ZnO-TiO$_2$ Composites and Ternary ZnTiO$_3$ Electrospun Nanofibers: Influence on annealing on Photocatalytic Response and Reusable Functionality

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Supporting Information

Synthesis of TiO$_2$ Nanofibers

Synthesis of TiO$_2$ nanofibers was accomplished through an electrospinning process. To prepare the precursor solution, 0.5 g of polyvinylpyrrolidone (PVP, Mw = 1,300,000, Sigma-Aldrich) were dissolved in 2.5 mL of ethanol by stirring. 0.5 ml of titanium tetra butoxide (Ti(OBu)$_4$) were used as Ti precursor and stirred for 20 mins in 1 ml of ethanol and 0.3 ml of acetic acid; this solution was then added to the polymer solution. After stirring for 3 h, the precursor solution was drawn into a 3 mL plastic syringe with needle diameter of 0.4 mm and displaced to the needle tip to an electrospinning system (KD Scientific, KDS101) at a flow rate of 0.5 mLh$^{-1}$; the distance between the tip of the needle and the grounded aluminum plate was approximately 15 cm. The needle was connected to a high-voltage power source, and a voltage of 15 kV was applied from a high voltage power supply (Spellman, SL series, USA). The electrospun TiO$_2$/polymer nanofibers were dried at 80 °C in an oven for 6 hours and then calcined at 500 °C for 3 h in air.

Electrospinning of ZnO nanofibers

The electrospinning solution was prepared by dissolving polyvinyl alcohol (PVA, 7.5% w/v) in water at 80 °C followed by addition of zinc acetate dihydrate (4%, w/v). The resulting solution was stirred for 2 hours to obtain a homogeneous solution. Furthermore, the solution was loaded in a 3 mL plastic syringe with needle diameter of 0.8 mm and placed horizontally on a syringe pump (KD Scientific, KDS101). The flow rate of the polymer solution was controlled by the syringe pump and fixed at 0.5 mL h$^{-1}$. The grounded metal collector was covered with aluminum foil and placed at a distance of 12 cm from the needle tip. The electric field (15.0 kV) was applied from a high voltage power supply (Spellman, SL series, USA). Electrospinning procedure was carried out at 22 °C and 19% relative humidity in a Plexiglas box. The obtained zinc acetate/PVA composite NF were further calcined at 400 °C for 3 h in air to obtain ZnO NF.
Fig. S1 XRD spectra and SEM images of Zn(OAc)$_2$-Ti(OBu)$_4$-PVP NF annealed at 500 °C, 600 °C, 700 °C, 800 °C respectively.
Fig. S2 (a) C 1s XPS spectra of ZnO-TiO$_2$ composite and ternary ZnTiO$_3$ NFs. (b, c) EDAX spectra of ZnO-TiO$_2$ composite and ternary ZnTiO$_3$ NFs, respectively.

Fig. S3 EDAX-SEM image mapping of ZnO-TiO$_2$ composite NF coated on copper tape.
Fig. S4 BET adsorption–desorption curve for the composite and ternary NFs. (a) ZnO-TiO$_2$ NF and (b) ZnTiO$_3$ NF. The inset shows the distribution of pore volume vs pore radius.

Fig. S5. Self-degradation of MB dye solution under visible irradiation without any catalyst respect to time.
**Fig. S6** Photo degradation activity of the composite and ternary NFs over the colorless 4-chlorophenol in 120 min under visible irradiation.
**Fig. S7** Comparative photocatalytic properties over the MB dye molecules with composite and ternary NFs under visible photo irradiation

**Fig. S8** Quantifying the superoxide radical anions (O$_2^-$) and hydroxyl radicals (OH) production rate, from the degradation of NBT and p-CBA were used as a probe molecules under visible irradiation.
**Fig. S9** Optical images of (a) ZnO-TiO$_2$ composite and (d) ternary ZnTiO$_3$ NFs before irradiation. Optical and low magnified SEM images of the (a, b) ZnO-TiO$_2$ composite and (c, d) ternary ZnTiO$_3$ NFs after photocatalytic process.

**Fig. S10** XRD spectra of the ZnO-TiO$_2$ composite and ternary ZnTiO$_3$ NFs before and after photocatalytic process.