Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Surface Photovoltage Phase Spectra in Analysing Photogenerated Charge Transfer and Photocatalytic Activity of $ZnFe_2O_4$-TiO_2 Nanotube Arrays

Liping Chen, Shuo Li, Zhipeng Liu, Yongchun Lu, Dejun Wang, Yanhong Lin and Tengfeng Xie*

College of Chemistry, Jilin University, Changchun 130012, People's Republic of China.

Supplementary Information

Synthesize different contents of $ZnFe_2O_4$ modified TNAs

For synthesizing different contents of $ZnFe_2O_4$ modified TNAs, the as-anodized TNAs were soaked in different concentration of $Fe(NO_3)_3$ and $Zn(NO_3)_2$ mixed solutions for 2 h. The concentration the mixed solutions are list in **Table S1**. Afterward the nanotube arrays were dried in air for 14 h and then annealed at 500 °C for 2 h with heating and cooling rates of 2 °C min^{-1}. Different samples were denoted as ZFO1-TNAs to ZFO4-TNAs.

Table S1. Concentration of $Fe(NO_3)_3$ and $Zn(NO_3)_2$ in mixed solutions for synthesizing different contents of $ZnFe_2O_4$ modified TNAs.

Sample	$Fe(NO_3)_3$ Concentration /M	$Zn(NO_3)_2$ Concentration /M	Denote as
1	0.250	0.125	ZFO1-TNAs
2	0.500	0.250	ZFO2-TNAs
3	1.000	0.500	ZFO3-TNAs
4	1.500	0.750	ZFO4-TNAs

Synthesize pure $ZnFe_2O_4$ loaded on Ti foil

For synthesizing pure $ZnFe_2O_4$ loaded on Ti foil, ammonia solution (25 wt.%) was added into 10 mL of $Fe(NO_3)_3$ and $Zn(NO_3)_2$ mixed solution (with the concentration of 1M and 0.5M, respectively) in drops under vigorous agitation until the mixed solution changed to pasty mixture. After drying at 50 °C in air for 48 h, the yellow power was followed by annealing at 500 °C for 2 h with heating and cooling rates of 2 °C min^{-1}. Then the obtained $ZnFe_2O_4$ power was ultrasonically dispersed in ethanol and subsequently spread on a Ti foil (1cm × 2 cm). Finally the $ZnFe_2O_4$ loaded on Ti foil sample was obtained after drying at 50 °C for 10 min.

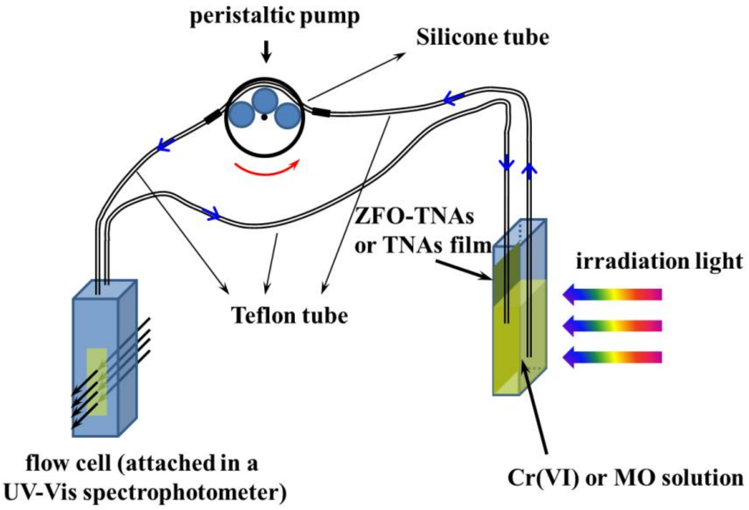
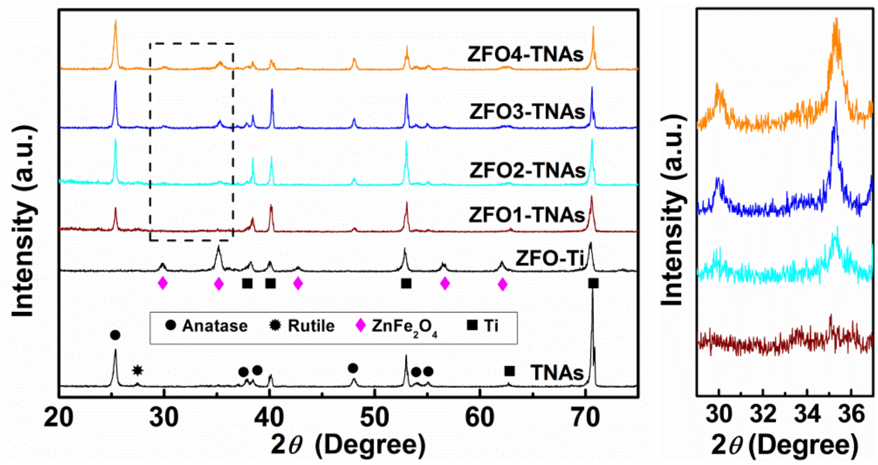


