One-step calcination method for synthesis of mesoporous g-C_3N_4/$NiTiO_3$ heterostructure photocatalyst with improved visible light photoactivity

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Materials

Dicyandiamide ($C_2H_4N_4$), tetrabutyl titanate ($Ti(O\text{-}C_4H_9)_9$), Nickel acetate ($Ni(CH_3COO)_2{\cdot}4H_2O$), ethylene glycol ($C_2H_6O_2$), ethanol ($C_2H_5OH$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents and solvents were of analytical reagent grade and used as received from commercial suppliers.

Preparation of C_3N_4/$NiTiO_3$ hybrid materials

The g-C_3N_4 was prepared by calcination with dicyandiamide as precursor. 10 g of dicyandiamide was put into a covered crucible, and heated at 550 °C in a muffle furnace for 2 h. The yellow g-C_3N_4 powders were obtained after cooling.

In a typical run, the dicyandiamide was dissolved into 100 mL ethylene glycol under magnetic stirring. Then 2.48 g ($Ni(CH_3COO)_2){\cdot}4H_2O$)·and 3.4 mL ($Ti(O\text{-}C_4H_9)_9$) was added into the above solution. After a light blue precipitate appeared, the stirring was continued for another 2 h to ensure the reaction completed. The obtained precipitate was collected by centrifugation, purified thoroughly with absolute ethanol and dried at 60 °C in an oven for 6 h. Finally, the resulted product was putted into a muffle furnace and then calcined at 550 °C for 2 h in air to obtain the g-C_3N_4/$NiTiO_3$ nanocomposites. As reference, normal $NiTiO_3$ was synthesized via the same strategy but without dicyandiamide. The as-prepared g-C_3N_4/$NiTiO_3$ samples with expected g-C_3N_4 contents of 10.1, 18.4 and 27.3 wt% were labeled as CT1, CT3, CT5, respectively.

Characterization

XRD patterns were recorded using Bruker AXS D8 Advance diffractometer equipped with Cu-K*a* source ($\lambda = 1.541$ Å). The surface morphologies and the energy dispersive X-ray spectra of the prepared samples were characterized by an environmental scanning electron microscopy (SEM) (JSM-7001F, Japan). The X-ray Photoelectron Spectroscopy spectrum (XPS) (Thermo Fisher Scientific, UK) was carried out to analyze the surface elemental composition analyses. UV-visible diffuse-reflectance spectra (UV-vis DRS) of the samples were recorded using a Varian Cary 300 spectrometer outfitted with an integrating sphere. The specific surface area and pore size of the samples were measured with Brunauer–Emmett–Teller (BET) measurement (ASAP2020, Micromeritics, USA). Steady-state photoluminescence (PL) spectra were examined by Perkin-Elmer LS-55 spectrofluorimeter.

Photocatalytic activity measurement

Photocatalytic removal of NB was conducted vertically irradiated by a 300 W xenon lamp (Beijing China Education Au-light Co. Ltd) with a 420nm cutoff filter. The visible light source (14 V, 16 A, 15 cm) far away from the photocatalytic reactor. Typically, 40 mg powdered catalysts were dispersed in 100 mL of 20 mg·L^{-1} NB solution. Then, the solution was magnetically stirred for 1 h in darkness to attain adsorption equilibrium. Aliquots were drawn out of the solution at defined time intervals, centrifuged, and examined at 268 nm using a UV-vis spectrophotometer (UV-2250, SHIMADZU Corporation, Japan). Five successive cyclic tests were carried out over the optimal hybrid as follows. After the every run, the photocatalyst was washed several times with deionized water, dried at 60 °C in air and subjected to the next run.

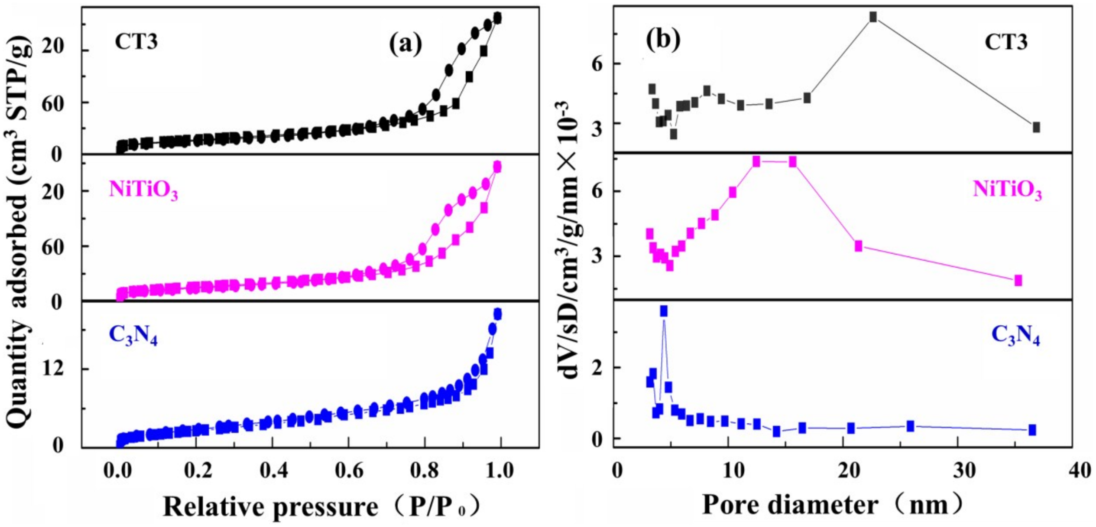

Fig.S1. (a) N_2 adsorption and desorption isotherms and (b) pore-size distribution curves for g-C_3N_4, $NiTiO_3$, CT3.

