Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


# Synchrotron Infrared Spectroscopic High-Throughput Screening of Multi-composite Photocatalyst Films for Air Purification

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**Photocatalyst library preparation**

The photocatalyst library was fabricated using thin-film deposition method by a multi-target magnetron sputtering system. Layers of precursors were deposited sequentially through the masks. $TiO_2$ was grown firstly on the ultra-clean glass (10 mm ×10 mm) without mask in 12 h. Then, the mask was moved to generate a compositional gradient of $Fe^{3+}$ and $Nb^{5+}$ on substrate in 10 min, respectively. After this, C was deposited on the thin film to form FNT library. The deposition of C on thin file was beneficial for the homogeneous distribution of $Fe^{3+}$ and $Nb^{5+}$. The details of synthesis process have been described elsewhere (*Chemcatchem, 2014, 6, 2535*). Considering the preparation method of gradating FNT library, the compositions on the different plots can be estimated as depicted in Fig. S1. Along the solid diagonal, the content of $Fe^{3+}$ gradually increases from 0 to a maximum on the top left corner (1% $Fe^{3+}$), while the content of $Nb^{5+}$ gradually decreases from the maximum on the bottom right corner (0.7% $Nb^{5+}$) to 0. Along the dashed diagonal, the composition are theoretically equal of ca. 0.5% $Fe^{3+}$/0.35% $Nb^{5+}$-$TiO_2$.

**Photocatalytic activity tests of FNT library**

The photocatalytic activity of FNT library was tested in a homemade reaction cell under gaseous HCHO atmosphere with a fixed flow rate of ca. 10 sccm. 20 vol%$O_2$/$N_2$ was first bubbled through saturator containing formaldehyde, and then supplied to the reaction cell via drier. Water vapor was supplied to the cell via a by-pass line. The relative humidity (R.H.) in the cell was determined using the electronic hygrometer

fixed in the reaction cell. In-situ FTIRM image measurements were performed with a 64×64 (4096 pixels) mercury cadmium telluride focal plane array (FPA) detector, which has the advantage of high spatial resolution in a wide field within a relatively short data collection time. Infrared spectra can be collected from an individual pixel or from spots formed by several pixels. The details of in-situ FTIRM image measurements have been provided elsewhere (*Chemcatchem, 2014, 6, 2535*).

**Bulk powder photocatalyst preparation**

Once an active photocatalyst was obtained from the high-throughput screening process, the bulk powder sample was synthesized by a sol-gel method. 10 mL tetra-n-butyl titanium ($Ti(OC_4H_9)_4$) mixed with 40 mL ethanol were added drop-wise into a mixture solution containing 3 mL distilled water, 4 mL acetic acid and 40 mL ethanol under vigorous stirring for 2 h. The obtained transparent colloidal suspension was then aged for 48 h to form $Ti(OC_4H_9)_4$ gel. A certain amount of iron nitrate ($Fe(NO_3)_3$) and niobium chloride ($NbCl_5$) according to the desired dopant content (Fe:0.1-1 wt%, Nb: 0.07-0.7 wt%) dissolved in distilled water were mixed with the $Ti(OC_4H_9)_4$ gel. Finally, the resulting gel was dried at 353 K for 48 h followed by calcination at 753 K for 3 h to obtain powder samples.

**Photocatalytic activity tests of bulk powder photocatalyst**

The photocatalytic activity of bulk powder samples were tested using a 300 mL photoreactor. 1.7 g sample was coated on the 14.4 $cm^{-2}$ sample holder for photocatalytic degradation. The initial HCHO concentration was 45 ppm, and the R.H. level was 60%.

