Supplementary Information

In-situ carbonization of soft-template to directly synthesize the crystalline mesoporous metal oxides with high surface area

Limin Guo,[a,*] Shintaro Ida,[b] Takashi Daio,[c] Hidehisa Hagiwara,[b] Tatsumi Ishihara[a,*]
[a]International Institute for Carbon-Neutral Energy Research (WPI-I^{2}CNER),
[b]Department of Applied Chemistry and [c]International Research Center for Hydrogen Energy, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.
*E-mail: lmguo1982@gmail.com (L.G.); ishihara@cstf.kyushu-u.ac.jp (T. I.).

Experimental Section

Preparation of Crystalline Mesoporous Nb_2O_5. Pluronic P-123 (1 g) was dissolved in ethanol (10 g) with constant stirring for 30 min. Then, $NbCl_5$ (1 g) was added to the solution under vigorous stirring. After further 1.5 h stirring, the sol solution was transferred into Petri dishes for aging at room temperature for 7 days to obtain a gel. The gel was heated to partially decompose the P-123 and condensate the Nb_2O_5 related species at 250 °C for 12 h. Thereafter, the powder was heated in a tube furnace to crystallize the Nb_2O_5 species at 650 °C under N_2 gas flow for 1 h and the black powder was obtained. Finally, the carbon was removed at 500 °C by calcination in air. The obtained sample was named Nb_2O_5-R3.

Preparation of Crystalline Mesoporous TiO_2. 1 g of polymer SDA (Pluronic P-123) was dissolved in ethanol (10 g) under constant stirring for 30 min. Then, $TiCl_4$ (1.1 mL) was added to the solution under vigorous stirring. After further 1.5 h stirring, the sol solution was transferred into Petri dishes for aging at room temperature for 7 days to obtain the gel. The gel was heated to partially decompose the P-123 and condensate the TiO_2 related species at 250 °C for 12 h. Thereafter, the powder was heated in a tube furnace to crystallize the TiO_2 at 700 °C under N_2 gas flow for 1 h and the black powder was obtained. Finally, the carbon was removed at 500 °C by calcination in air. The obtained sample was named TiO_2-R3.

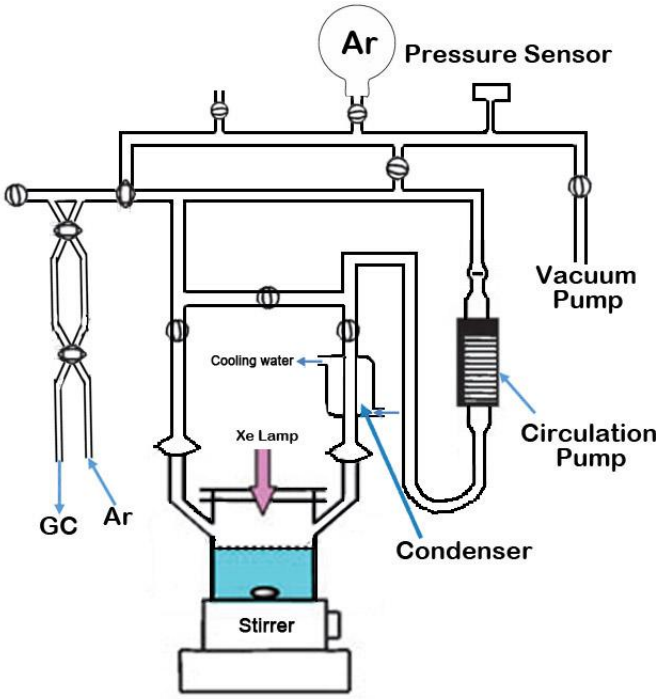

Figure 1. Schematic illustration of the photocatalytic water splitting system.

