

Supporting information

Preparation of p-aminobenzoic acid grafted TiO_x semiconductive aerogels for photocatalytic reduction of CO₂ to methanol

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Scheme S1 Photocatalytic reactor.

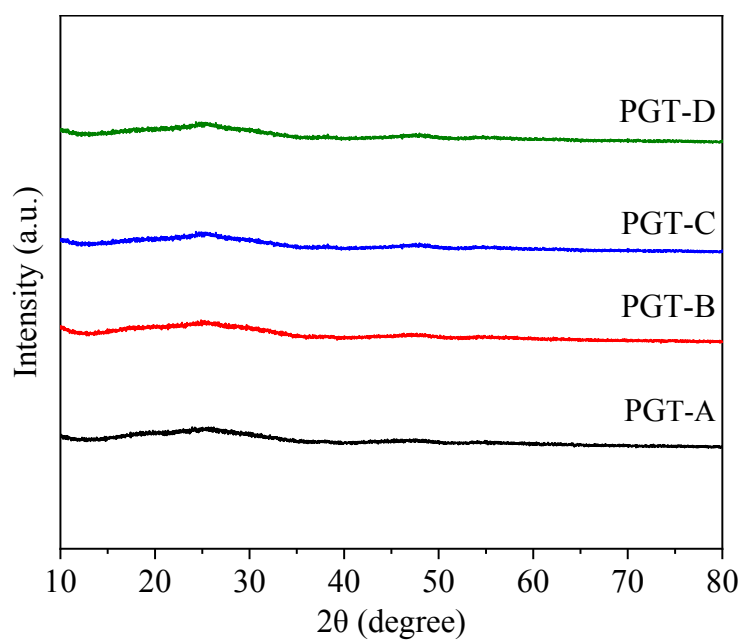


Fig. S1 XRD patterns of the grafted TiO_x aerogels.

