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## **Electronic Supplementary Information**

# Graphene nanoclusters decorated niobium oxide nanofibers for

## visible light photocatalytic applications

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### Contents

- 1. HR-TEM images for the samples prepared at intermediate concentrations
- 2. Photocatalytic results for all the samples prepared at various glucose concentrations
- 3. Cyclic photocatalytic efficiency data for G@Nb<sub>2</sub>O<sub>5</sub> NFs and C@Nb<sub>2</sub>O<sub>5</sub> NFs
- 4. Comparison of the photocatalytic activity with similar systems

1. HR-TEM images for the samples prepared at intermediate concentrations



Figure S1. HR-TEM of samples prepared at (a) 1 g/L, (b) 5 g/L, (c) 10 g/L and (d) 20 g/L.

The composite nanofibers were prepared at different intermediate glucose concentrations of 1 g/L, 5 g/L, 10 g/L and 20 g/L. Firstly, the Nb<sub>2</sub>O<sub>5</sub> nanofibers were synthesized. Then, the composite nanofibers were fabricated by the hydrothermal method by adding glucose solution of 1 g/L, 5 g/L, 10 g/L and 20 g/L. The composite nanofibers were first uniformly dispersed in ethanol, and then several drops of the solution were dipped on a copper mesh to carry out the TEM characterization.

**Figure S1** shows the HR-TEM images for the samples prepared at intermediate glucose concentrations. By increasing the glucose concentration from 0.5 g/L to 10 g/L, the carbon changed from graphene clusters to discontinuous carbon layers, which were consisted of randomly oriented small "carbon sheet". The evolution could be clearly seen from **Figure S1a** to **Figure S1c**. However, the small "carbon sheets" were turned to oriented parallel to the surface of the nanofibers and typical core-shell structured composite fibers with continuously coated carbon layers could be seen as displayed in **Figure S1d** (20 g/L). And the thickness of carbon layers on the surface of the nanofibers was thinner than that of the C-Nb<sub>2</sub>O<sub>5</sub> NFs (30 g/L). Based on the above images, we could conclude that the morphology of the carbon layers exhibited a close dependence on the carbon content.

2. Photocatalytic results for all the samples prepared at various glucose concentrations



**Figure S2** Photocatalytic degradation efficiency for G@Nb<sub>2</sub>O<sub>5</sub> NFs, C@Nb<sub>2</sub>O<sub>5</sub> NFs and samples prepared at intermediate concentrations ranging from 1 g/L to 20 g/L.

The photocatalytic degradation experiments were carried out for the samples of 1 g/L, 5 g/L, 10 g/L and 20 g/L following the process described in the manuscript. **Figure S2** shows the Photocatalytic degradation efficiency for G@Nb<sub>2</sub>O<sub>5</sub> NFs, C@Nb<sub>2</sub>O<sub>5</sub> NFs and samples prepared at intermediate concentrations ranging from 1 g/L to 20 g/L. It could be clearly seen that the photo-degradation efficiency of the four samples (1 g/L to 20 g/L) decreased with the increase of the glucose concentration. And they were in the range between G@Nb<sub>2</sub>O<sub>5</sub> NFs and 20 g/L exhibited degradation efficiency of 90%, 85%, 85% and 75%, respectively. The decrease of the efficiency indicated a carbon-content dependent relationship for our composite nanofibers. With slight increase of the carbon layer's thickness, the degradation efficiency obviously decreased.

3. Cyclic photocatalytic efficiency data for G@Nb<sub>2</sub>O<sub>5</sub> NFs and C@Nb<sub>2</sub>O<sub>5</sub> NFs



**Figure S3** Photocatalytic degradation efficiency for G@Nb<sub>2</sub>O<sub>5</sub> NFs and C@Nb<sub>2</sub>O<sub>5</sub> NFs in the cycling experiment.

Cyclic photocatalytic experiments were repeated three times for sample  $G@Nb_2O_5$  NFs and  $C@Nb_2O_5$  NFs. After every photocatalytic reaction, the samples were obtained by centrifuging the solution. The collected samples were used in the next photocatalytic degradation experiment. From the results shown in **Figure S3**, it could be seen that the efficiency of  $C@Nb_2O_5$  NFs exhibited almost no changes and the  $G@Nb_2O_5$  NFs showed a slightly decreased efficiency in the second and third cycling run. However, the obtained efficiency of  $G@Nb_2O_5$  NFs was still much higher than that of  $C@Nb_2O_5$  NFs. And the stability of the  $C@Nb_2O_5$  NFs could be mainly attributed to the uniformly coated thick carbon layers. The efficiency decrease for the  $G@Nb_2O_5$  NFs might be related with the loss of the graphene nanoclusters during the centrifuging process.