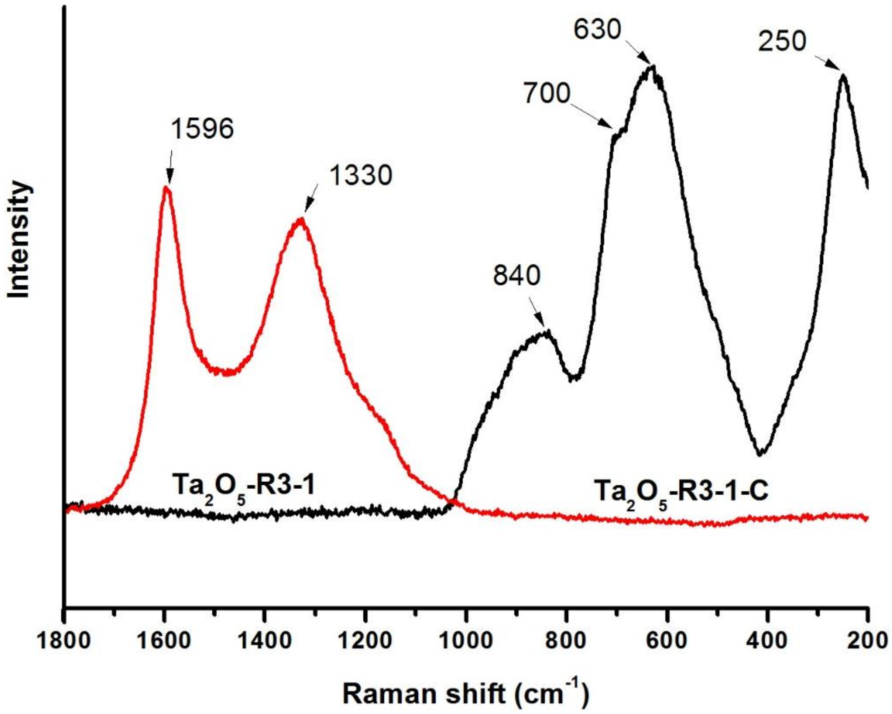

Figure 2. The Raman spectrum of samples Ta_2O_5-R3-1-C and Ta_2O_5-R3-1.

