Electronic Supplementary Information

Synthesis of Visible-light Responsive C, N and Ce Co-Doped TiO₂

Mesoporous Membranes via Weak Alkaline Sol-gel Process

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Fourier-transform infrared spectroscopy spectra



Fig. S1 FTIR spectra of N-TiO₂-450 and N-Ce-TiO₂-450.

In order to explain the influence of Ce-doping on the structure of the resulted materials better, the Fourier transform infrared spectroscopy (FTIR) spectra of TiO_2 samples with different dopant calcined at 450 0 C was added, shown in Fig.S1. In undoped sample exhibits a peak at 502 cm⁻¹, which is the characteristic peak of titania. But in the case of Ce-doped samples, this peak shifted to the range of 465-480 cm⁻¹ due to the formation of Ti-O-Ce bond. ^{1, 2}

X-ray diffraction patterns



Fig. S2 Wide angle XRD patterns for the TiO₂ films. A: N-P123-TiO₂-450 and B: N-Ce-P123-TiO₂-450 From the wide angle XRD results in Fig.S2, the crystallite size was estimated to be approximately 16.7 nm in the N-P123-TiO₂-450 sample and 10.5 nm in N-Ce-P123-TiO₂-450 sample.



X-ray photoelectron spectroscopy studies

Fig. S3 XPS spectra of a. Ti 2p, b. O 1s, c. C 1s, and d. N 1s of N-Ce-P123-TiO₂-450

To get a better understanding about the chemical state of all elements on the membrane surface, N-Ce-P123-TiO₂-450 was investigated by XPS technique and the XPS spectra of Ti 2p, O 1s, C 1s, and N 1s were presented in Fig. S3.

In Fig. S3 (a), the XPS peaks of Ti $2p_{3/2}$ and Ti $2p_{3/2}$ observe at 458.5 eV and 464.4 eV, were due to Ti⁴⁺ in pure anatase form.³ The O 1*s* spectrum was also well fitted by two components with O 1*s* binding energies at 531.1 eV and 529.7 eV, respectively. The O 1*s* peak with the binding energy at 529.7 eV can be unambiguously assigned to the oxygen bound to Ti⁴⁺ and another peak at 531.1 eV ascribe to the typical values of O 1*s* binding energy for oxygen in OH groups.⁴ In Fig. S3 (c), primary C 1*s* relevant peaks were found mainly at 284.8 eV, 286.5 eV, 288.5 eV. The peak (284.8 eV) is thought to signal the presence of adventitious elemental carbon and the other two suggest the existence of C-O and C=O, respectively, which indicates the formation of carbonated species. These data reveal that carbon may substitute for some of the lattice titanium atoms and form a Ti–O–C

structure via the hybridization between P123 and titanium dioxide.⁵⁻⁶ Fig. S3 (d) confirms the states of the doped N atom, N 1*s* XPS spectrum of the sample, there is only one strong peak observed at 400.1 eV (at. %: 2.04), which probably reflects a chemical structure like O-Ti-N in the surface.⁷⁻¹⁰

Optical absorption properties

The band of the semiconductor can be deduced from the equation below: ^{11, 12}

$$\alpha h v = A (h v - E_g)^{n/2}$$
(1)

where α , v, E_g and A are the sbsorption coefficient, light frequency, band gap, and a constant, respectively. Among them, n is determined by the type of optical transition of a semiconductor (for TiO₂, n=4). Therefore, the band gap energy of TiO₂ was determined from a plot of (ahv) ^{1/2} versus energy (hv) (Fig. S4) and is found to be 2.14 eV for N-Ce-P123-TiO₂-450 and 2.65 eV for N-P123-TiO₂-450.



Fig. S4 Plots of (ahv))1/2 versus energy (hv) for the band gap energy of N-P123-TiO₂-450 (A) and N-Ce-P123-TiO₂-450 (B)

Photolysis experiment of methyl orange



Fig.S5 The direct photolysis of methyl orange solution (5mg/L, pH=3) under visible light (800 nm> λ > 400 nm) The direct photolysis of methyl orange solution was shown in Fig. S5, we can see that the concentration of methyl orange was almost unchanged in 80 min. The influence of photolysis on methyl orange can be neglected.

References

- 1 C. Sibu, S. R. Kumar, P. Mukundan and K. Warrier, Chem. Mater., 2002, 14, 2876.
- 2 B. M. Reddy, B. Chowdhury, P. G. Smirniotis. Appl. Catal., A, 2001, 219, 53.
- 3 Y. Li, D. S. Hwang, N. H. Lee and S. J. Kim, Chem. Phys. Lett., 2005, 404, 25.
- 4 J. Chastain. Handbook of X-ray photoelectron spectroscopy. Perkin-Elmer Corporation, Minnesota, 1992.
- 5 Y. Park, W. Kim, H. Park, T. Tachikawa, T. Majima and W. Choi, Appl. Catal., B: Environmental, 2009, 91, 355.
- 6 W. Ren, Z. Ai, F. Jia, L. Zhang, X. Fan and Z. Zou, Appl. Catal., B: Environmental, 2007, 69, 138.
- 7 F. Dong, W. Zhao and Z. Wu, Nanotechnology, 2008, 19, 365607.
- 8 C. Liu, X. Tang, C. Mo and Z. Qiang, J. Solid State Chem., 2008, 181, 913.
- 9 H. Li, J. Li and Y. Huo, J. Phys. Chem., B, 2006, 110, 1559.
- 10 J. Wang, W. Zhu, Y. Zhang and S. Liu, J. Phys. Chem., C, 2007, 111, 1010.
- 11 Tauc, J. Mater. Res. Bull. 1970, 5, 721.
- 12 J. Zeng, H. Wang, Y. C. Zhang, M. K. Zhu and H. Yan, J. Phys. Chem. C, 2007, 111, 11879.

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