

Supporting Information for

**Ion exchange synthesis of PAN/Ag₃PO₄ core-shell nanofibers with
enhanced photocatalytic properties**

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Experimental Section

1. Materials

PAN (molar mass $M_w=150000$) was purchased from J&K Scientific Ltd, other materials such as PVP(K-30), AgNO₃ and Na₂HPO₄ were purchased from Sinopharm Chemical ReagentCo. Ltd. DMF was used as solvent of the PAN without further purification.

2. Preparation of AgNO₃/PAN electrospun mats

In a typical synthesis, polyacrylonitrile (PAN) was initially dissolved in N,N-dimethyl formamide (DMF) to form a PAN solution of 10 wt %, 0.5 g silver nitrate powder was then added to the as-prepared PAN/DMF solution with magnetic stirring to get a viscous transparent solution. For electrospinning, the electrospun solution was transferred into a 10 mL plastic syringe and electrospun at a positive voltage of 20 kV with a constant rate of 0.8 mL/h through a syringe pumps. A sheet of grounded aluminum foil was placed 10 cm under the syringe as the collector. All experiments were conducted at room temperature and atmosphere pressure. The obtained AgNO₃/PAN fiber mats were dried for 2 h in the air to allow the residual solvent to evaporate for in situ generation of Ag₃PO₄ nanoparticles.

3. Fabrication of PAN/Ag₃PO₄ core-shell nanofibers

For the preparation of PAN/Ag₃PO₄ core-shell nanofibers, the obtained AgNO₃ electrospun mats were immersed into a Na₂HPO₄ aqueous solution (0.2 M) containing 0.1 M PVP at room temperature for ion exchange. The color of the composite fibers rapidly changed from white to

yellow, thus, Ag_3PO_4 nanoparticles were synthesized on the surface polymer nanofibers via the reaction of Ag^+ with $(\text{HPO}_4)^{2-}$. The obtained samples for morphology and structure analysis were washed three times with distilled water to remove the PVP residue and subsequently dried at 60°C for 1 h.

4. Photocatalytic Reactions

In a typical test, the sample (0.6 g, mass ratio of Ag_3PO_4 : PAN was 1:2) was mixed with an aqueous solution of RhB dye (100 mL, 8 mg/L). The reaction system was irradiated with a 300 W Xe arc lamp equipped with an ultraviolet cutoff filter to provide visible light with $\lambda \geq 420$ nm. The degradation of RhB dye was monitored by UV/Vis spectroscopy. Before the spectroscopy measurement, this photocatalyst was removed from the photocatalytic reaction systems by a dialyzer (Millipore, Millex-LH 0.45 μm).

5. Characterizations

The morphologies were observed by field-emission scanning electron microscope (FE-SEM, JSM 6701F) operated at an accelerating voltage of 5 kV. The X-ray diffraction (XRD) measurements were performed on X'pert PRO diffractometer using $\text{Cu K}\alpha$ radiation (40 kV). The XRD patterns were recorded from 10° to 90° with a scanning rate of $0.067^\circ/\text{s}$. The XPS was performed by an ESCALAB 250 Xi XPS system of Thermo Fisher Scientific, England and excited by monochromatic $\text{Al K}\alpha$ radiation (1486.6 eV). The infrared spectra were obtained on a TENSOR27 FT-IR spectrometer using the KBr disk method. UV/vis absorption spectra were taken at room temperature on a UV-2550 (Shimadzu) spectrometer.

Additional Figures and Discussions

Reasons for using PAN in the photocatalytic system.

It has been generally known that electrospinning could serve as a universal and versatile method to generate 1D nanostructure with controlled morphology and composition compared with other fabrication methods. The electrospun nanofibers can further serve as the templates to obtain multifunctional nanostructures by controlling the fiber compositions. Thereby, we expect that the rational design and fabrication of well-defined PAN-Ag₃PO₄ composite nanofibers may greatly improve the current photochemical reactivity and open up new applications.

