

## Visible light-induced photocatalytic activity of modified titanium (IV) oxide with zero-valent bismuth clusters

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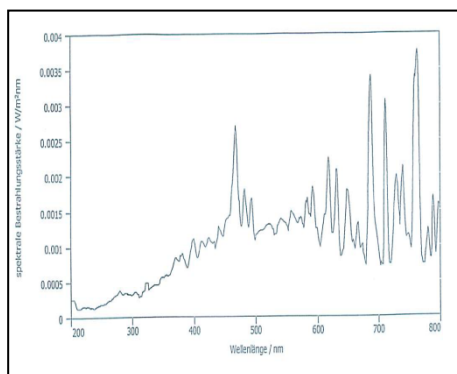
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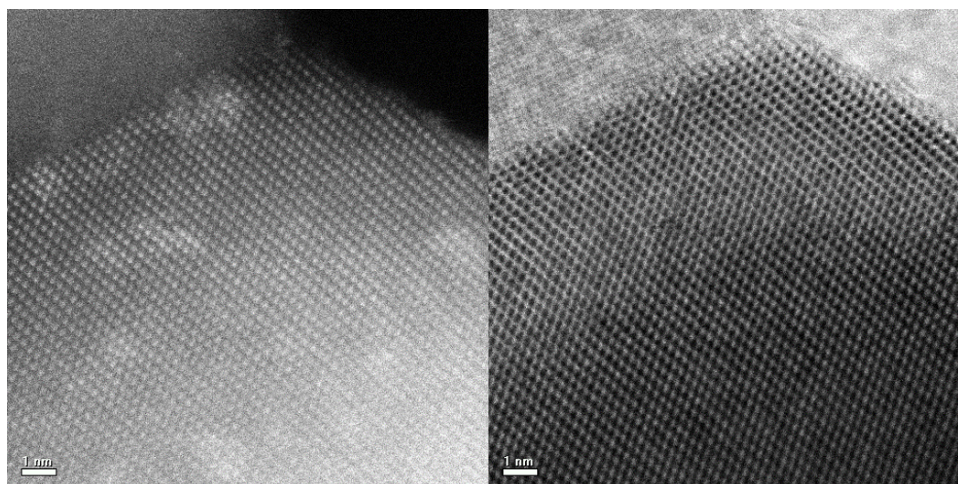
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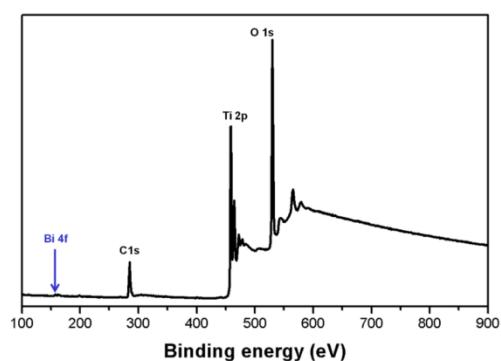
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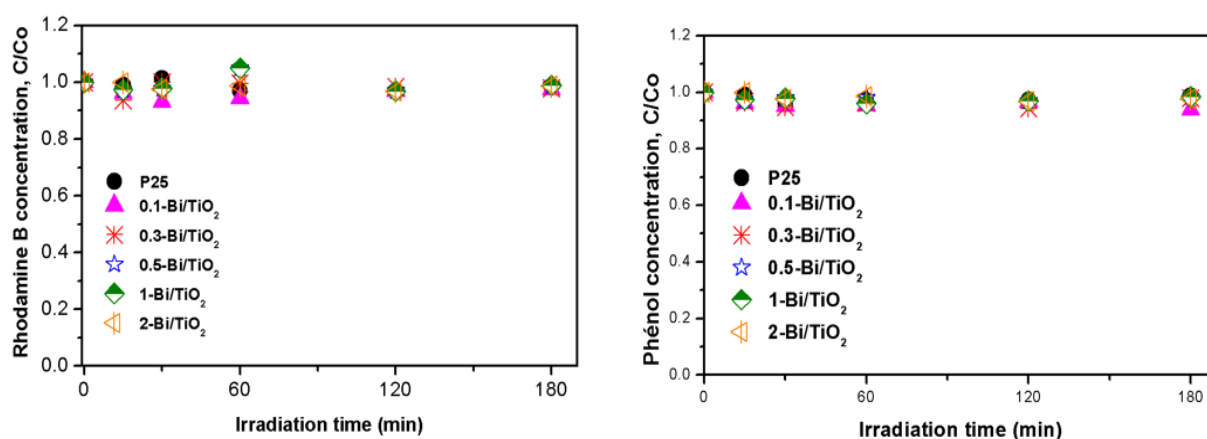
**Fig. S1.** Emission spectrum of xenon TXE 150 W lamp.