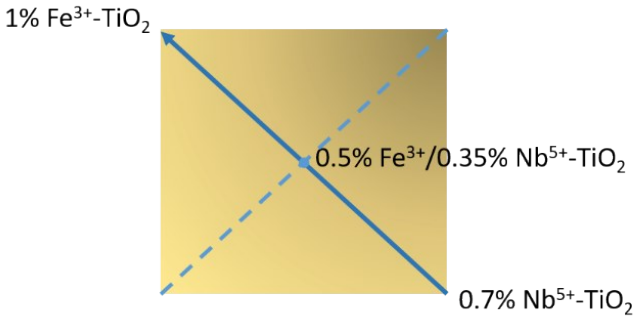


Fig. S1 The compositional gradient of FNT library.

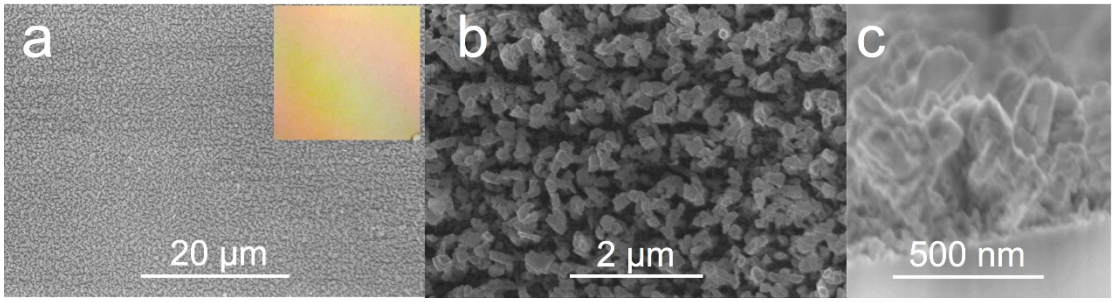


Fig. S2 SEM images of the as-synthesized FNT library (a)(b) vertical view (inset is a digital image of FNT library) and (c) cross-section view.

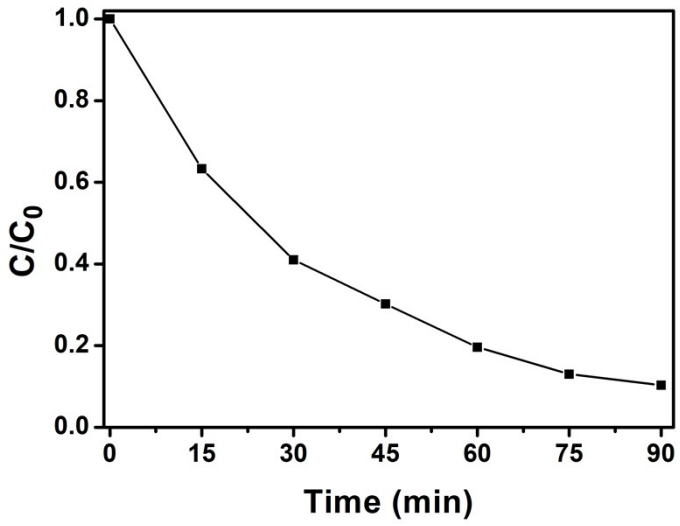


Fig. S3 Photocatalytic activity of bulk powder 0.9%$Fe^{3+}$/0.07%$Nb^{5+}$-$TiO_2$ under visible light.