In the PAN/Ag₃PO₄ hetero-structures, PAN acted as polymer template to make the Ag₃PO₄ nanoparticles expose completely and densely on the fiber surface without agglomeration, thus they could share the photo-excited electrons and achieve novel collective photocatalytic properties. Furthermore, it has been widely known that after photocatalytic reaction, the recovery process is very difficult for the conventional powder photocatalysts. However, the PAN-based electrospun nanofibers can be easily separated from solution by filtration or sedimentation due to its hydrophobic property with a low density. Besides, PAN possesses some clear advantages over other polymers, such as its straightforward synthesis, high environmental stability, and good processibility.

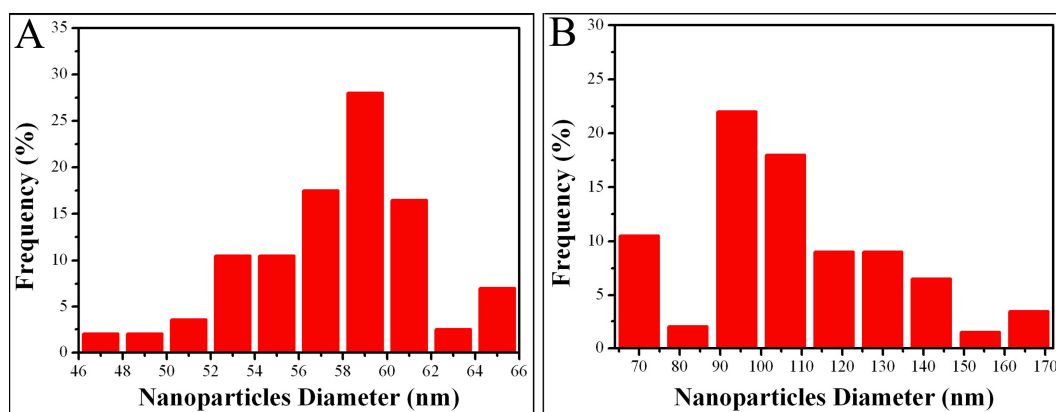


Fig. S1 Histogram showing the diameter distribution of the PAN/Ag₃PO₄ core-shell nanofibers, as measured by SEM. (A) Prepared from the Na₂HPO₄ aqueous solution in the presence of PVP, (B) prepared from the Na₂HPO₄ aqueous solution in the absence of PVP.

