considering the larger surface area and “rough” surface morphology of  $\text{TiO}_{2-x}$ , Ru may have better dispersion on  $\text{TiO}_{2-x}$ . Furthermore, oxygen vacancies or  $\text{Ti}^{3+}$  in  $\text{TiO}_{2-x}$  may also be helpful for anchoring metal particles and, thus, leading to better dispersion than that on pristine P25.<sup>18</sup>

Recent reports showed that the electron-rich transition metals could facilitate the hydrogenation of N-heterocycles.<sup>32</sup> The reduced state of  $\text{TiO}_{2-x}$  may also be favorable in electron transfer between support and Ru. As we expected, the XPS of Ru

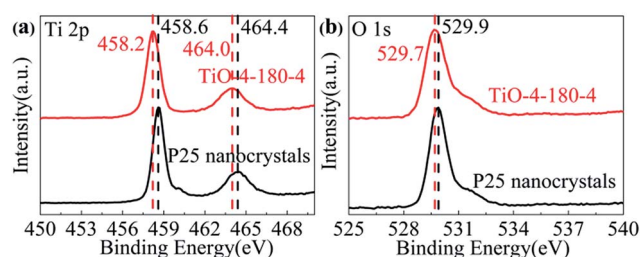


Fig. 5 (a) Ti 2p and (b) O 1s XPS of P25 nanocrystals and TiO-4-180-4.



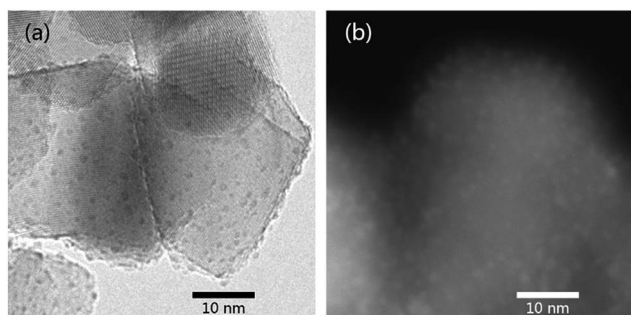


Fig. 6 (a) TEM image of 5 wt% Ru/TiO<sub>2</sub>. (b) HAADF-STEM image of 5 wt% Ru/TiO<sub>2-x</sub>.

3d<sub>5/2</sub> signal shows that the binding energy of Ru supported on TiO<sub>2-x</sub> down shifts 0.5 eV as compared with that on TiO<sub>2</sub> (Fig. S6†), indicating an electron rich state of Ru on TiO<sub>2-x</sub>, which also suggests a stronger interaction between support and metal particles.<sup>33</sup> Although Ru is known to catalyze the hydrogenation of *N*-methylpyrrole well,<sup>34</sup> the effect of catalyst support has not been well investigated. As shown in Fig. 7a, about 80% and 88% *N*-methylpyrrole can be hydrogenated to *N*-

methylpyrrolidine in 60 min at 90 °C and 100 °C by using Ru/TiO<sub>2</sub> catalyst, respectively. Ru/TiO<sub>2-x</sub>, on the other hand, shows superior catalytic performance compared to that of Ru/TiO<sub>2</sub>, *i.e.*, about 91% and 95% *N*-methylpyrrole can be hydrogenated under the same condition. Furthermore, the initial hydrogenation rate on Ru/TiO<sub>2-x</sub> at 100 °C is about twofold as that with Ru/TiO<sub>2</sub> (Table S1†), showing encouraging promotion effect of TiO<sub>2-x</sub> as support. Calculated from the Arrhenius plots (Fig. 7b), the activation energies for the hydrogenation reaction are 50.9 kJ mol<sup>-1</sup> and 50.0 kJ mol<sup>-1</sup> for Ru/TiO<sub>2</sub> and Ru/TiO<sub>2-x</sub>, respectively, suggesting similar hydrogenation mechanism for both catalysts. Therefore, the improved catalytic activity of Ru/TiO<sub>2-x</sub> can be probably attributed to the better dispersion of Ru on the support, which is confirmed by the larger pre-exponential factor (*A*) as shown in Table S1.† We suggest that in addition to the larger specific surface area of TiO<sub>2-x</sub> (113 m<sup>2</sup> g<sup>-1</sup>), oxygen vacancies or Ti<sup>3+</sup> in TiO<sub>2-x</sub> may intensify the interaction between Ru particles and TiO<sub>2-x</sub>, and therefore, enhancing the better dispersion of Ru particles by inhibiting Ru migration and agglomeration.<sup>11</sup> However, the strong interaction between TiO<sub>2-x</sub> and metal particles is an interesting subject that needs to be further investigated and elucidated over reactions that are sensitive to the electronic state of transition metals.