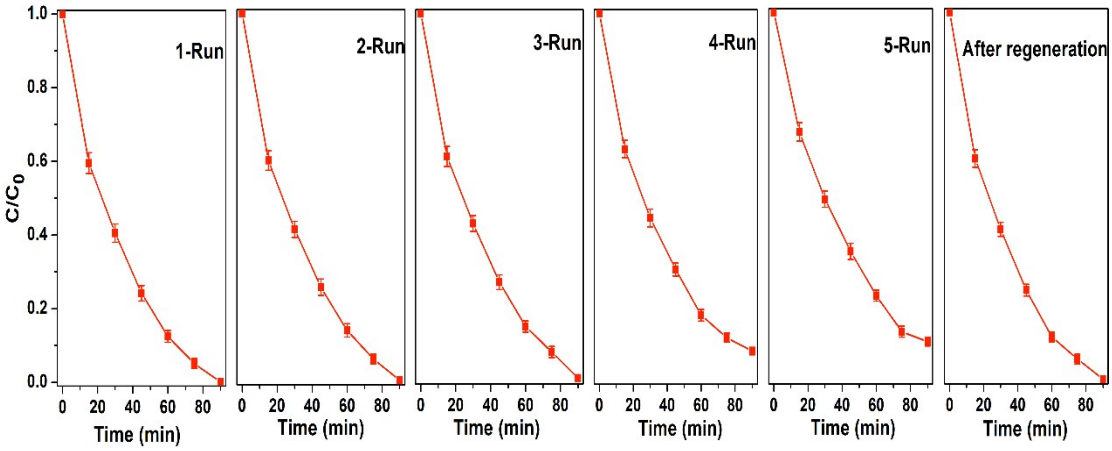


Fig. S4 Stability test of bulk powder 0.9%$Fe^{3+}$/0.07%$Nb^{5+}$-$TiO_2$ for repeated photocatalytic degradation of HCHO. The initial concentration of HCHO is 45 ppm. The regeneration of photocatalysts were conducted at 300°C for 4h followed by exposure to R.H. 80%.

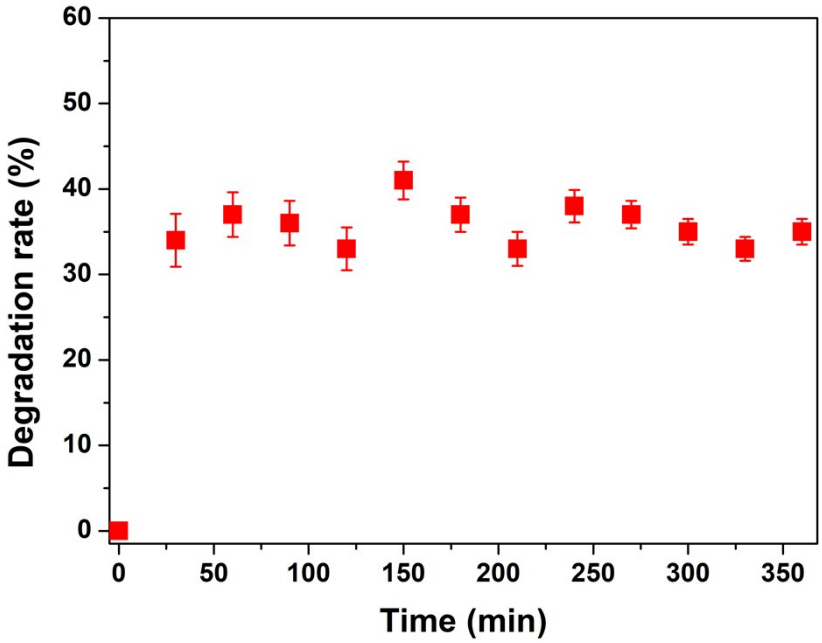


Fig. S5 Stability test of bulk powder 0.9%$Fe^{3+}$/0.07%$Nb^{5+}$-$TiO_2$ for photocatalytic degradation in HCHO flow.