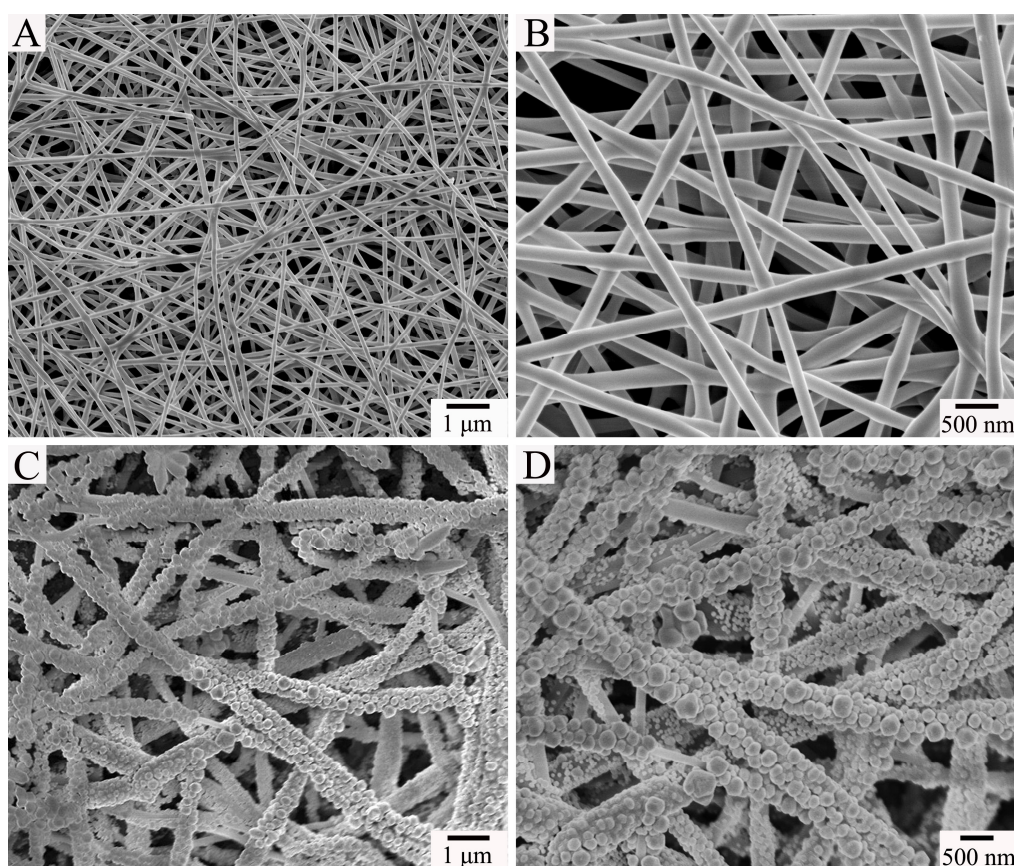


Fig. S2 (A, B) SEM images of AgNO₃/PAN nanofibers with mass ratio of AgNO₃ and PAN 1.5:1;
(C, D) SEM images of corresponding PAN/Ag₃PO₄ core-shell nanofibers

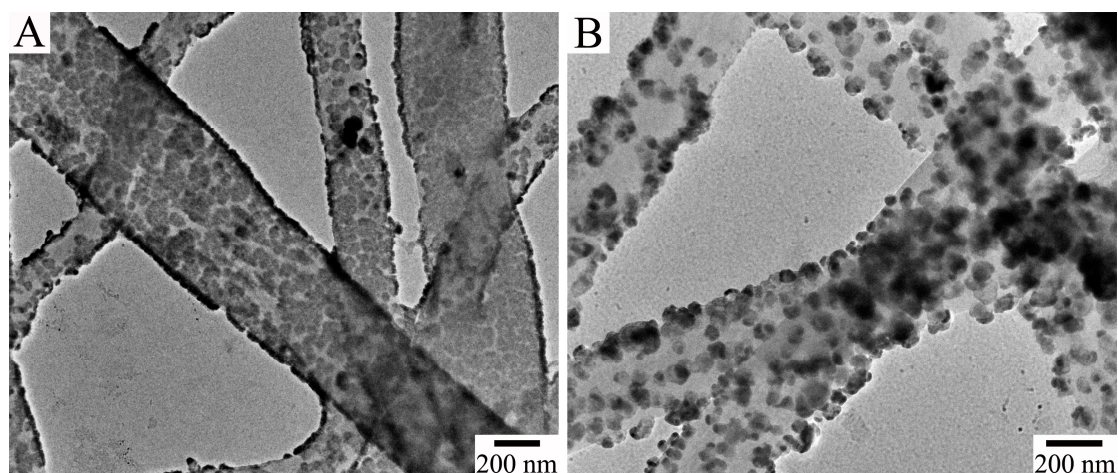


Fig. S3 (A, B) TEM images of as-prepared PAN/Ag₃PO₄ core-shell nanofibers with mass ratio of AgNO₃ and PAN 1:1; (C, D) TEM images of PAN/Ag₃PO₄ composite nanofibers with mass ratio of AgNO₃ and PAN 0.25:1

Results and discussion

Fig. S3A and S3B show the typical transmission electron microscopy (TEM) images of the as-prepared PAN/Ag₃PO₄ core-shell nanofibers. It can be clearly seen from Fig. S3A that the surface of the fibers was covered completely and densely by the Ag₃PO₄ nanoparticles and the nanofibers present a rough surface, corresponding to the observation of the SEM images. To further investigate the structure of PAN fiber nanocores and Ag₃PO₄ nanoshells, the nanofibers with incompletely covered were obtained via decreasing the content of the AgNO₃ in the AgNO₃/PAN electrospun mats. As shown in Fig. S3B, it can be clearly seen that the PAN fibers possessed unbroken fibrous structure to form the cores of the composite nanofibers, while the Ag₃PO₄ nanoparticles resided on the outside surface of the PAN nanofibers to constitute the shells of the fibers. Thereby, we believe that the composite nanofibers with Ag₃PO₄ nanoparticles completely coated have undoubtedly a core-shell structure.