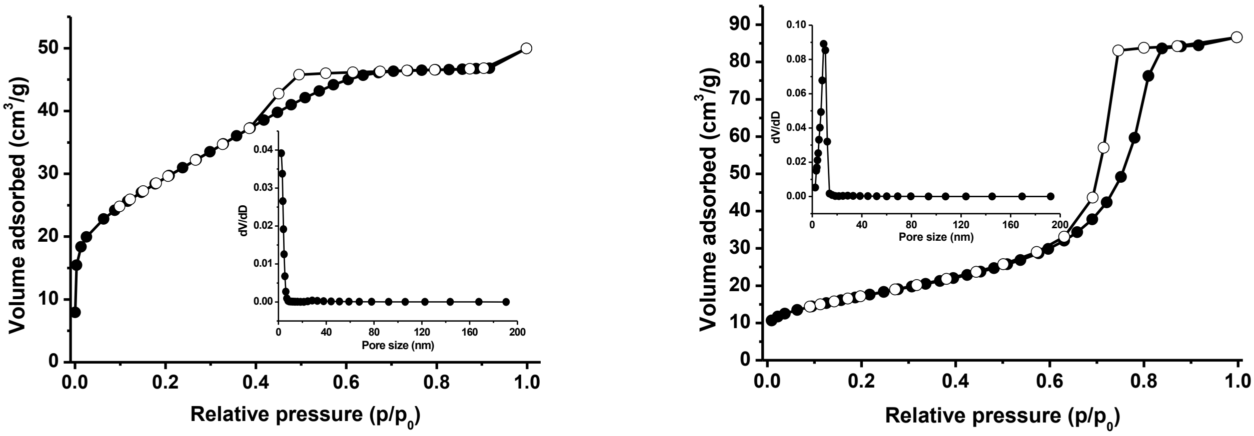

Figure 3. The N_2 sorption isotherm and pore size distribution of Ta_2O_5-R3-1-C (left) and Ta_2O_5-R3-1 (right). Herein, in order to well understand the difference, the data of Ta_2O_5-R3-1 is also enclosed. The BET surface area and pore volume of Ta_2O_5-R3-1-C are 95.9 m^2/g and 0.06 cm^3/g, respectively. And the BET surface area and pore volume of Ta_2O_5-R3-1 are 56.6 m^2/g and 0.13 cm^3/g, respectively. From the N_2 sorption isotherm, very obvious difference can be observed. Before the carbon removal, there is no obvious adsorption leap. After carbon removal, the adsorption leap around $p/p_0 = 0.6$-0.8, which is typical phenomena for the mesoporous materials, can be clearly observed. From the pore size distribution, we can further see the difference. The pore size centers around 10 nm for Ta_2O_5-R3-1 and no such pore size distribution is observed in the mesopore range. In addition, the pore volume of Ta_2O_5-R3-1-C is much smaller compared with that of Ta_2O_5-R3-1. Based on the above analysis, the mesoporous channels of Ta_2O_5-R3-1-C should be filled with the in-situ formed carbon. The higher surface area of Ta_2O_5-R3-1-C can be ascribed to the microporous structure of in-situ formed carbon.