#### 4. Comparison of the photocatalytic activity with similar systems

The degradation efficiency was compared with previous reports for popular systems and the information was clearly displayed in Table I. The degradation efficiency of our composite nanofibers was comparable with some similar systems, like TiO<sub>2</sub>, ZnO and CdS.<sup>2, 6-8</sup> Since the sample was prepared from raw materials of low lost, it shows great potential as a promising visible light photocatalyst. However, the efficiency for our sample was lower than some systems with much smaller dimensions, such as RGO-CdS nanorods, RGO-ZnO nanoparticles, C-Bi<sub>12</sub>TiO<sub>20</sub> nanorods and G-SnO<sub>2</sub> aerosol.<sup>1, 5, 11, 12</sup> We believed that the efficiency could be further enhanced by reducing the diameter of the nanofibers.

Composite	Light Region	Degradation Efficiency	Morphology	Reference
G@Nb2O5	Visible Light	95%/300min	Nanofibers	This work
RGO-CdS	Visible Light	90%/120min	Nanorods	[1]
CdS-GR	Visible Light	80%/300min	Nanoparticles	[2]
		(Best efficiency in p-		
		methoxybenzyl alcohol)		
G-ZnO	UV Light	80%/240min	Nanofibers	[3]
ZnO/graphene	UV Light	95%/40min	Nanoparticles	[4]
RGO-ZnO	Visible Light	100%/120min	Nanoparticles	[5]
GO-TiO <sub>2</sub>	Visible Light	25%/180min	Nanocrystals	[6]
Graphene@TiO2	Visible Light	70%/200min	Nanoparticles	[7]
TiO2/C	Visible light	84%/360min	Core-Shell	[8]
			Nanofibers	
G-TiO <sub>2</sub>	UV Light	75%/180min	Nanoparitcles	[9]
G-TiO2	UV Light	91%/90min	Mesoporous	[10]
			Nanospheres	
C-Bi <sub>12</sub> TiO <sub>20</sub>	Visible Light	120min	Nanorods	[11]
SnO <sub>2</sub> -Graphene	Visible Light	100%/40min	Aerosol	[12]
Zn <sub>2</sub> TiO <sub>4</sub> @C	UV Light	100%/40min	Core-Shell	[13]
			Nanofibers	

 Table I Comparison on degradation efficiency of popular photocatalysts modified by graphene or reduced graphene oxide

### References

1 X. Q. An, X. L. Yu, J. C. Yu and G. J. Zhang, J. Mater. Chem. A, 2013, 1, 5158-5164.

2 N. Zhang, Y. H. Zhang, X. Y. Pan, X. Z. Fu, S. Q. Liu and Y. J. Xu, *J. Phys. Chem. C*, 2011, **115**, 23501-23511.

3 S. An, B. N. Joshi, M. W. Lee, N. Y. Kim and S. S. Yoon, *Appl. Surf. Sci.*, 2014, **294**, 24-28.

4 T. G. Xu, L. W. Zhang, H. Y. Cheng and Y. F. Zhu, *Appl. Catal. B-Environ.*, 2011, **101**, 382-387.

5 B. J. Li and H. Q. Cao, J. Mater. Chem., 2011, 21, 3346-3349.

6 C. Chen, W. M. Cai, M. Long, B. X. Zhou, Y. H. Wu, D. Y. Wu and Y. J. Feng, ACS Nano, 2010, 4, 6425-6432.

7 D. L. Zhao, G. D. Sheng, C. L. Chen and X. K. Wang, *Appl. Catal. B-Environ.*, 2012, **111-112**, 303-308.

8 P. Zhang, C. L. Shao, Z. Y. Zhang, M. Y. Zhang, J. B. Mu, Z. C. Guo and Y. C. Liu, *Nanoscale*, 2011, **3**, 2943-2949.

9 K. F. Zhou, Y. H. Zhu, X. L. Yang, X. Jiang and C. Z. Li, *New J. Chem.*, 2011, **35**, 353-359.

10 J. Zhang, Z. P. Zhu, Y. P. Tang and X. L. Feng, J. Mater. Chem. A, 2013, 1, 3752-3756.

11 J. G. Hou, S. Q. Jiao, H. M. Zhu and R. V. Kumar, CrystEngComm, 2011, 13, 4735-4740.

12 S. D. Zhuang, X. Y. Xu, B. Feng, J. G. Hu, Y. Pang, G. Zhou, L. Tong and Y. X. Zhou, *ACS Appl. Mater. Inter.*, 2014, **6**, 613-621.

13 P. Zhang, C. L. Shao, M. Y. Zhang, Z. C. Guo, J. B. Mu, Z. Y. Zhang, X. Zhang, P. P. Liang and Y. C. Liu, *J. Hazard. Mater.*, 2012, **229-230**, 265-272.