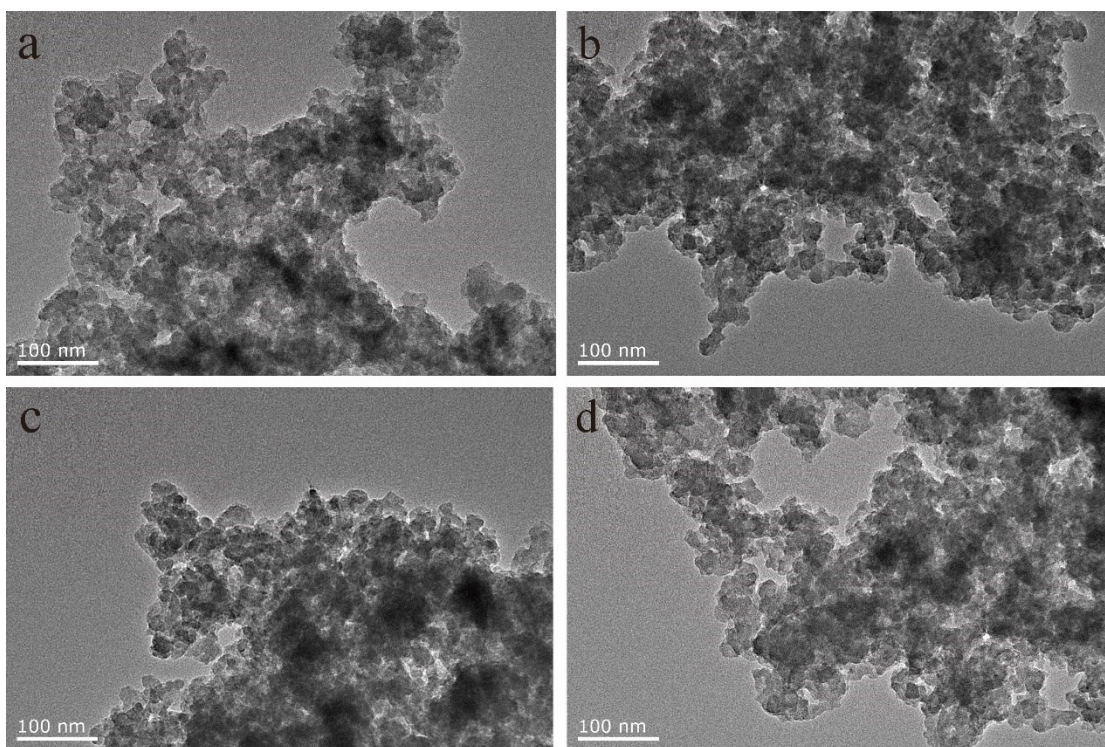


Fig. S2 The TEM images of (a) PGT-A, (b) PGT-B, (c) PGT-C and (d) PGT-D

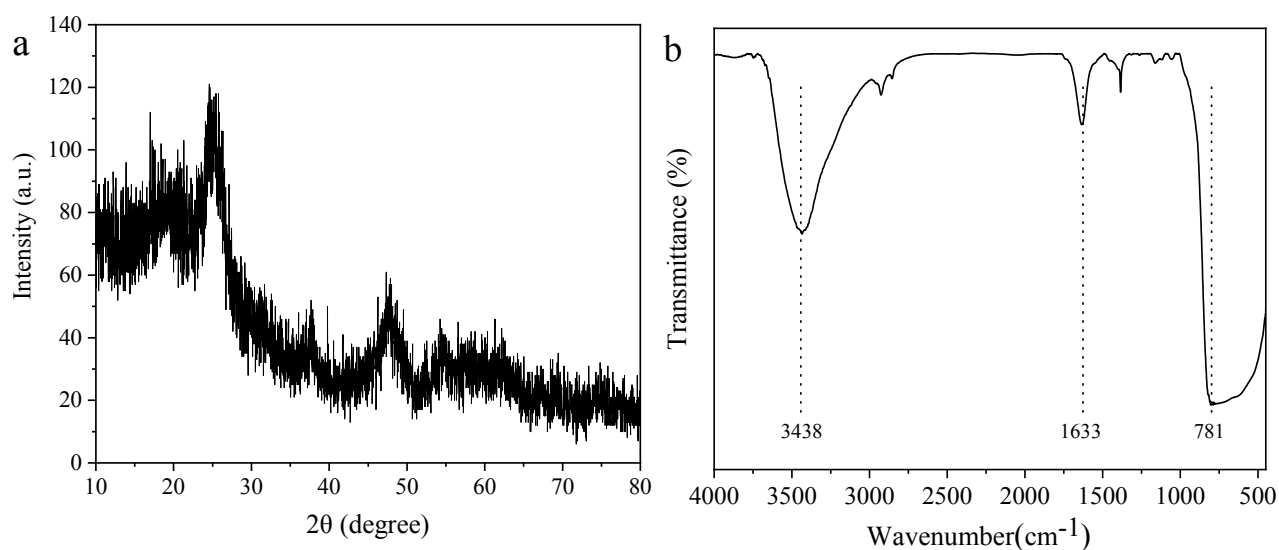


Fig. S3 (a) XRD pattern and (b) FT-IR spectrum of the TiO_2 aerogel without grafting PABA.

In Fig. S3(a), the observed weak peaks at $2\theta = 25.3^\circ, 48.1^\circ$ matched the anatase phase, they can be assigned to (101) and (200) lattice planes,^[1] respectively. It is possible that small amount of anatase nucleus formed during the drying process. Therefore, a few weak peaks can be observed.

In Fig. S3(b), the FTIR spectrum of TiO_2 clearly shows three bands. The two absorption bands at 3438 and 1633 cm^{-1} in the materials can be recognized as the stretching and bending vibrations of water molecules.^[1] In addition, the band at 781 cm^{-1} is ascribed to the stretching vibration of the Ti-O-Ti.^[2]