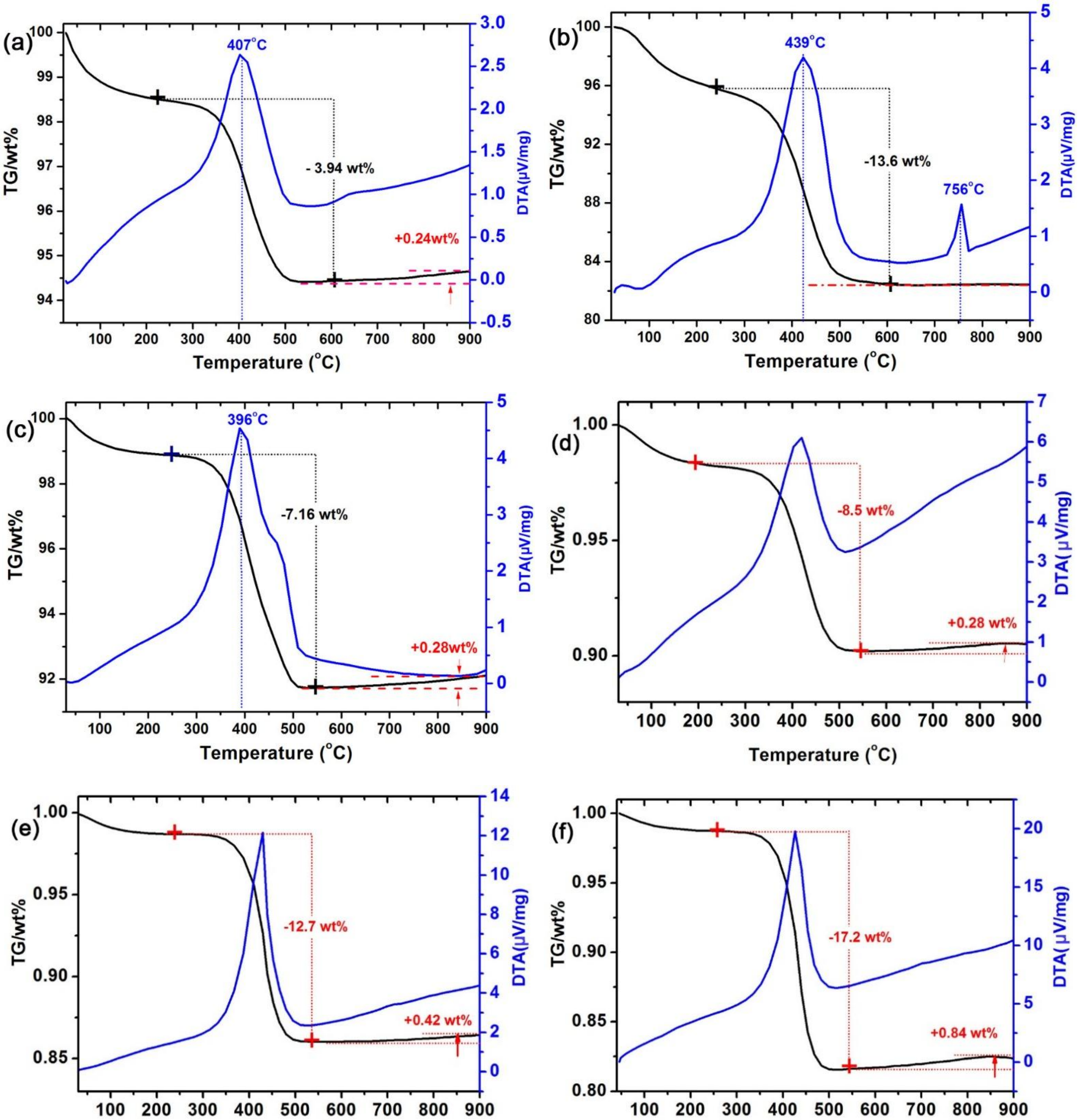

Figure 4. TG–DTA curves of the as-synthesized mesoporous Ta_2O_5 samples (a) Ta_2O_5-R1-1-C; (b) Ta_2O_5-1-250; (c) Ta_2O_5-R3-1-C; (d) Ta_2O_5-R3-2-C; (e) Ta_2O_5-R3-3-C and (f) Ta_2O_5-R3-4-C.

The evaluation of reduced Ta species.

The ratio of reduced Ta species has been calculated according to some simple hypothesis and on the basis of TG data (Fig. 2), which can be used to directly understand the trend influenced by the amount of in-situ formed carbon.

The hypothesis:

1. After TG-DTA measurement (the final calcination temperature is 900 °C), all the Ta species are Ta^{5+}. The final mass of Ta_2O_5, m_1, can be given by TG results;
2. Before all the carbon has been removed, no reduced Ta species are oxidized. On the basis of this hypothesis, we can get the mass change (m_2) from TG results due to reduced Ta species were oxidized to Ta^{5+} state;
3. All the reduced Ta species are Ta^{4+};

The crystal structure or phase demonstrated the single phase of Ta_2O_5, which means there are O vacancies sites in the crystalline Ta_2O_5 lattice.

M_O is molecular weight of O and the value is known as 16 g/mol. M_{Ta2O5} is molecular weight of Ta_2O_5 and the value is known as 441.9 g/mol.

The equation to calculate the ratio of O vacancies to the total O lattice sites is:

$$N_{OV} = (m_2/M_O)/[5*(m_1/M_{Ta2O5})]$$

The equation to calculate the ratio of reduced Ta species (atoms or sites) to the total Ta species is:

$$N_{Ta4+} = (m_2/M_O)/(m_1/M_{Ta2O5})$$

The ratio of Ta/O for the standard Ta_2O_5 is 2/5 (0.4). If the calcination is just remove the carbon and all reduced Ta species have not been oxidized. The equation to calculate the ratio of Ta/O at the condition is:

$$R_{Ta/O} = [2*(m_1/M_{Ta2O5})]/\{ [5*(m_1/M_{Ta2O5})] - (m_2/M_O)\}$$

According to above mentioned equations, the as-calculated values for samples are summarized in the table.

Sample name	N_{OV}	N_{Ta4+}	$R_{Ta/O}$
Ta_2O_5-R1-1	0.014	0.069	0.406
Ta_2O_5-R2-1 (proposed to ideal state)	0.000	0.000	0.400
Ta_2O_5-R3-1	0.023	0.114	0.409
Ta_2O_5-R3-2	0.021	0.103	0.408
Ta_2O_5-R3-3	0.027	0.137	0.411
Ta_2O_5-R3-4	0.064	0.320	0.427

From the evaluation, the ratio of reduced Ta species or O vacancies in the final synthesized crystalline mesoporous Ta_2O_5 increased with the amount of in-situ formed carbon of corresponding sample preparation process.