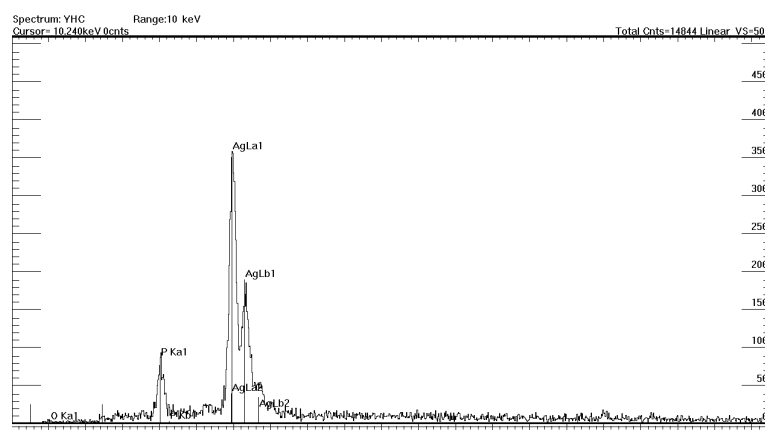


Fig. S4 EDS spectra of the as-synthesized PAN/Ag₃PO₄ core-shell nanofibers.

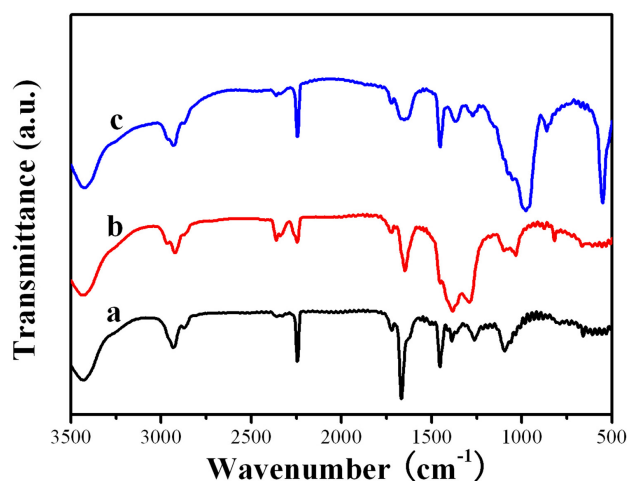


Fig. S5 FTIR spectra of the a) PAN nanofibers, b) AgNO₃/PAN nanofibers, c) PAN/Ag₃PO₄ core-shell nanofibers

FTIR analysis of the as-prepared PAN/Ag₃PO₄ core-shell nanofibers

Fourier transformation infrared spectroscopy (FTIR) analysis was performed in our study in order to investigate the interaction between the polymer and the inorganic phase by comparing the infrared absorption of the composite fibers and pure PAN nanofibers. Fig. S5a shows the typical FTIR spectrum of PAN nanofibers, it can be clearly seen that the PAN displays the characteristic absorption peaks of the CN nitrile group at around 2241 cm⁻¹, besides, a series of characteristic bands in the regions 2930-2870 cm⁻¹, 1460-1450 cm⁻¹, 1380-1360 cm⁻¹ and 1290-1260 cm⁻¹ are ascribed to the vibrations of different modes in methylene group of PAN. As shown in Fig. S5b, a new set of bands are observed due to the presence of AgNO₃, including the bands at 1037 cm⁻¹, 818 cm⁻¹, attributed to the N-O stretching vibration and the bending vibration of nitrate, respectively. These peaks are undetectable after the ion exchange reaction (Fig. S5c), on the other hand, significant spectroscopic bands at 980 cm⁻¹ and 818 cm⁻¹ appear which assigned to the P-O stretching vibrations of the PO₄³⁻, indicating the formation of the Ag₃PO₄.