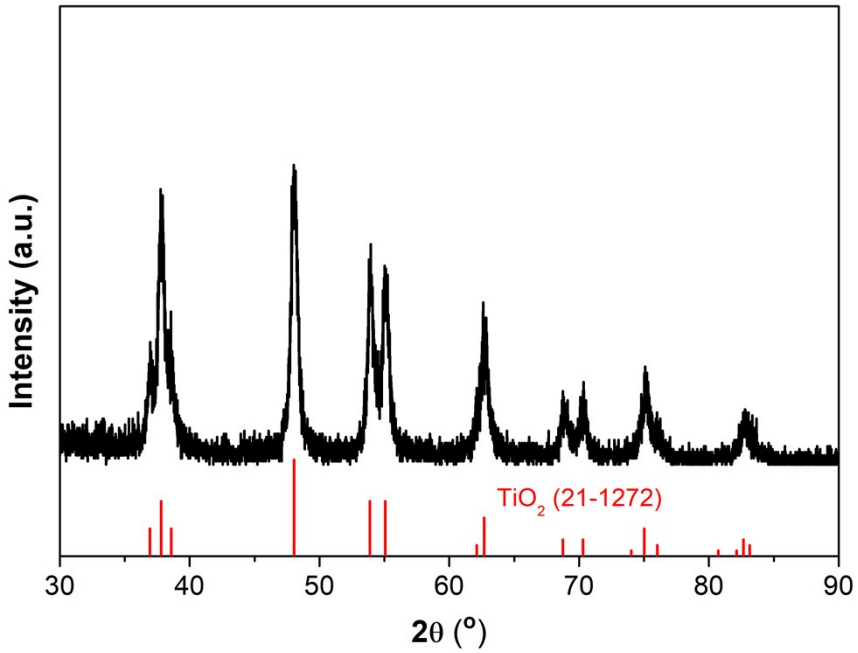


Fig. S6 XRD pattern of bulk powder 0.9%$Fe^{3+}$/0.07%$Nb^{5+}$-$TiO_2$ photocatalyst.

The as-synthesized bulk 0.9%$Fe^{3+}$/0.07%$Nb^{5+}$-$TiO_2$ photocatalyst show typical $TiO_2$ phase (PDF#21-1272).

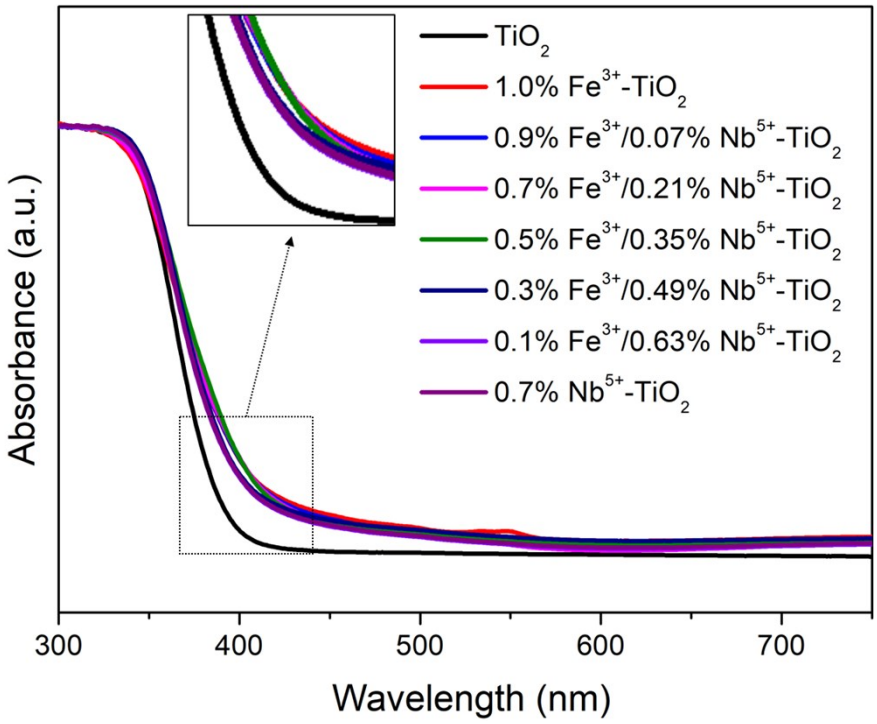


Fig. S7 UV-vis absorbance spectra of the bulk powder samples.

The absorbance intensity of 0.9%$Fe^{3+}$/0.07%$Nb^{5+}$-$TiO_2$ especially in the region from 400 to 650 nm, displays a significant enhancement compared with $TiO_2$. According to the UV-vis DRS spectra, we speculated that 0.9%$Fe^{3+}$/0.07%$Nb^{5+}$-$TiO_2$ may have an excellent photocatalytic effect in the visible light region.