**Fig. S2.** HAADF-STEM (left) and BF-STEM (right) images of 2-Bi/TiO<sub>2</sub>.



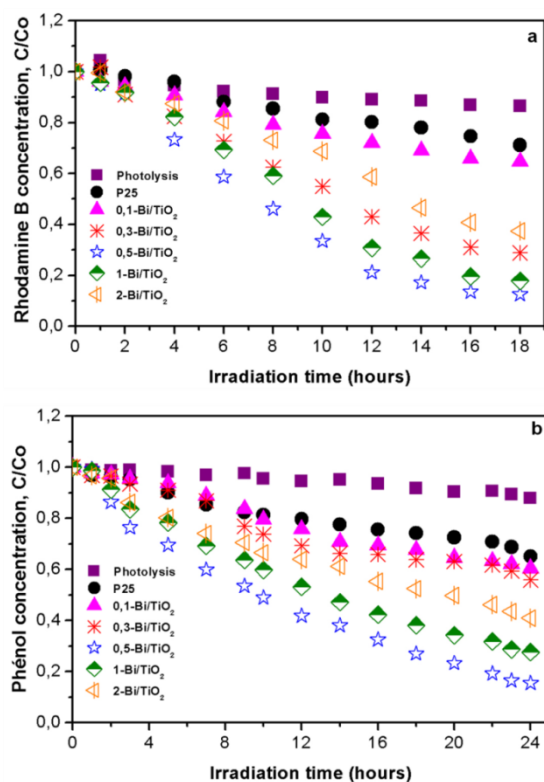
**Fig. S3.** XPS spectrum of 1-Bi/TiO<sub>2</sub>.



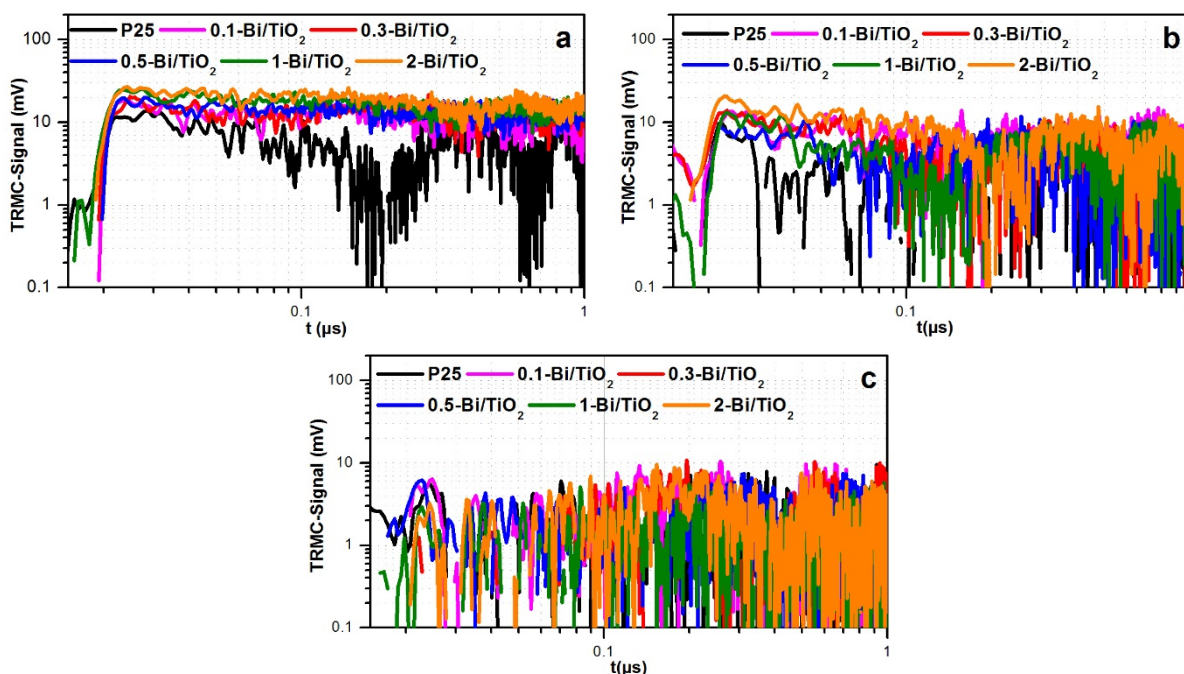
**Fig. S4.** Adsorption test of phenol and rhodamine B with  $x$ -Bi/TiO<sub>2</sub> (1 g.L<sup>-1</sup>) in the dark.