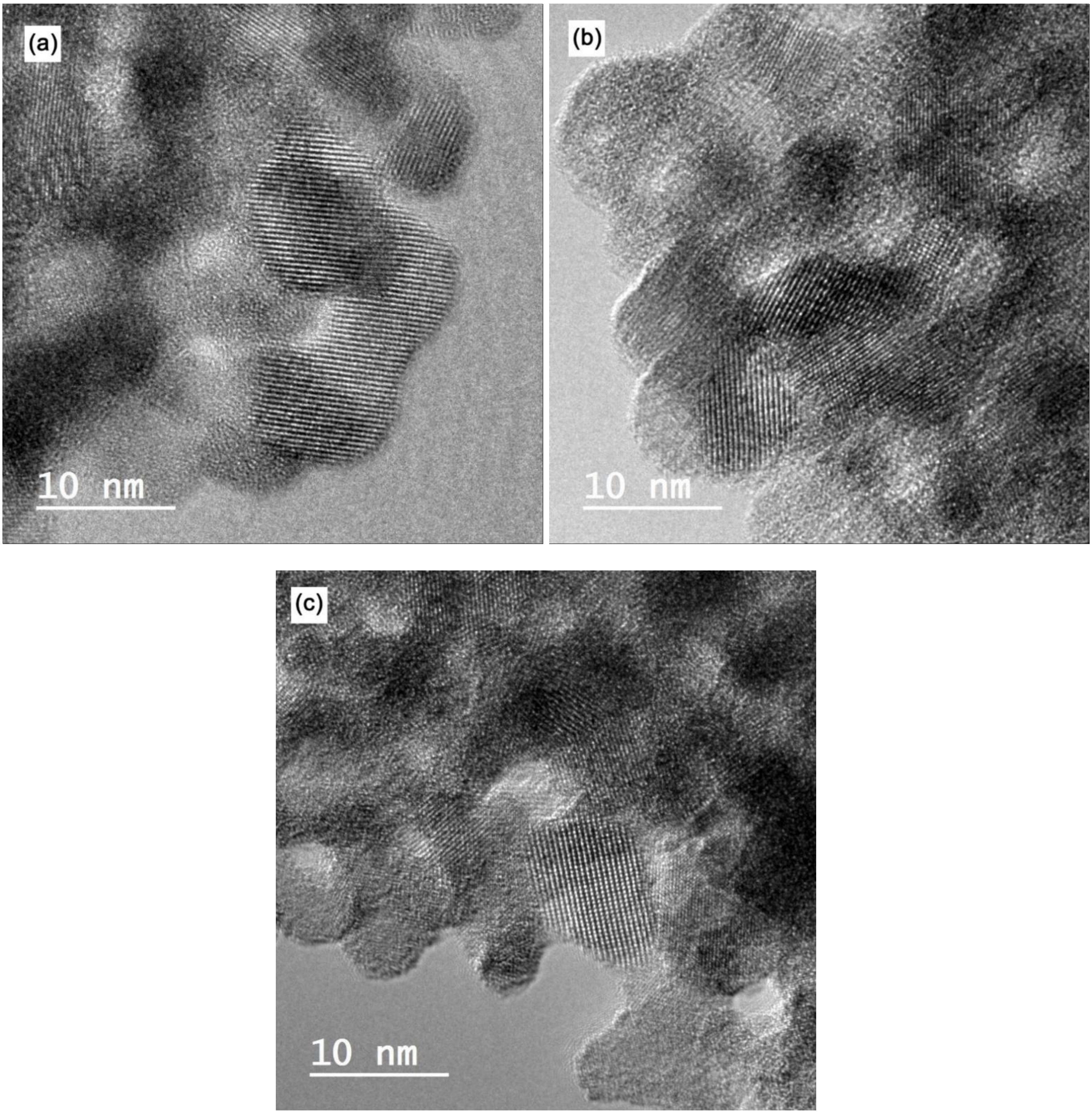

Figure 5. High resolution TEM images of (a) Ta_2O_5-R3-2, (b) Ta_2O_5-R3-3 and (c) Ta_2O_5-R3-4.