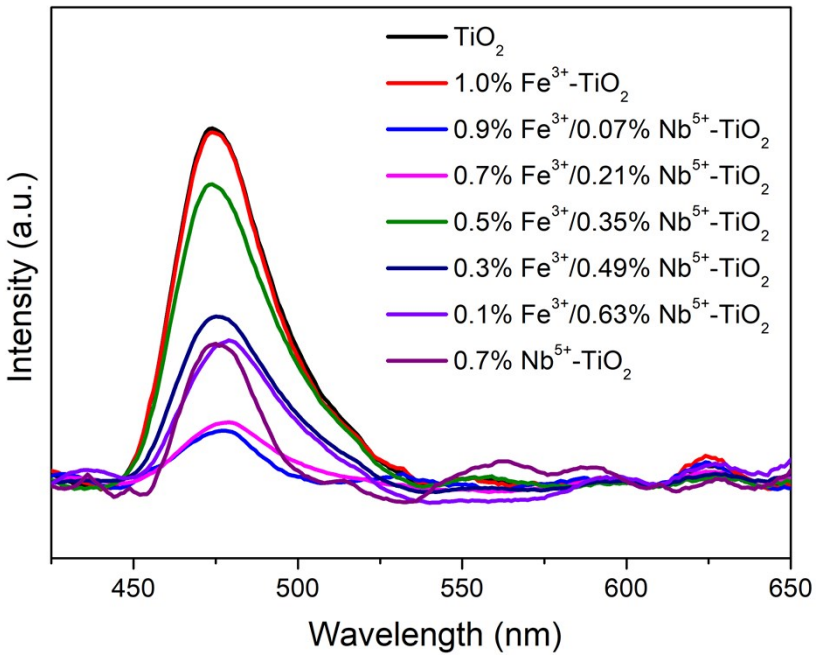


Fig. S8 Photoluminescence (PL) spectra of the bulk powder samples.

It is widely accepted PL spectra is closely related to the recombination of photo-excited electrons and holes. A lower PL intensity indicates a lower recombination rate of electron-hole pairs. The bulk powder samples corresponding to some picked spots in FTIRM image in Fig. 2 were examined by PL. As shown in Fig. S6, it can be seen the 0.9%$Fe^{3+}$/0.07%$Nb^{5+}$-$TiO_2$ shows the lowest intensity of PL emission, which means it has the highest charge separation efficiency.

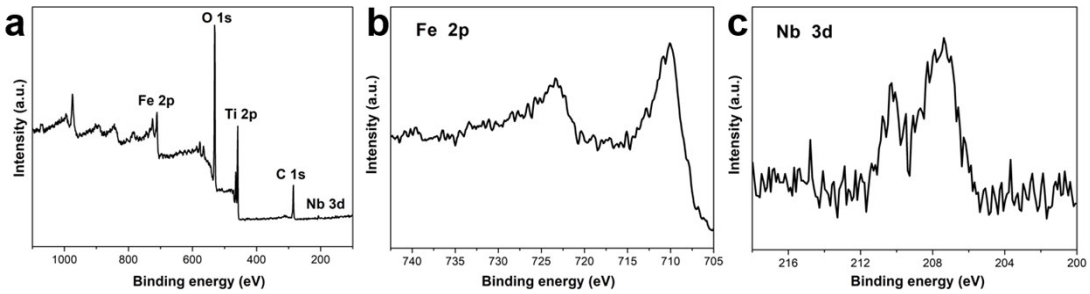


Fig. S9 XPS spectra of the bulk powder 0.9%$Fe^{3+}$/0.07%$Nb^{5+}$-$TiO_2$ photocatalyst.

Table S1 Intermediate species detected by GC.

| Time (min) | Species | | |
|---|---|---|---|
| | HCHO (ppmV) | $CO_2$ (ppmV) | HCOOH (ppmV) |
| 0 | 45 | 0 | 0 |
| 30 | 18.2 | 25.2 | 1.6 |
| 60 | 5.6 | 37.5 | 1.9 |
| 90 | trace | 43.1 | 1.9 |