

*Electronic Supplementary Material*

**Detoxification of DON by photocatalytic degradation and quality  
evaluation of wheat**

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## **Preparation of NaYF<sub>4</sub>:Yb,Tm@TiO<sub>2</sub>**

Typically, YCl<sub>3</sub>•6H<sub>2</sub>O, YbCl<sub>3</sub>•6H<sub>2</sub>O and TmCl<sub>3</sub>•6H<sub>2</sub>O with a stoichiometric ratio of 79.5: 20: 0.5 were dissolved in 6 mL oleic acid along with 15 mL 1-octadecene. Then the solutions were heated to 160 °C under the N<sub>2</sub> atmosphere to form a homogeneous solution. After the obtained solution was cooled to room temperature, 10 mL of a methanol solution containing 4 mmol of NH<sub>4</sub>F and 2.5 mmol of NaOH was added dropwise. The solution was stirred and heated to completely evaporate the methanol. Then, the solution was heated to 300 °C and maintained for 1 h under the N<sub>2</sub> atmosphere. After the solution was cooled naturally, the obtained nanoparticles were precipitated by adding ethanol and were separated by centrifugation. The final precipitation was dispersed in cyclohexane to obtain 0.1 M NaYF<sub>4</sub>:Yb,Tm nanomaterial dispersion. 0.05 g of cetyltrimethyl ammonium bromide (CTAB) and 1 mL of cyclohexane with prepared nanoparticles were added to 20 mL of deionized water stirring until it formed a milky solution. The obtained solutions were heated to 80 °C to evaporate the cyclohexane until the milky solution became transparent. After the mixture cooled to room temperature, the product was collected by centrifugation, washed with deionized water two times, and finally re-dispersed in 10 mL of isopropanol. Then 10 mL isopropanol containing 36 μL TDAA was slowly added to the above solution. The solution was stirred continuously for 12 h at room temperature. The TiO<sub>2</sub> coated NaYF<sub>4</sub>:Yb<sup>3+</sup>,Tm<sup>3+</sup> nanoparticles were collected by centrifugation, washed with deionized water and ethanol several times, and then dried at 70 °C in air. To finally obtain a crystalline anatase TiO<sub>2</sub> shell, the products were annealed at 500 °C for 3 h in an oven under an atmosphere of air.

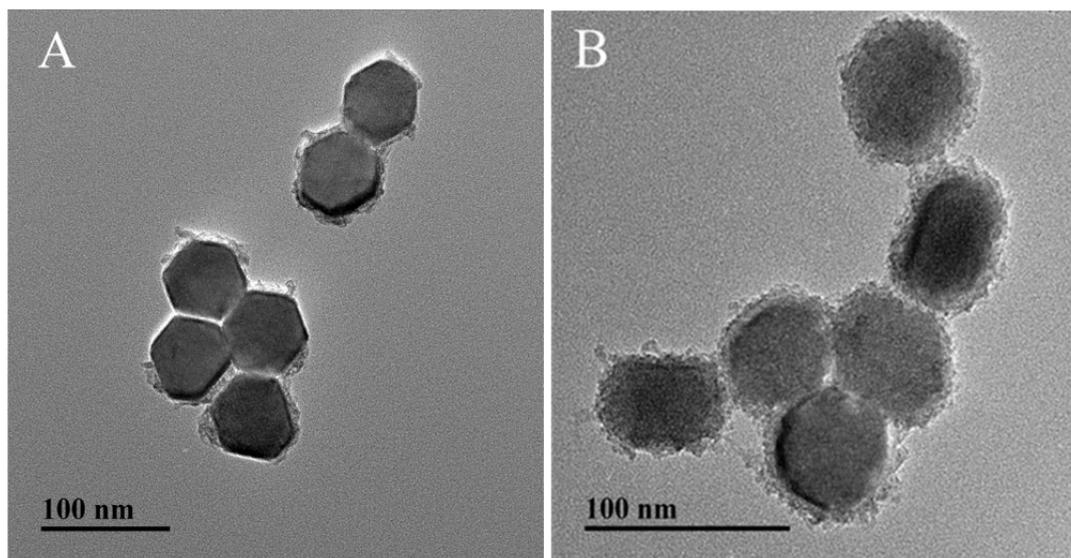


Fig. S1 TEM images of  $\text{NaYF}_4:\text{Yb,Tm}@\text{TiO}_2$  nanoparticles at different synthetic stages: (A)  $\text{NaYF}_4:\text{Yb,Tm}$ , (B)  $\text{NaYF}_4:\text{Yb,Tm}@\text{TiO}_2$ .