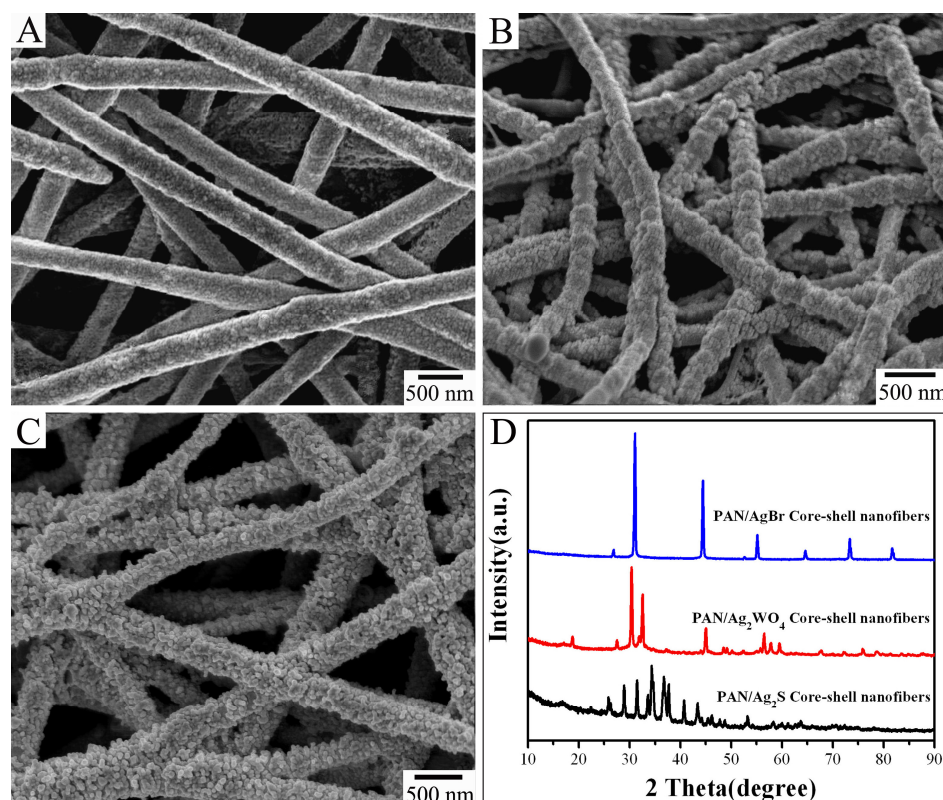


Fig. S6 SEM images of the nanoproducts prepared with different compounds: (A) Na₂S solution, (B) KBr solution, (C) Na₂WO₄ solution; (D) their XRD patterns.

Results and discussion

Here, we extend the approach combining electrospinning and ion exchange reaction to develop a general methodology for generation of other Ag-based core-shell nanostructures using AgNO₃/PAN electrospun mats as precursor and template. The morphology of nanoproducts prepared with other compounds has also been investigated. As shown in Fig. S6A, in the case of Na₂S aqueous, dense and homogeneous Ag₂S nanoparticles reside on the PAN fibers to form PAN/Ag₂S core-shell structure. Moreover, when NaBr solution is used in this process, PAN/AgBr core-shell nanofibers are obtained (Fig. S6B), the same goes for Na₂WO₄ aqueous (Fig. S6C). Their crystalline structures have also been studied, and the XRD results are shown in Fig. S5D. The ultraviolet-visible diffuse reflectance spectra have also been studied and presented in Fig. S7. These demonstrations suggest that the method combining electrospinning with ion exchange reaction can be served as a general and facile synthesis process for the generation of polymer/inorganic composites with core-shell structures.