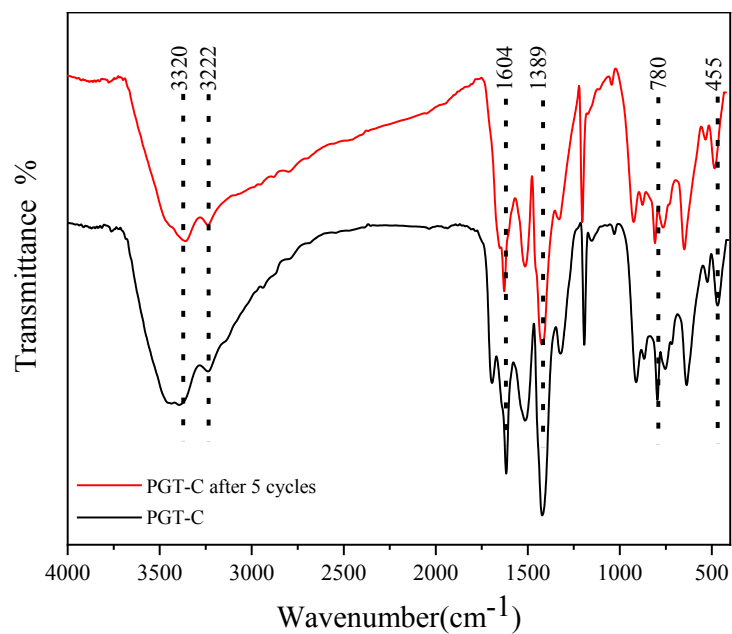


Fig. S4 FT-IR spectra of the PGT-C. (a) the fresh one and (b) the used one after the recycle experiments.

The FTIR spectra of the used aerogels are shown in Fig. S4. The asymmetrical and symmetrical stretching vibrations of -CO_2^- can be still observed at 1604 and 1389 cm^{-1} , and they had the nearly same band intensity as the fresh sample.

Preparation of NH₂-MIL-125(Ti).

0.5 g of BDC-NH₂ was dissolved in a solution containing 10 mL of DMF and 1 mL of methanol. Then, 0.26g of TBOT was added to the above solution. The mixture was stirred at room temperature for 30 min and was transferred to a 50 mL Teflon lined autoclave and heated at 130°C for 15 hours. After reaction, the resulting suspension was filtered and washed with methanol and acetone. Finally, the yellow powder was dried under vacuum at 50°C for 12h to obtain final product.

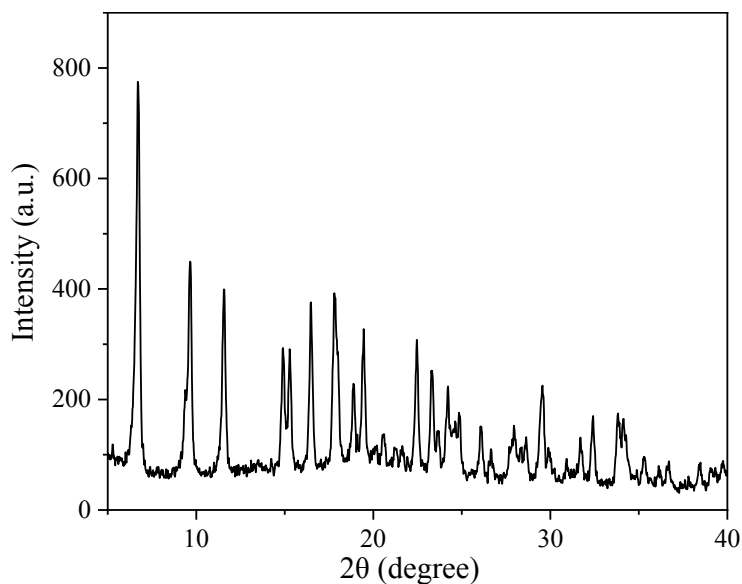


Fig. S5 XRD pattern of NH₂-MIL-125(Ti)

The XRD pattern in Fig.S5 reveals that the product matched with the reported NH₂-MIL-125(Ti) well. The characteristic peaks appeared at $2\theta = 6.74^\circ, 9.44^\circ, 9.72^\circ, 11.6^\circ, 13.54^\circ, 14.96^\circ, 15.36^\circ, 16.56^\circ, 17.86^\circ, 18.02^\circ, 18.96^\circ, 19.5^\circ, 22.52^\circ$ and 23.38° , which can be assigned to (101), (200), (002), (211), (220), (310), (103), (222), (312), (213), (400), (004), (204) and (422) lattice planes, respectively.^[3]