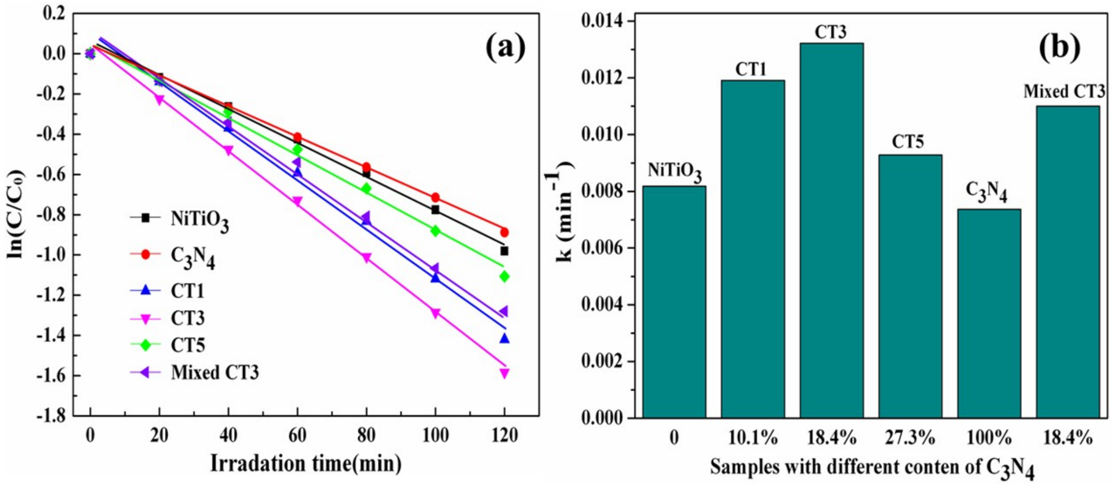

Fig.S2. The model fitting plots (a) and corresponding *k* values (b) of g-C_3N_4, $NiTiO_3$ and g-C_3N_4/$NiTiO_3$ composites.

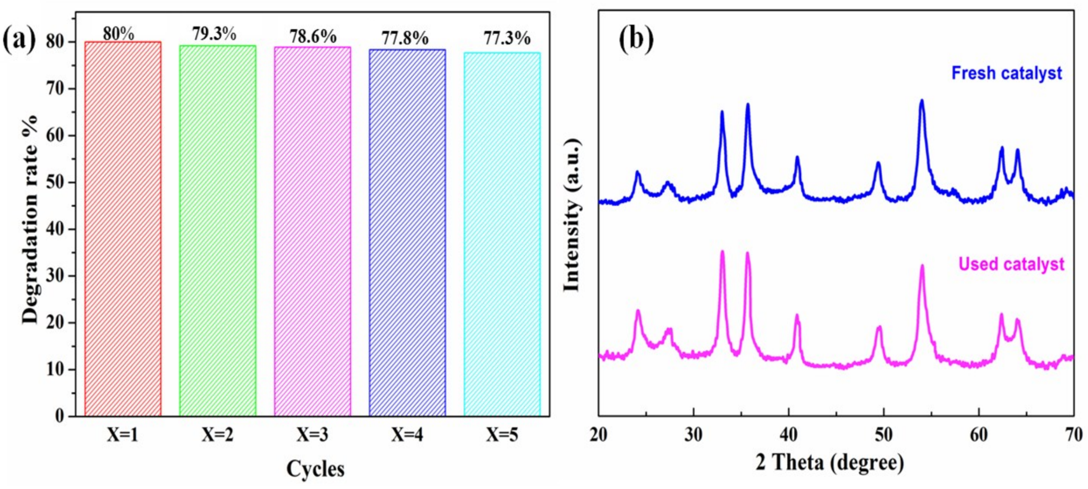

Fig.S3. (a) Recycling test of CT3 in photocatalytic removal of NB; (b) the XRD patterns of CT3 before and after irradiation.

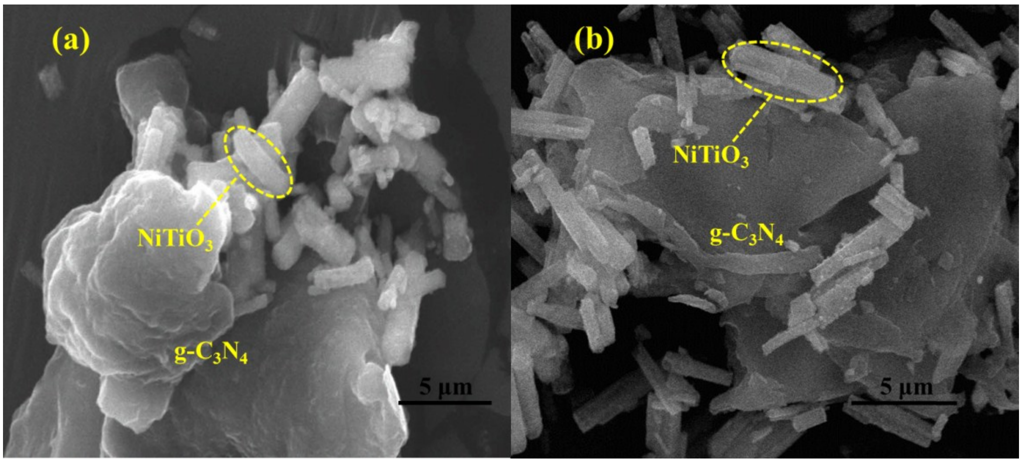

Fig.S4. SEM images of CT3 before (a) and after (b) visible light irradiation.