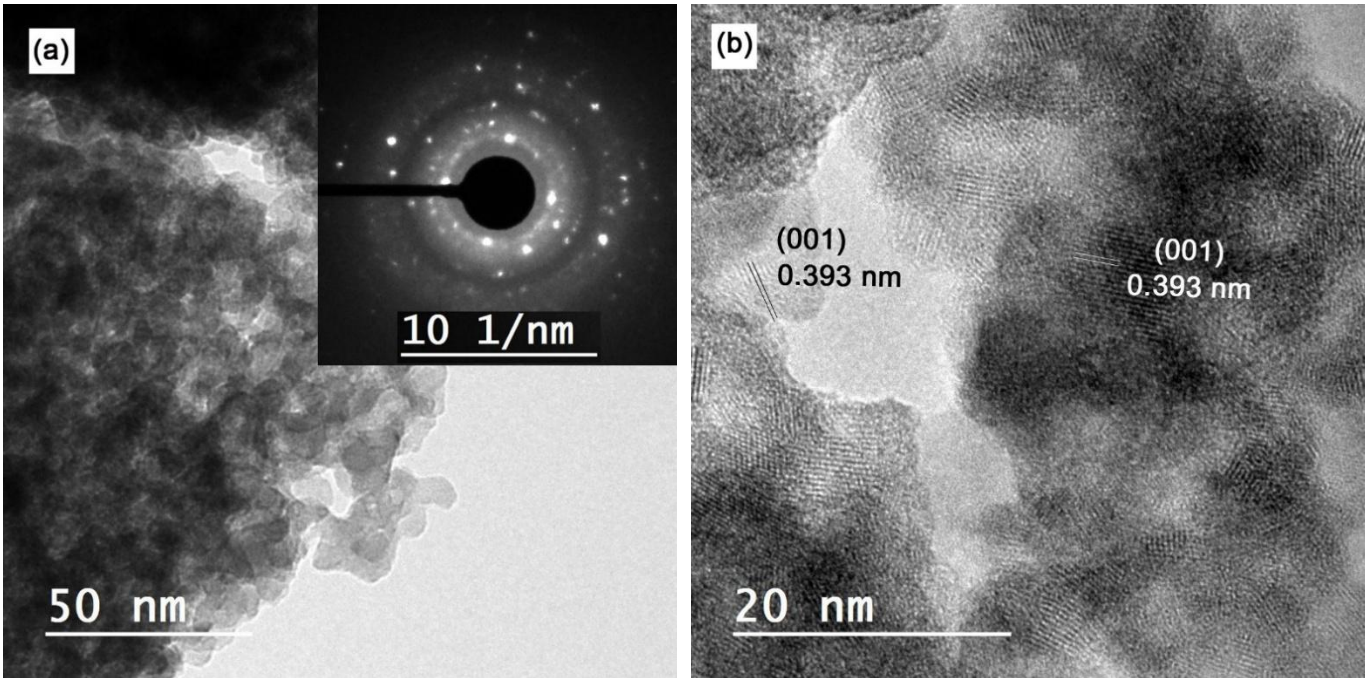

Figure 6. (a) Low magnification TEM image and diffraction pattern (inset) and (b) high resolution TEM image of Nb_2O_5-R3.

