Supplementary Information for

Metal oxide sensitized TiO_2 and $TiO_{2-x}N_x$ with efficient charge transport conduits

Xin Shu, Zhe An, Lianying Wang and Jing He*

State Key Laboratory of Chemical Resource Engineering, Beijing UniVersity of Chemical Technology, Beijing 100029, China

Layered Metal Hydroxides.

Ni-Ti layered hydroxides with CO_3^{2-} as charge balancing anion: 0.5 mL of $TiCl_4$ solution (the solution was prepared from $TiCl_4$ and HCl with a volume ratio of 1:1, in which $TiCl_4$ is 0.002 mol), 0.005 mol of $Ni(NO_3)_2$, and 0.1 mol of urea were dissolved in 100 mL of deionized water under vigorous stirring. The resulting suspension was stirred for 1 h at refluxing temperature. Then the solid was filtered, washed with deionized water until pH=8. The filter cake was re-dispersed in 80 mL of deionized water, and 0.0085 mol of Na_2CO_3 was added to the suspension under stirring. The resulting slurry was transferred into a Teflon-lined autoclave and heated at 100 °C for 10 h. The precipitate was then filtered, washed well with deionized water and anhydrous ethanol, and dried at room temperature.

Ni-Ti layered hydroxides with CNO^- as charge balancing anion: 0.5 mL of $TiCl_4$ solution (the solution was prepared from $TiCl_4$ and HCl with a volume ratio of 1:1, in which $TiCl_4$ is 0.002 mol), 0.005 mol of $Ni(NO_3)_2$, and 0.1 mol of urea were dissolved in 100 mL of deionized water under vigorous stirring. The resulting suspension was stirred for 10 h at refluxing temperature. The solid was filtered, washed with deionized water and anhydrous ethanol, and dried at 60 °C.

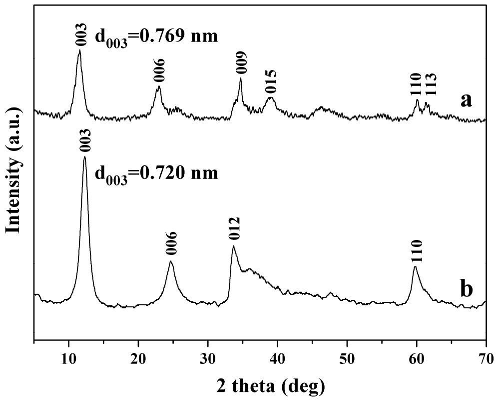

Fig. S1 Powder XRD patterns of Ni-Ti layered hydroxides. The (00*l*) reflections correspond to the layer stacking along the *c* axis. The (110) reflections originate from the layers of metal hydroxides. $a=2d_{110}$ reflects the distance between two metal cations in the layers. The value of d_{003} suggests that the interlayer anions balancing the layer charges are (a) carbonate[1] and (b) cyanate[2].

Photocatalysts.

The NiO-sensitized TiO_2 and $TiO_{2-x}N_x$ are synthesized by calcination of Ni-Ti layered hydroxides with CO_3^{2-} and CNO^- as charge-balancing anions, respectively, in air at 500 °C for 4 h. The temperature-programmed rate was 10 °C/min. To remove NiO, 1.0 g of calcined solids was treated with 100 mL of sulfuric acid solution (5 mol/L) for 24 h under moderate stirring.

Pure NiO powder: 0.005 mol of $Ni(NO_3)_2$ and 0.1 mol of urea were dissolved in 100 mL of deionized water and stirred for 10 h at refluxing temperature. The resulting solid was filtered, washed with deionized water, dried at 60 °C, and then calcined in air at 800 °C for 4 h.

Pure TiO_2 powder: 0.5 mL of $TiCl_4$ solution (the solution was prepared from $TiCl_4$ and HCl with a volume ratio of 1:1, in which $TiCl_4$ is 0.002 mol), and 0.1 of mol urea were dissolved in 100 mL of deionized water and stirred for 10 h at refluxing temperature. The resulting solid was filtered, washed with deionized water, dried at 60 °C, and then calcined in air at 500 °C for 4 h.

NiO+TiO_2 or NiO+$TiO_{2-x}N_x$ as reference: physically mixing pure powders of NiO (81.5 wt %) and TiO_2 (18.5 wt %) or NiO (81.5 wt %) and $TiO_{2-x}N_x$ (18.5 wt %).

$TiO_{2-x}N_x$ was prepared following the procedure in ref. 7 in article.