## Conclusions

In summary, we have developed a room temperature solid reduction approach for the synthesis of nanosized TiO<sub>2-x</sub> from TiO<sub>2</sub> crystals. A series of TiO<sub>2-x</sub> with controllable reduction degree have been successfully synthesized by ball-milling of TiO<sub>2</sub> crystal with finely dispersed Na/NaCl powders. The obtained TiO<sub>2-x</sub> with high surface area can be employed as an effective support for Ru particles and the Ru/TiO<sub>2-x</sub> catalyst exhibited superior activity in catalytic hydrogenation of *N*-methylpyrrole, a commercial available heterocycle with large annual global production. We believe that this highly efficient room temperature reduction approach for the production of TiO<sub>2-x</sub> offers a promising opportunity for the practical applications of TiO<sub>2-x</sub> in different areas.

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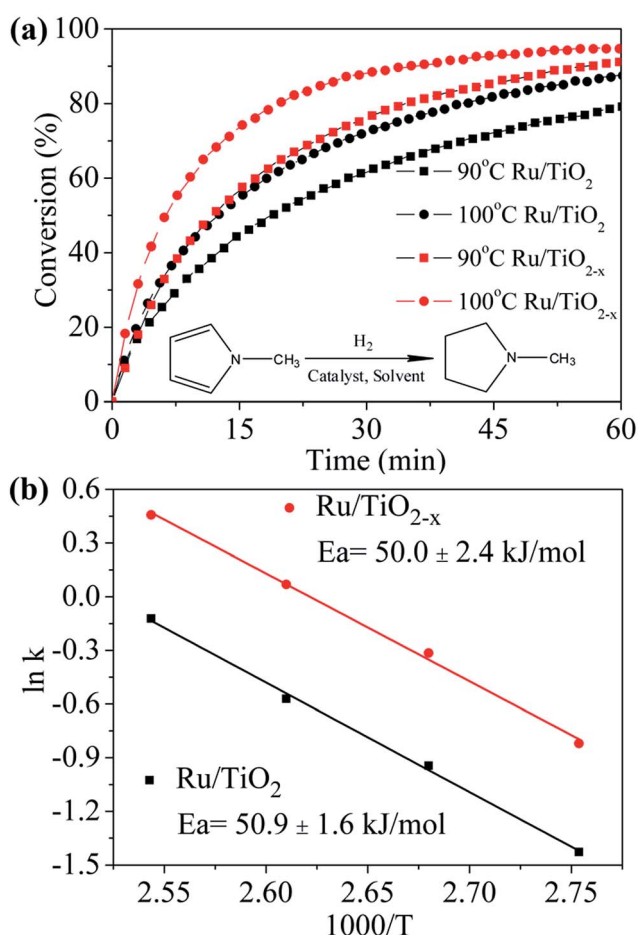


Fig. 7 (a) Hydrogenation of *N*-methylpyrrole with catalysts Ru/TiO<sub>2</sub> or Ru/TiO<sub>2-x</sub> at 30 atm H<sub>2</sub> pressure, 90 °C and 100 °C, catalyst/substrate molar ratio is 1 : 100. (b) The Arrhenius plots in the temperature range of 363–393 K.



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