#### **UPLC -TQD-MS detection conditions**

UPLC was performed on a Waters Acquity UPLC system equipped with an ultraviolet detector. Chromatography separation was achieved using a Waters Acquity UPLC BEH C18 column (2.1 mm  $\times$  50 mm). The column temperature was 35°C, the injection volume was 5  $\mu\text{L}$  and the flow rate was 0.3 mL/min. The mobile phase comprised (A) acetonitrile and (B) 0.1% formic acid aqueous solution. The total operation time was 10 min.

Mass spectrometry was performed on a Waters Synapt Q-TOF system fitted with an electron spray ionization source. The ESI source operated in the positive ionization mode. The optimum conditions were set as follows: capillary voltage to 2.5 kV, cone voltage to 30 kV, source temperature to 120°C, and desolvation temperature to 350°C. The gas flow rate for cone and desolvation were 50 L/h and 600 L/h, respectively. The mass spectrometry was operated in a scan range from 200 m/z to 1000 m/z.

#### **Recyclability of photocatalyst**

The photocatalytic activity of photocatalyst was measured in five consecutive DON degradation reactions. As shown in Fig. S2, the degradation rate decreased from 100% to 92% after five cycle tests. Considering the inevitable loss in the recycling

process (such as the centrifuge, washing with distilled water and drying), UCNP@TiO<sub>2</sub> has good stability and can be used as a recyclable photocatalyst.

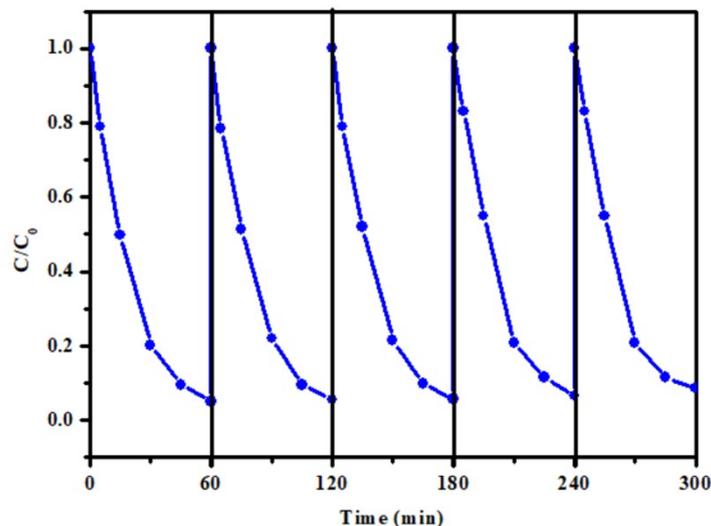


Fig. S2. The recyclability of the UCNP@TiO<sub>2</sub> nanoparticles for the degradation of DON (the UCNP@TiO<sub>2</sub> nanoparticles was 6 mg·mL<sup>-1</sup>, DON 10 μg·mL<sup>-1</sup>)

### Free radical capture experiments

Generally, the reactive oxygen species, including  $\bullet\text{OH}$ ,  $\text{h}^+$  and  $\bullet\text{O}_2^-$ , is produced in the photocatalytic reaction. tBuOH was used for trapping the hydroxyl radical  $\bullet\text{OH}$ , EDTA-2Na as an  $\text{h}^+$  scavenger, and N<sub>2</sub> as a detective molecular to  $\bullet\text{O}_2^-$ . Three captured agents were added to the reaction system respectively under the same reaction conditions. The results (Fig. S3) showed that the degradation rate of DON was decreased slightly with N<sub>2</sub> blowing, indicating that  $\bullet\text{O}_2^-$  is not the main effect. The degradation rate decreased both with EDTA-2Na and tBuOH, but the latter was much higher than the former. Based on the above analysis, it can be concluded that  $\bullet\text{OH}$ , with its strong oxidation ability, is mainly responsible for the degradation of DON in the photocatalytic process.