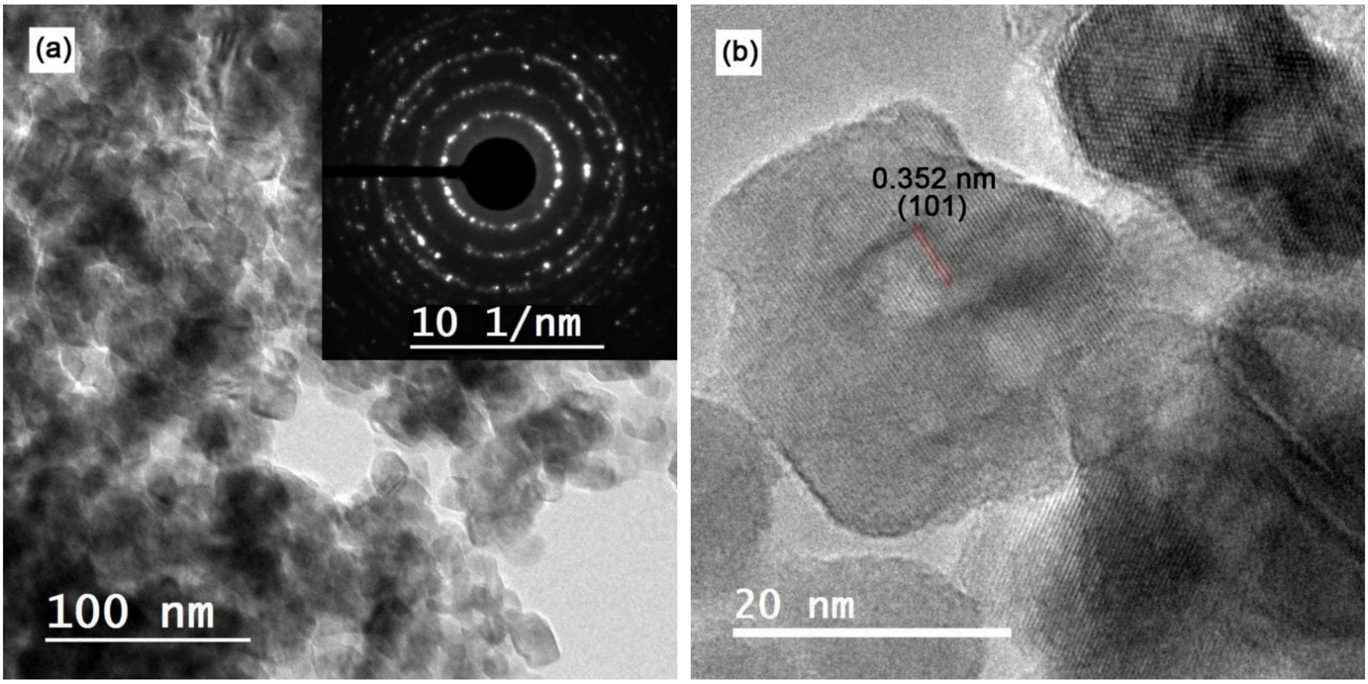

Figure 7. (a) Low magnification TEM image and diffraction pattern (inset) and (b) high resolution TEM image of TiO_2-R3.