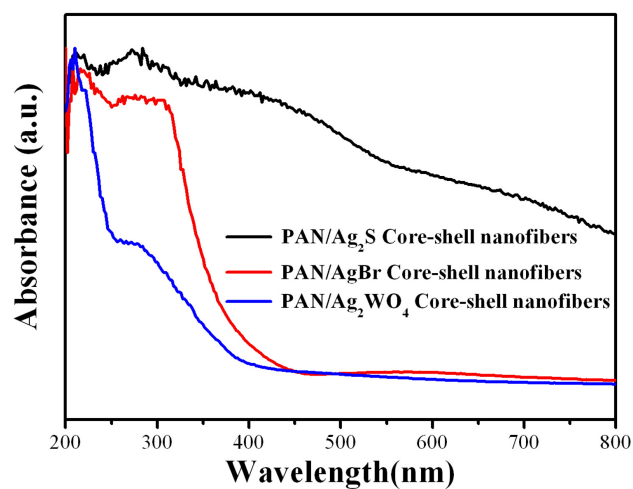


Fig. S7 The ultraviolet-visible diffusive absorption spectrums of different core-shell hetero-structures: PAN/Ag₂S core-shell nanofibers, PAN/AgBr core-shell nanofibers and PAN/Ag₂WO₄ core-shell nanofibers.

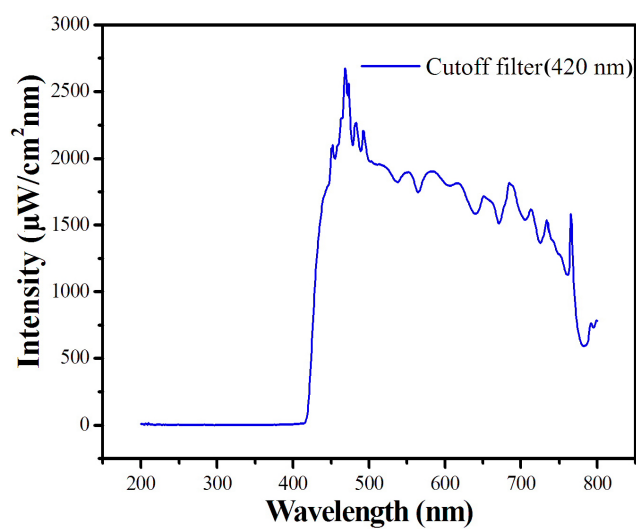


Fig. S8 The intensity and wavelength distribution of the irradiation light employed in the organic decomposition experiments. Integral intensities were measured under the actual experimental conditions.