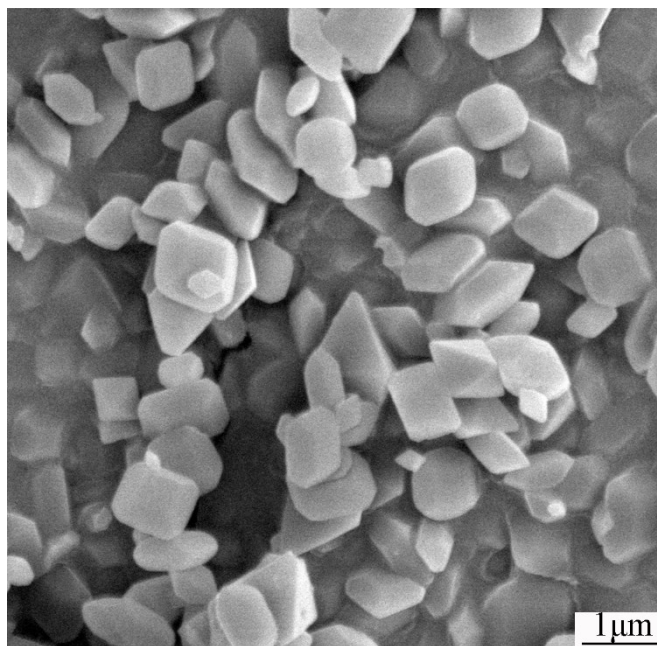


Fig. S6 SEM image of the NH₂-MIL-125(Ti)

The crystals have regular truncated bipyramid morphology as shown in Fig. S6, which is consistent with other reports.^[4-5]

Preparation of NH₂-BDC grafted TiO_x aerogel: The preparation procedures were similar to that described for PABA grafted TiO_x aerogels. Briefly, 0.75g of NH₂-BDC was dissolved in 10mL of DMF under vigorous stirring at room temperature for 30 min, followed by addition of 10mL of TiCl₄ ethanol solution (0.4M) and kept stirring for another 30min. Then 0.5 mL of deionized water was added into the above solution. After stirring for 30min, the above solution was transferred to a Teflon-lined autoclave and heated at 100°C for 12 h to form solid gel. The obtained gel was soaked with 30 mL of t-BuOH at 60°C for 12 h, and then repeatedly soaked for 5 times. The gel was freeze-dried for 24h to obtain aerogel. The sample was denoted as BDCT.

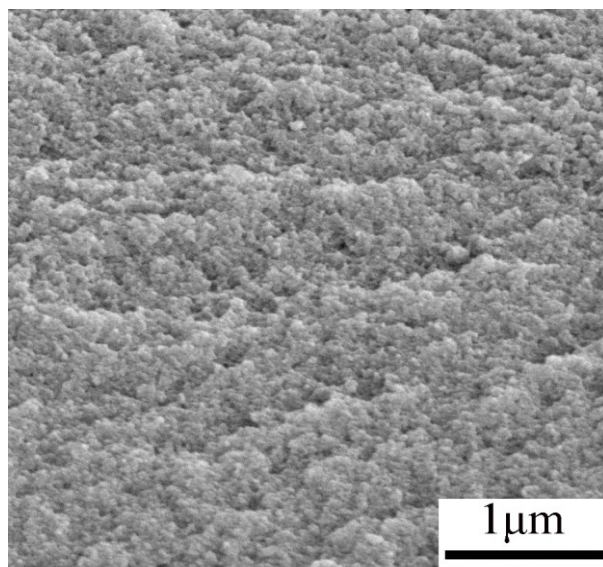


Fig. S7 SEM image of the BDCT aerogel.

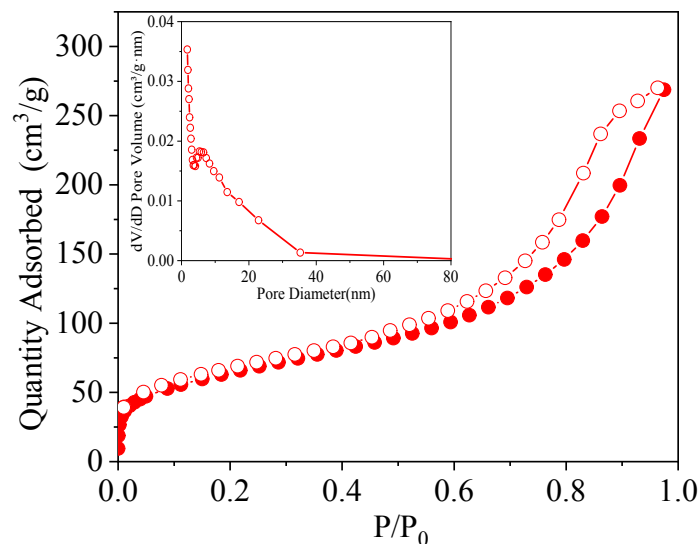


Fig. S8 N₂ adsorption-desorption isotherms of the BDCT aerogel. Inset: the pore size distribution.

