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To confirm the influence of annealing atmosphere orders on the photocatalytic activity of TiO<sub>2</sub>, we conduct the contrast test of N-H-TiO<sub>2</sub>-E and H-N-TiO<sub>2</sub>-E as presented in Fig .S1. N-H-TiO<sub>2</sub>-E was obtained by annealing in NH<sub>3</sub> for 2h and then held in H<sub>2</sub> for 4 h. Similarly, H-N-TiO<sub>2</sub>-E was obtained by treating in H<sub>2</sub> for 4h and NH<sub>3</sub> for 2h.The photocatalytic activity of N-H-TiO<sub>2</sub>-E behaves better than H-N-TiO<sub>2</sub>-E, which is accorded with the contrast between N-H-TiO<sub>2</sub> and H-N-TiO<sub>2</sub>. It proves that N doping followed by H doping is better for improving the performance of TiO<sub>2</sub>. In addition, the positive effect of H doping is also confirmed by the contrast of H-N-TiO<sub>2</sub> and H-N-TiO<sub>2</sub>-E, as well as N-H-TiO<sub>2</sub> and N-H-TiO<sub>2</sub>-E respectively, shown in Fig .S2. Because of the special disordered surface layer by H doping, the absorption ability is efficiently enhanced and the surface active sites are more produced, thus results in the higher mineralization rate of benzene.





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Fig. S2. (a, b) the contrast tests of the photocatalytic activity between H-N-TiO<sub>2</sub> and H-N-TiO<sub>2</sub>-E under visible light; (c, d) the contrast tests of the photocatalytic activity between N-H-TiO<sub>2</sub> and N-H-TiO<sub>2</sub>-E under visible light.