| Pollutants  | Photocatalysts          | $k_{app} \times 10^{-3} \text{ (min}^{-1}\text{)}$ | $R^2$ |
|-------------|-------------------------|----------------------------------------------------|-------|
| Rhodamine B | P25                     | 1.7                                                | 98.91 |
|             | 0.1-Bi/TiO <sub>2</sub> | 13.3                                               | 99.1  |
|             | 0.3-Bi/TiO <sub>2</sub> | 12.4                                               | 98.95 |
|             | 0.5-Bi/TiO <sub>2</sub> | 17.5                                               | 98.93 |
|             | 1-Bi/TiO <sub>2</sub>   | 8.0                                                | 98.96 |
|             | 2-Bi/TiO <sub>2</sub>   | 7.1                                                | 98.91 |
| Phenol      | P25                     | 0.2                                                | 98.9  |
|             | 0.1-Bi/TiO <sub>2</sub> | 1.0                                                | 98.91 |
|             | 0.3-Bi/TiO <sub>2</sub> | 1.1                                                | 98.95 |
|             | 0.5-Bi/TiO <sub>2</sub> | 2.0                                                | 98.92 |
|             | 1-Bi/TiO <sub>2</sub>   | 1.0                                                | 99.09 |
|             | 2-Bi/TiO <sub>2</sub>   | 0.5                                                | 99    |

**Table S1.** Apparent rate constants of the first-order kinetics for phenol and rhodamine B photodegradation with  $x$ -Bi/TiO<sub>2</sub> (1 g.L<sup>-1</sup>) under visible illumination ( $\lambda > 450 \text{ nm}$ ) (measurements at 230 min).



**Fig. S5.** Photodegradation of (a) Rhodamine and (b) Phenol with  $x\text{-Bi/TiO}_2$  under solar light (the tests were conducted with 0.5 g of modified TiO<sub>2</sub> per L).



**Fig. S6.** TRMC signals of bare and modified samples excited at 410 nm (a), 500 nm (b) and 550 nm (c). The Excitations density for each wavelength was respectively 3.38, 4.5 and 3.18  $\text{mJ}\cdot\text{cm}^{-2}$ . At 410 nm the signal is slightly higher and with a slower decay for the Bi-modified titania, suggesting an electron injection from Bismuth into titania. There is no signal after excitation at 500 and 550 nm.

| $\lambda$ (nm) | Sample                  | $I_{\max}$ (mV) | $I_{50\text{ns}}/I_{\max}$ | $I_{5\mu\text{s}}/I_{\max}$ |
|----------------|-------------------------|-----------------|----------------------------|-----------------------------|
| 355            | P25                     | 65.8            | 0.69                       | 0.19                        |
|                | 0.1-Bi/TiO <sub>2</sub> | 82.6            | 0.72                       | 0.19                        |
|                | 0.3-Bi/TiO <sub>2</sub> | 83.6            | 0.70                       | 0.23                        |
|                | 0.5-Bi/TiO <sub>2</sub> | 91.1            | 0.69                       | 0.18                        |
|                | 1-Bi/TiO <sub>2</sub>   | 108.7           | 0.68                       | 0.16                        |
|                | 2-Bi/TiO <sub>2</sub>   | 97.1            | 0.74                       | 0.19                        |
| 410            | P25                     | 11.9            | 0.74                       | 0.45                        |
|                | 0.1-Bi/TiO <sub>2</sub> | 16.1            | 0.78                       | 0.47                        |
|                | 0.3-Bi/TiO <sub>2</sub> | 16.3            | 0.68                       | 0.64                        |
|                | 0.5-Bi/TiO <sub>2</sub> | 17.6            | 0.97                       | 0.48                        |
|                | 1-Bi/TiO <sub>2</sub>   | 23.1            | 0.84                       | 0.58                        |
|                | 2-Bi/TiO <sub>2</sub>   | 24.2            | 0.88                       | 0.55                        |
| 450            | P25                     | -               | -                          | -                           |
|                | 0.1-Bi/TiO <sub>2</sub> | 19.9            | 0.76                       | 0.34                        |
|                | 0.3-Bi/TiO <sub>2</sub> | 19.1            | 0.80                       | 0.46                        |
|                | 0.5-Bi/TiO <sub>2</sub> | 14.8            | 0.83                       | 0.62                        |
|                | 1-Bi/TiO <sub>2</sub>   | 24.7            | 0.68                       | 0.39                        |
|                | 2-Bi/TiO <sub>2</sub>   | 24.2            | 0.60                       | 0.44                        |

**Table S2:** Maximum of the intensities of the TRMC signals ( $I_{\max}$ ) and ratio between the TRMC signals after 50 ns and  $I_{\max}$  ( $I_{50\text{ns}}/I_{\max}$ ) and between the signals after 5  $\mu\text{s}$  and  $I_{\max}$  ( $I_{5\mu\text{s}}/I_{\max}$ ) obtained by 355, 410 and 450 nm excitations. These ratios are respectively representative of the short time charge carrier decay (mainly due to direct recombination) and the long lifetime charge carriers. These data confirm that the presence of Bi induce a rise of the signal intensity at 355 nm without significant change of the decay. 0.5-Bi/TiO<sub>2</sub> has the highest short time ratio at 410 nm and 450 nm and the highest long time ratio at 450 nm. That indicates a longer charge carrier lifetime under excitation with visible light for this sample, which is in correlation with the photocatalysis results.