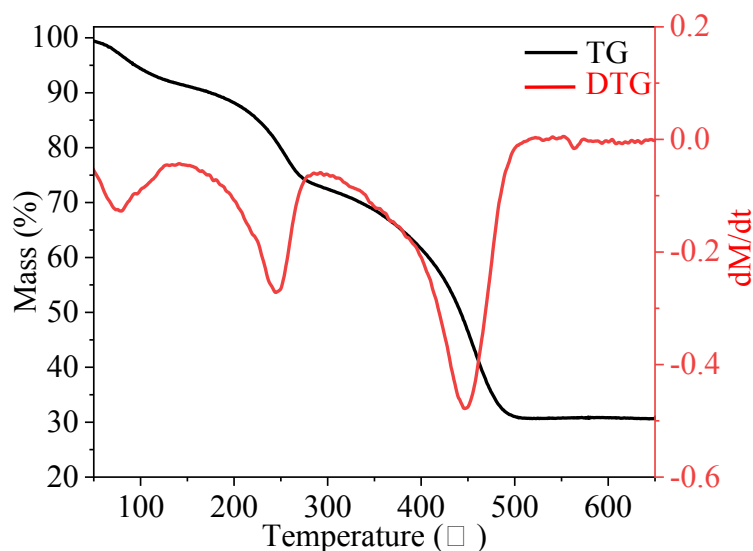


Fig. S9 Thermal analysis of the BDCT aerogel.

The thermal stability of the BDCT aerogel was evaluated by thermogravimetry (TG) analysis under air flow. Three temperature ranges of weight loss were observed. The one at 30~100 °C was attributed to physisorbed water. The second that occurred between 100 and 250°C corresponded to the loss of physisorbed NH₂-BDC that was not involved in the coordination reaction.^[6] Whereas the most obvious weight loss in a range of 250~450°C could be assigned to the decomposition of NH₂-BDC that coordinated with Ti⁴⁺, which led to collapse of aerogel framework. According to TG curves, the weight loss was 43.87% for BDCT. And the residual mass was 30.61% for BDCT. Therefore, the actual molar ratios of NH₂-BDC to Ti in the BDCT aerogel can be calculated as 0.83.

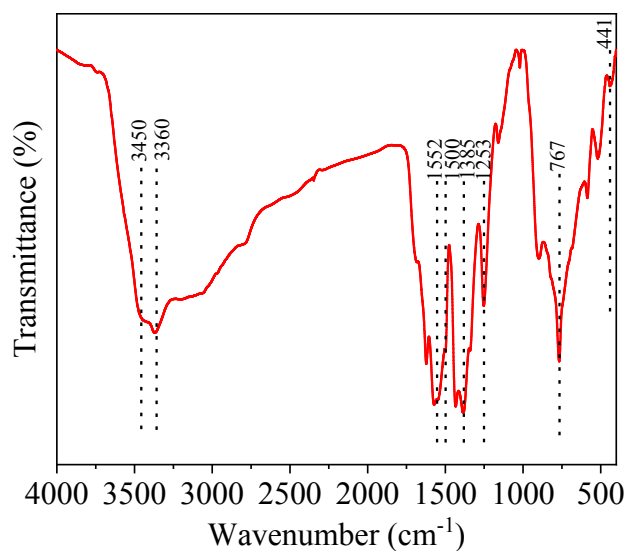


Fig. S10 FT-IR spectrum of the BDCT aerogel.

FT-IR spectrum of the BDCT aerogel is displayed in Fig.S10. The bands at 3450 and 3360 cm^{-1} are related to the asymmetrical and symmetrical stretching bands of NH_2 ,^[6] respectively. Additionally, the asymmetrical and symmetrical stretching vibrations of $-\text{COO}^-$ are also observed at 1552 and 1385 cm^{-1} ,^[6] respectively. The bands centered at 1500 and 1253 cm^{-1} are assigned to the stretching vibrations of $\text{C}=\text{C}$ and $\text{N}-\text{C}$,^[6-7] respectively. The bands at 767 and 441 cm^{-1} correspond to the stretching and bending vibrations of $\text{O}-\text{Ti}-\text{O}$,^[5,9] respectively.