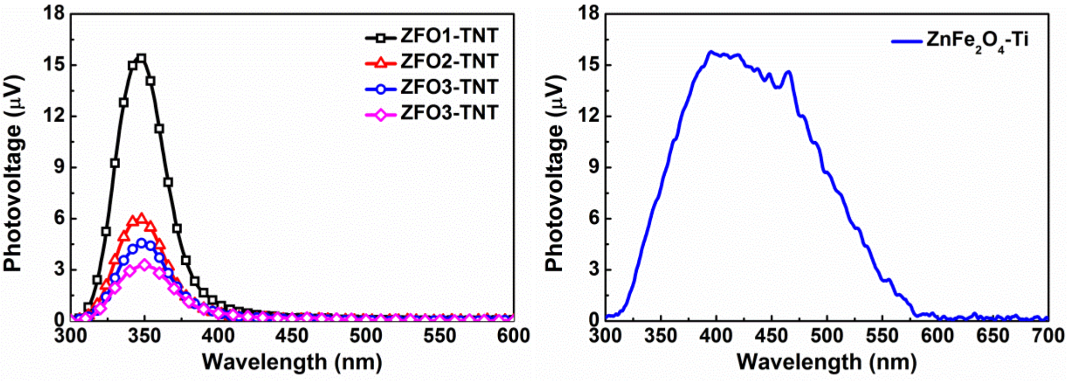
Fig. S1. Schematic diagram of on-line detection system for photo-catalytic reduction of Cr(VI) and degradation of MO solution.



(a) (b)

Fig. S2. (a) XRD patterns of TNAs, pure $ZnFe_2O_4$ (loaded on Ti foil) and different contents of $ZnFe_2O_4$ modified TNAs; (b) magnified XRD patterns of the ZFO1-TNAs ~ ZFO4-TNAs at 2θ of 29°–37°.

As the concentration of the $Fe(NO_3)_3$ and $Zn(NO_3)_2$ mixed solution increased in the soaking procedure, the content of $ZnFe_2O_4$ in the obtained ZFO-TNAs increased accordingly, which enhanced the strength of the diffraction peaks of $ZnFe_2O_4$.



(a) (b)

Fig. S3. SPV spectra of (a) different contents of $ZnFe_2O_4$ modified TNAs and (b)pure $ZnFe_2O_4$ (loaded on Ti foil).

When the content of $ZnFe_2O_4$ increases, the probability of the photo-generated charge carriers that excitated from TiO_2 transferring to $ZnFe_2O_4$ and recombining in $ZnFe_2O_4$ increases too. As a result, the SPV responses decrease.

The pure $ZnFe_2O_4$ cannot be obtained via the same procedure as the synthesis of ZFO-TNAs, so a different scheme was adopted. That’s the reason why the SPV response of $ZnFe_2O_4$-Ti shows much stronger in the visible light region compared with those different $ZnFe_2O_4$ modified TNAs.

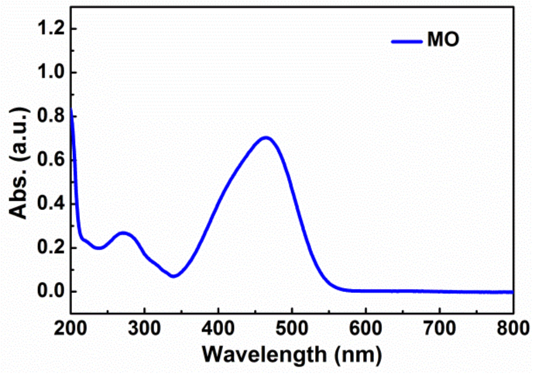


Fig. S4. Absorption spectrum of MO solution (10 mg L^{-1}).

When the cutoff filter ($\lambda > 400$ nm) was used, only visible light can pass through and reach the MO solution. As shown in the schematic diagram of our on-line detection system (Fig. S1), the TNAs or ZFO-TNAs film was placed at the back of the MO solution. Due to the strong absorption of MO in the 400–550 nm region, the intensity of visible light in this region decreased rapidly before reaching TNAs or ZFO-TNAs film. This may be the reason why both the TNAs and ZFO-TNAs show no photocatalytic activity for the degradation of MO.