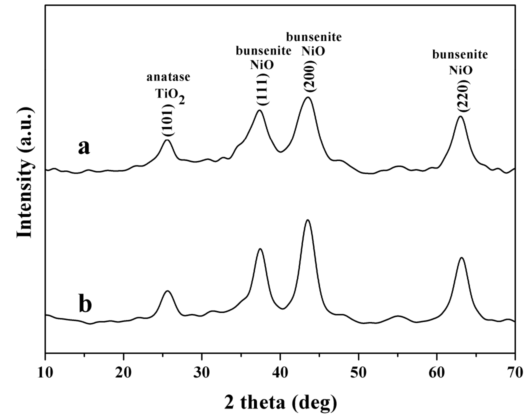

Fig. S2 Powder XRD patterns of NiO-sensitized TiO_2 (a) and NiO-sensitized $TiO_{2-x}N_x$ (b). The reflection characteristic of (101) plane of anatase TiO_2 (JCPDS no. 21-1272), as well as the (111), (200) and (220) reflections of bunsenite NiO (JCPDS no. 47-1049) are observed.

Table S1. The Crystallite Sizes of the Photocatalysts Determined by the Scherrer Equation.

Sample	crystallite size $TiO_{2\,(101)}$ (nm)	crystallite size NiO $_{(111)}$ (nm)	crystallite size NiO $_{(200)}$ (nm)	crystallite size NiO $_{(220)}$ (nm)
NiO-sensitized TiO_2	8.1	9.9	5.9	7.6
NiO-sensitized $TiO_{2-x}N_x$	9.2	7.2	6.6	8.3

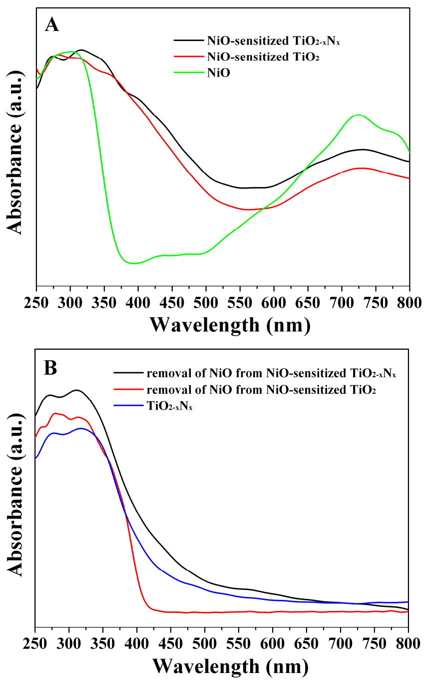

Fig. S3 (A) UV-vis diffuse reflectance spectra of NiO-sensitized TiO_2, NiO-sensitized $TiO_{2-x}N_x$ and pure NiO. (B) UV-vis diffuse reflectance spectra of the remaining TiO_2 after removal of NiO and the reference sample of $TiO_{2-x}N_x$.

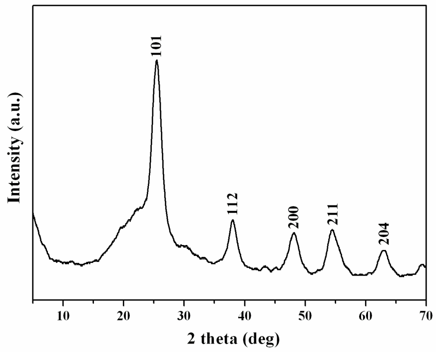

Fig. S4 Powder XRD pattern of the remaining TiO_2 after removal of NiO from NiO-sensitized $TiO_{2-x}N_x$. The basal reflections of (101), (112), (200), (211) and (204) planes are characteristic of anatase TiO_2 (JCPDS no. 21-1272).

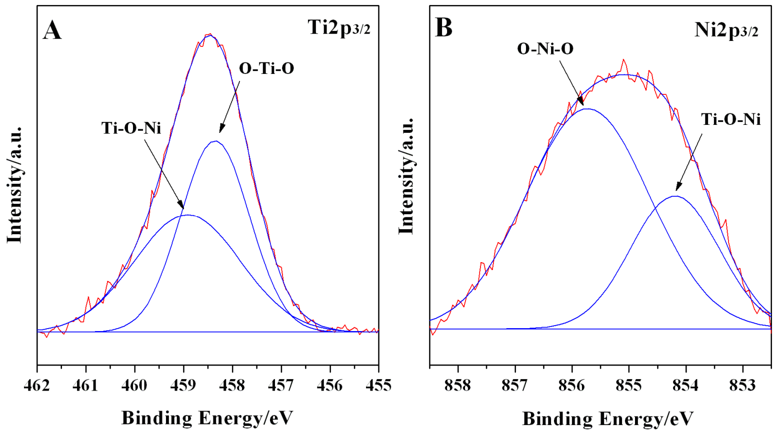

Fig. S5 The Ti $2p_{3/2}$ (A) and Ni $2p_{3/2}$ (B) XPS spectra of NiO sensitized TiO_2. In (A), the peaks at 458.9 and