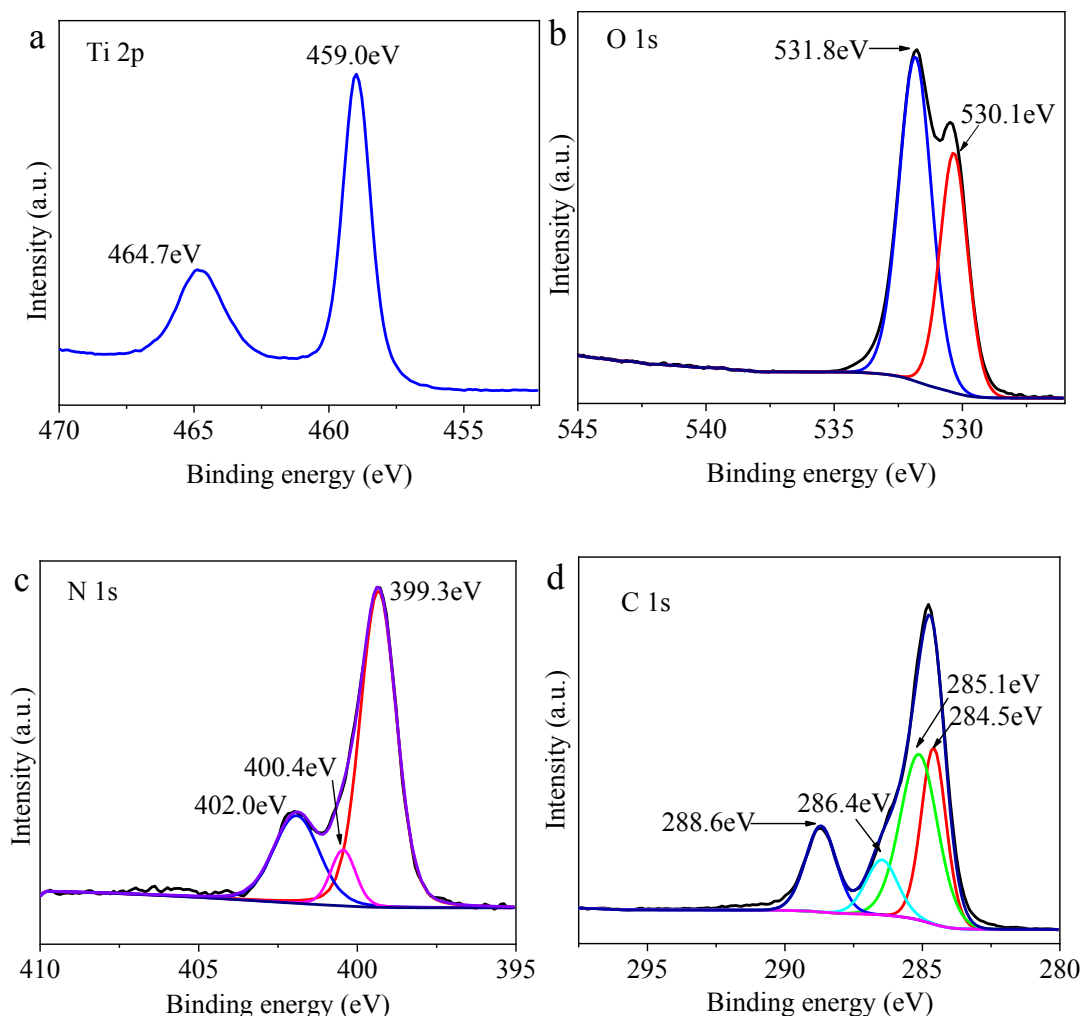


Fig. S11 XPS spectra of the BDCT aerogel

The bind energies of $Ti2p_{3/2}$ and $Ti2p_{1/2}$ of Ti^{4+} shifted to lower binding energies as compared with the reported 459.4 and 465.2 eV for pure TiO_2 ,^[8-9] as shown in Fig. S11a. The O1s spectra (Fig.S11b) show two peaks at 531.8 and 530.1 eV, corresponding to the O1s in the $-CO_3^{2-}$ and the TiO_x .^[4] In the N1s spectra of Fig.S11c, the peak is fitted at 399.3 eV corresponding to free $-NH_2$.^[10] Furthermore, appearance of a small peak at 402.0 eV can be attributed to the positively charged nitrogen species ($-NH_3^+$) under the acidic condition.^[5,11] One more peak at ~ 400.4 eV can be attributed to $-NH_2$ coordinated with Ti^{4+} .^[5-6] The bind energies of C1s were detected at 288.6, 286.4, 285.1 and 284.5 eV as shown in Fig.S11d, corresponding to C=O, C-O, C-N and C=C,^[5] respectively.

References

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