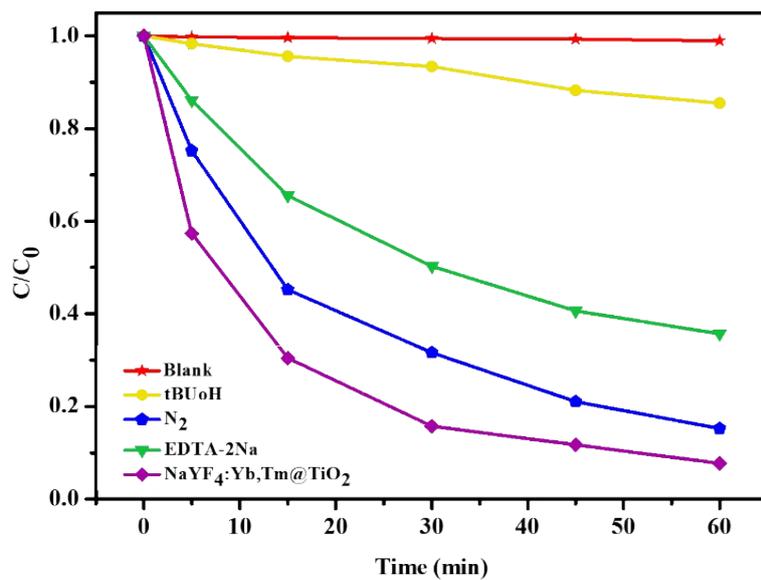


Fig. S3. Photodegradation rate curves of DON with the addition of  $h^+$  and  $\bullet OH$  scavengers and  $N_2$  under the irradiation of simulated sunlight.

Table S1 Effect of illumination on amino acids content in wheat

Amino acids (g/100g)	Time (min)			
	0	30	60	90
Asp	0.575	0.497	0.503	0.532
Glu	3.236	3.585	3.268	3.442
Ser	0.396	0.360	0.353	0.365
His	0.246	0.203	0.192	0.227
Gly	0.438	0.439	0.403	0.421
Thr	0.313	0.270	0.274	0.287
Arg	0.457	0.457	0.443	0.442
Ala	0.398	0.366	0.366	0.378
Tyr	0.192	0.186	0.181	0.161
Sys-S	0.119	0.112	0.071	0.069
Val	0.511	0.493	0.469	0.493
Met	0.158	0.121	0.125	0.122
Phe	0.505	0.501	0.475	0.497
Ile	0.435	0.419	0.401	0.421
Leu	0.743	0.717	0.678	0.708
Lys	0.277	0.233	0.245	0.251
Pro	1.737	1.504	1.689	1.349
EAA	3.032	2.844	2.757	2.869
TAA	10.736	10.463	10.136	10.166
EAA/TAA	0.282	0.272	0.272	0.282

Table S2 Effect of photocatalytic technology on amino acids content in wheat

Amino acids (g/100g)	Time (min)			
	0	30	60	90
Asp	0.559	0.509	0.510	0.507
Glu	3.250	3.597	3.342	3.479
Ser	0.410	0.372	0.355	0.375
His	0.260	0.215	0.216	0.202
Gly	0.452	0.451	0.411	0.419
Thr	0.327	0.282	0.275	0.279
Arg	0.471	0.469	0.435	0.449
Ala	0.412	0.378	0.374	0.365
Tyr	0.206	0.198	0.166	0.179
Sys-S	0.133	0.814	0.071	0.072
Val	0.525	0.505	0.481	0.491
Met	0.172	0.133	0.129	0.117
Phe	0.519	0.513	0.483	0.499
Ile	0.449	0.431	0.408	0.419
Leu	0.717	0.729	0.691	0.718
Lys	0.291	0.245	0.241	0.244
Pro	1.751	1.316	1.550	2.006
EAA	3.090	2.928	2.798	2.857
TAA	10.904	10.426	10.165	10.821
EAA/TAA	0.283	0.281	0.275	0.264