458.4 eV correspond to the O-Ti-O-Ni and O-Ti-O-Ti structure. In (B), the peaks at 855.7 and 854.2 eV correspond to the O-Ni-O-Ni and O-Ti-O-Ni structure. The Ti $2p_{3/2}$ and Ni $2p_{3/2}$ XPS spectra display the formation of Ti-O-Ni linkage.

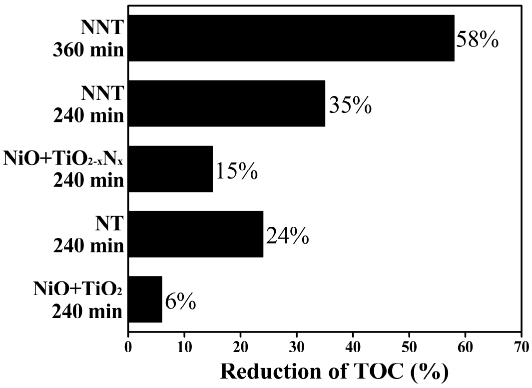

Fig. S6 TOC reduction in the photocatalytic degradation of MB (NT: NiO sensitized TiO_2; NNT: NiO sensitized $TiO_{2-x}N_x$).

Photocatalytic Activity.

Under visible light irradiation: the photocatalytic activity was evaluated by the degradation of methylene blue (MB) under visible light irradiation using a 300 W Xe lamp with the 400 nm cutoff filter. In each experiment, a mixture of MB solution (1×10^{-5} mol/L; 100 mL) and 30 mg of catalyst were vigorously stirred for 30 min to establish an adsorption/desorption equilibrium. Then light irradiation was started. 3 mL aliquots were sampled at intervals and centrifuged to remove the particles. The filtrates were analyzed by measuring the absorption at 665 nm on a Shimadzu UV-2501PC UV-vis spectrophotometer. The blank reaction was carried out following the same procedure without catalyst added.

Under 450 nm monochromatic irradiation: the photocatalytic activity was evaluated by the degradation of methylene blue (MB) under visible light irradiation using a 300 W Xe lamp with the 450±15 nm filter. In each experiment, a mixture of MB solution (2×10^{-6} mol/L; 100 mL) and 40 mg of catalyst were vigorously stirred for 30 min to establish an adsorption/desorption equilibrium. Then light irradiation was then started. 3 mL aliquots were sampled at intervals and centrifuged to remove the particles. The filtrates were analyzed by measuring the absorption at 665 nm on a Shimadzu UV-2501PC UV-vis spectrophotometer.

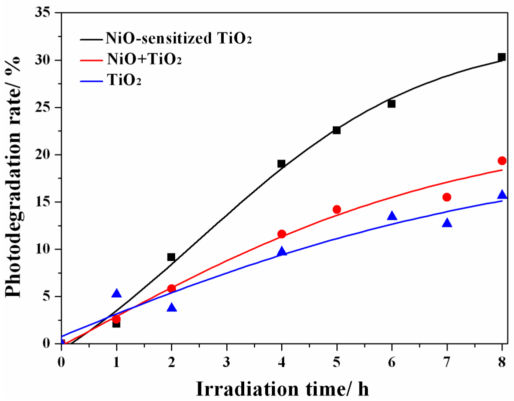

Fig. S7 Temporal course of MB photocatalytic degradation under monochromatic irradiation with 450±15 nm (2.66-2.85 eV). The physical mixture of NiO and TiO_2 shows slightly higher photocatalytic activity than bare TiO_2, meaning that NiO shows weak oxidization on MB. However, both of bare TiO_2 and NiO+TiO_2 (physical mixture) are apparently inferior to the NiO sensitized TiO_2. This fact further indicates the efficient electron transfer through Ti-O-Ni linkage has achieved a highly effective photosensitization in the visible light. The weak oxidizing ability of NiO on MB is quite important for the recovery of electron-injecting NiO.

Supplementary References.

[1] F. Cavani, F. Trifiro, A. Vaccari, *Catal. Today* **1991**, *11*, 173.

[2] X. Shu, W. H. Zhang, J. He, F. X. Gao, Y. X. Zhu, *Solid State Sci.* **2006**, *8*, 634.