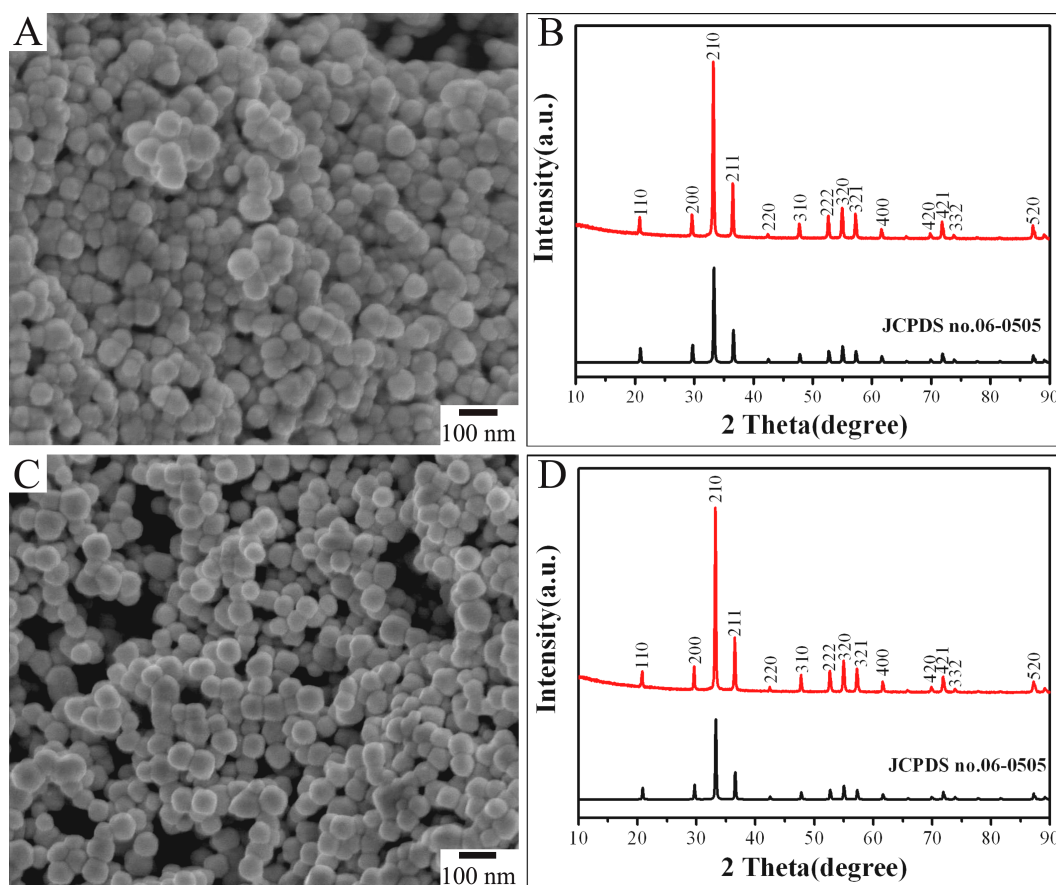


Fig. S9 (A, C) SEM images of the Ag_3PO_4 nanoparticles I and II ; (B, D) their XRD patterns.

Preparation of Ag_3PO_4 nanoparticles I and II

Ag_3PO_4 nanoparticles I was synthesized by precipitation of AgNO_3 and H_3PO_4 in the presence of oleylamine according to the method mentioned in previous literature^[1]. Ag_3PO_4 nanoparticles II was fabricated by a new method we are studying now. Fig. S9 show the SEM images of the products, indicating that both the samples with the average diameter of 65 nm, nearly the same as Ag_3PO_4 nanoparticles resided on the PAN fibers. From their XRD patterns, it can be clearly seen that all the diffraction peaks of the products could be perfectly indexed to the body-centered cubic structure of Ag_3PO_4 (JCPDS no 06-0505).

Reference

- [1]. C. T. Dinh, T. D. Nguyen, F. Kleitz and T. O. Do, *ChemComm.*, **2011**, 47, 7797.

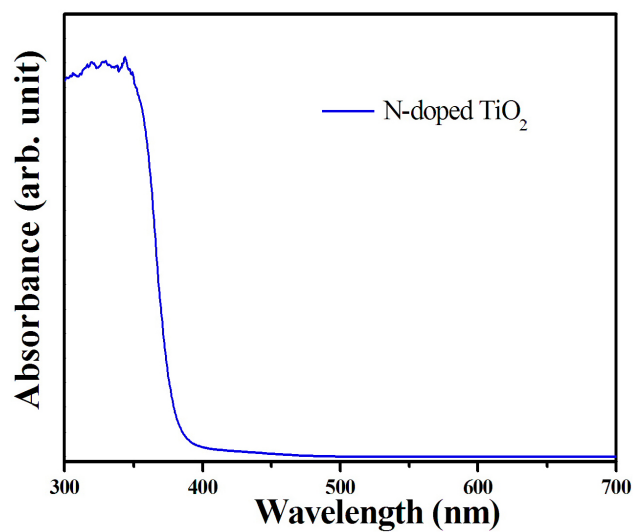


Fig. S10 The ultraviolet-visible diffusive reflectance spectrums of N-doped TiO_2 .