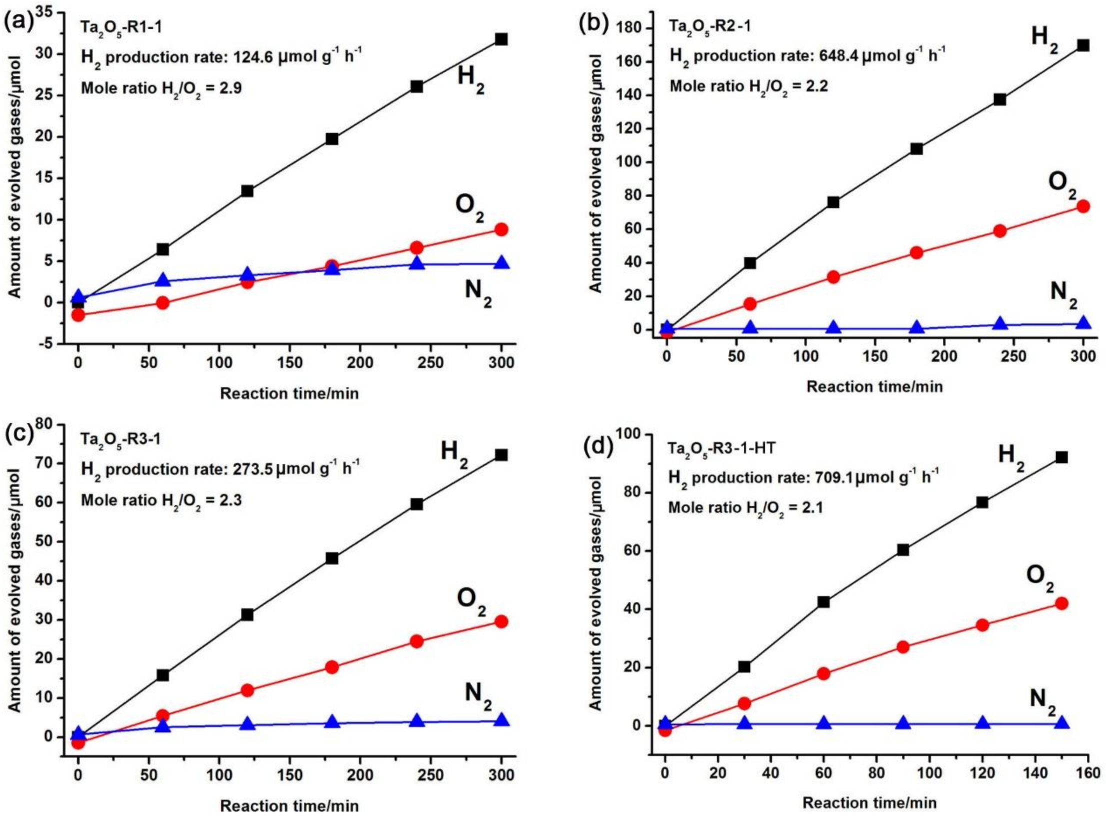

Figure 8. Time course of gas evolution from water splitting on NiO_x loaded mesoporous Ta_2O_5. (a) Ta_2O_5-R1-1-1.0 wt%NiO_x, (b) Ta_2O_5-R2-1-1.0 wt%NiO_x, (c) Ta_2O_5-R3-1-1.0 wt%NiO_x, and (d) Ta_2O_5-R3-1-HT-2.0 wt%NiO_x.

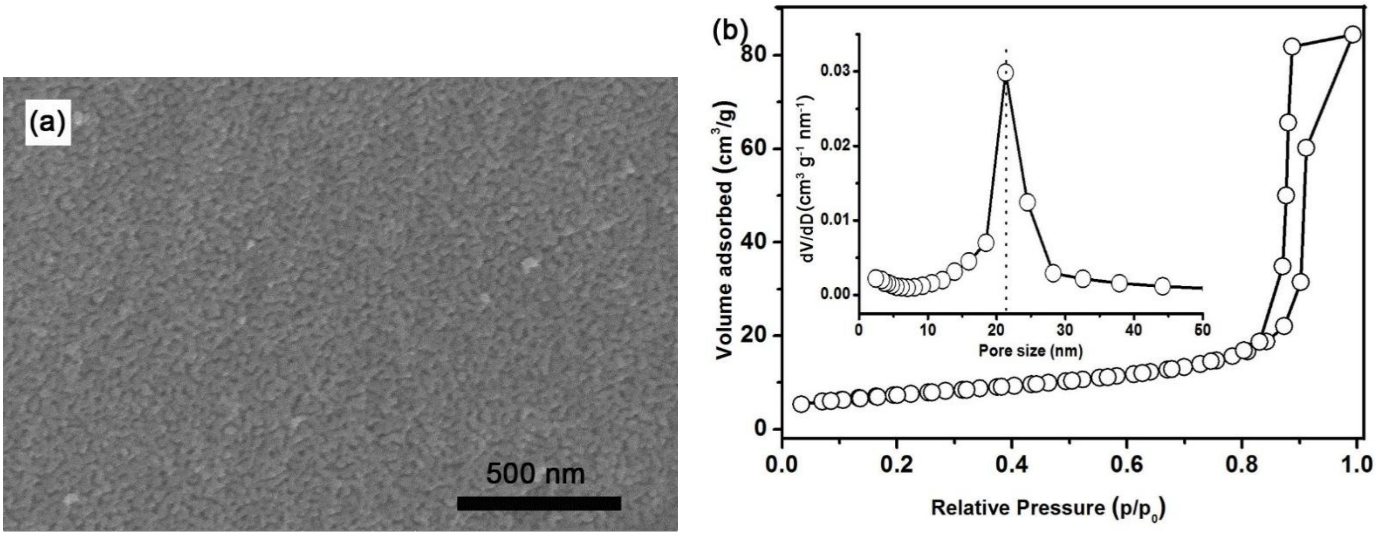

Figure 9. (a) SEM image and (b) N_2 sorption isotherm and pore size distribution (inset) of Ta_2O_5-R3-1-HT.