Table S3 Comparison of the developed method with previous methods for degradation DON in wheat

Reagents	Dosage	Initial DON	Reaction time	Removal rate	Reference
milling		20 $\mu\text{g}\cdot\text{mL}^{-1}$		19%	Bullerman et al., 2007
thermal	250 °C	3 $\mu\text{g}\cdot\text{mL}^{-1}$	15 min	31.8%	Numanoglu et al., 2012
electron beam	55.8 kGy	5 $\mu\text{g}\cdot\text{mL}^{-1}$		17.6%	Stepanik et al., 2007
sodium carbonate	0.1 M	3mg·kg <sup>-1</sup>	24 h	89.7%	Trenholm et al., 1992
aqueous ozone	80 mg·mL <sup>-1</sup>	10 $\mu\text{g}\cdot\text{mL}^{-1}$	7 min	83%	Sun et al., 2016
strain <i>S. cerevisiae</i>		100 $\mu\text{g}\cdot\text{mL}^{-1}$	24 h	33%	Chlebicz et al., 2019
strain WSN05-2		1000 $\mu\text{g}\cdot\text{mL}^{-1}$	7 d	90%	Ikunaga et al., 2011
dendritic-Like $\alpha\text{-Fe}_2\text{O}_3$	0.1 mg·mL <sup>-1</sup>	4 $\mu\text{g}\cdot\text{mL}^{-1}$	2 h	90.3%	Wang et al., 2019
UCNP@TiO <sub>2</sub>	6 mg·mL <sup>-1</sup>	10 $\mu\text{g}\cdot\text{mL}^{-1}$	60 min	100%	This study

## References

- Bullerman, L. B., & Bianchini, A. (2007). Stability of mycotoxins during food processing. *International Journal of Food Microbiology*, 119(1), 140-146.
- Chlebicz, A., Śliżewska, K.(2019). In Vitro Detoxification of Aflatoxin B1, Deoxynivalenol, Fumonisin, T-2 Toxin and Zearalenone by Probiotic Bacteria from Genus Lactobacillus and Saccharomyces cerevisiae Yeast. *Probiotics and Antimicrobial Proteins*, 4 , 1-13.
- Ikunaga, Y., Sato, I., Grond, S., Numaziri, N., Yoshida, S., & Yamaya, H., et al. (2011). Nocardioides sp. strain WSN05-2, isolated from a wheat field, degrades deoxynivalenol, producing the novel intermediate 3-epi-deoxynivalenol. *Applied Microbiology & Biotechnology*, 89(2), 419-427.
- Numanoglu, E., Gökmen, V., Uygun, U., & Koksel, H. (2012). Thermal degradation of deoxynivalenol during maize bread baking. *Food Addit Contam Part A Chem Anal Control Expo Risk Assess*, 29(3), 423-430.
- Stepanik, T., Kost, D., Nowicki, T., & Gaba, D. (2007). Effects of electron beam irradiation on deoxynivalenol levels in distillers dried grain and solubles and in

- production intermediates. *Food Additives & Contaminants*, 24(9), 1001-1006.
- Sun, C., Ji, J., Wu, S., Sun, C., Pi, F., & Zhang, Y., et al. (2016). Saturated aqueous ozone degradation of deoxynivalenol and its application in contaminated grains. *Food Control*, 69, 185-190.
- Trenholm, H. L., Charmley, L. L., Prelusky, D. B., et al. (1992). Washing procedures using water or sodium carbonate solutions for the decontamination of three cereals contaminated with deoxynivalenol and zearalenone. *Journal of Agricultural and Food Chemistry*, 40(11), 2147-2151.
- Wang, H., Mao, J., Zhang, Z., et al. (2019). Photocatalytic Degradation of Deoxynivalenol over Dendritic-Like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> under Visible Light Irradiation. *Toxins*, 11(2), 105.