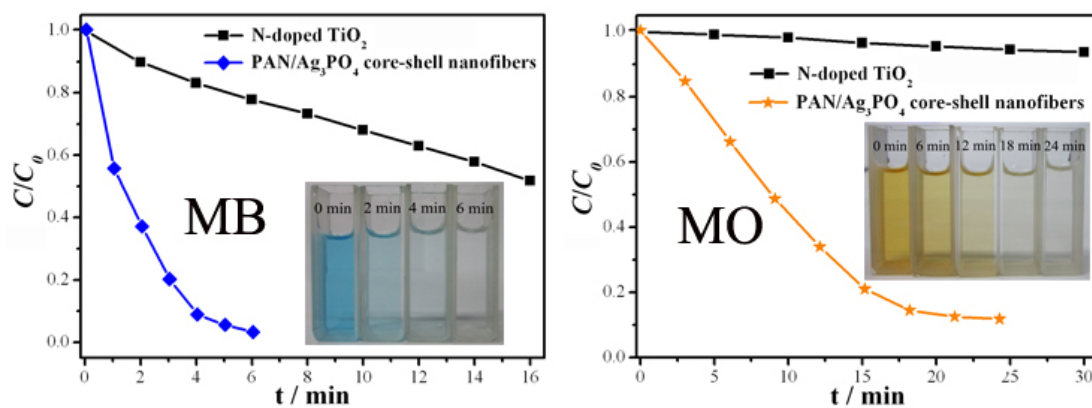


Fig. S11 Photocatalytic activities of PAN/ Ag_3PO_4 core-shell nanofibers for the degradation of (A) MB and (B) MO dye under visible light irradiation ($\lambda > 420 \text{ nm}$) at room temperature.

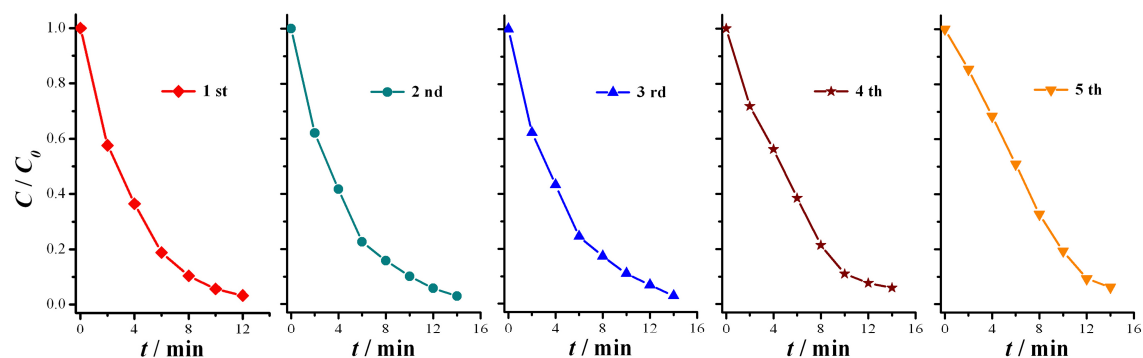


Fig. S12 Photocatalytic activities of the PAN/Ag₃PO₄ core-shell nanofibers for the degradation of RhB under visible light irradiation ($\lambda > 420$ nm) for five cycles.

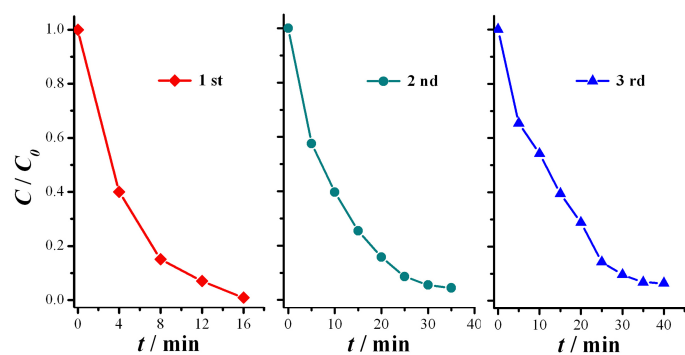


Fig. S13 Photocatalytic activities of the Ag₃PO₄/PAN Necklace-like nanofibers for the degradation of RhB under visible light irradiation ($\lambda > 420$ nm) for three cycles.