Supplementary material for

Development of spray pyrolysis-synthesised Bi_2O_3 thin films for photocatalytic applications

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Table S1 Comparative table of photocatalytic activity of Bi_2O_3 films prepared by different deposition methods

Deposition method	Precursor	Preparation temperature	Composition/Phase	Thick-ness, nm	Band gap, (eV)	Photo-catalytic activity	Ref
Sol-gel, spin coating	$Bi(NO_3)_3{\cdot}5H_2O$	Calcined at 450 °C	β-Bi_2O_3	200	3.2	ca 2 ppm of Rhodamine B in 300 min UV-C	[1]
Sol-gel, dip coating	$Bi(NO_3)_3{\cdot}5H_2O$	Preliminary heating at 371 °C and annealing at 400-700 °C	β-Bi_2O_3, $Bi_2O_{2.33}$ and Bi_2SiO_5	NR	3.63 - 3.74	ca 9.5 ppm of MO in 2 h under UV.	[2]
Sol-gel, dip coating	$Bi(NO_3)_3{\cdot}5H_2O$	Pre-heated at 390 °C and annealed at 450-600 °C	α-Bi_2O_3 and β-Bi_2O_3	120	NR	ca 10 ppm Rhodamine B in 210 min under UV-A.	[3]
Sol-gel, dip coating	$Bi(NO_3)_3{\cdot}5H_2O$	Heating at 250 °C for	β-Bi_2O_3	60	3.4	ca 5 ppb	[4]

		12 h and annealing at 400 °C for 15 min.				Rhodamine B in 150 min UV-C	
Ultrasonic spray pyrolysis	$[Bi_{38}O_45(Omc)_{24}(DMSO)_9]\cdot 2DMSO\cdot 7H_2O$	Deposition at 80 °C and annealing at 370 °C and 550 °C.	β-Bi_2O_3	5000-16000	2.34, 2.78	ca 3.8 ppm of Rhodamine B in 600 min under VIS light	[5]
Spray pyrolysis	$Bi(CH_3CO_2)_3$	Deposition temperatures 350-450 °C	BiO and β-Bi_2O_3	NR	2.6	ca 0.24 and 0.18 ppm of MO in 180 min under UV and VIS light, respectively	[6]
Photochemical solution deposition	Metal complex of Bi(III) and N-methyldiethanolamine	Dried at 150 °C for 10 min and heated at 250 °C with UV-irradiation.	β-Bi_2O_3 and δ-Bi_2O_3	50	3.0	ca 3 ppb MB in 250 min under UV-A.	[7]
Sputtering	α-$B_{i2}O_3$ target	Room temperature at $6.5x10^{-4}$ Pa at argon and oxygen atmosphere	δ- Bi_2O_3	450	2.0	ca 2 ppm MO in 180 min under UV.	[8]
Sputtering	Bismuth target	Room temperature at $2.2x10^{-2}$ mbar pressure at argon and oxygen atmosphere	Metallic bismuth and α-Bi_2O_3	NR	3.41 - 4.39	ca 17 ppm of MO in 240 min under Xenon lamp	[9]

NR – not reported.

Preliminary photocatalysis tests

To ensure that the decrease of the MO concentration on Bi_2O_3 thin films is due to the photocatalysis, the photolysis and adsorption experiments were performed (Fig S1).

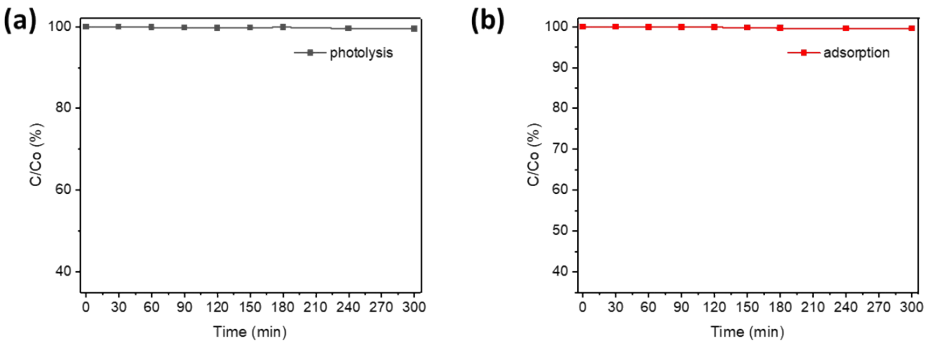

Fig S1 UV-A direct photolysis (a) and adsorption test on the Bi_2O_3 film deposited at 300 °C and annealed at 350 °C (b)

In the first experiment (Fig S1 a), 10 ppm MO solution was irradiated with UV-A lamp for 3 hours in the absence of the photocatalyst. In the second experiment (Fig S1 b), 10 ppm MO solution with Bi_2O_3 thin film was kept in the dark. No direct photolysis or adsorption were detected after 3 hours of measurements ($\eta \leq 1\%$).

Optimisation of precursor molarity

Bismuth (III) acetate is insoluble in water or ethanol; however, is soluble in acetic acid. Thus, 20% alcoholic solution was used for precursor preparation. To optimise the molarity of the precursor solution, Bi_2O_3 films were deposited from 0.025, 0.05 and 0.1 M bismuth (III) acetate solutions at a deposition temperature of 350 °C without annealing. The structural and optical properties of prepared Bi_2O_3 films are presented in Fig S2.

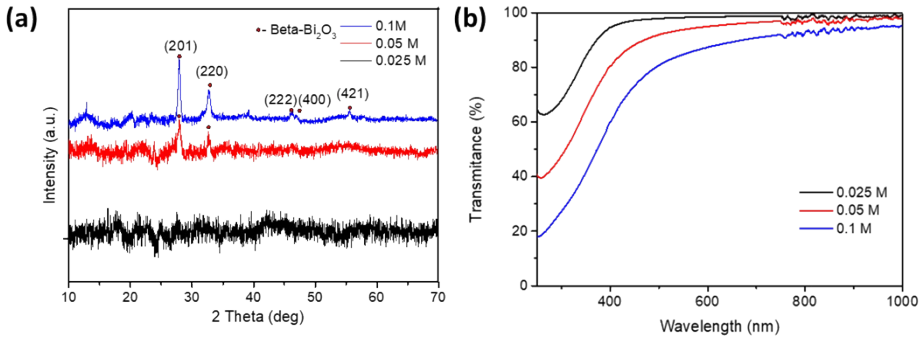

Fig S2 The X-ray diffraction (XRD) patterns (a) and total transmittance spectra (b) of Bi_2O_3 thin films prepared from different molar concentration of precursor

No peaks on the XRD pattern were detected for the sample deposited from a 0.025 M bismuth (III) acetate solution, indicating that the film was amorphous or not enough thick (Fig S2 a). The sample deposited from 0.05 M solution had two peaks of β-Bi_2O_3 phase at 2 theta of 27.9° and 32.9° corresponding to the reflections from (201) and (220) planes, respectively (JCPDS card number 01-077-5341). Increasing the molarity to 0.1 M leads to the presence of three more peaks of β-Bi_2O_3 at 2 theta of 46.2°, 47.1° and 55.6° corresponding to the reflections from (222), (400) and (421) planes, respectively (JCPDS card number 01-077-5341). The resulting films are polycrystalline.

Total transmittance spectra (Fig S2 b) reveal that films are transparent in the visible light spectrum. The transmittance in the visible light region decreased from 97% to 87% with the precursor concentration increase. It indicates that the films become thicker and more light is absorbed. The band gap values of the films deposited from 0.025, 0.05 and 0.1 M solutions were 3.5, 3.4 and 3.2 eV, respectively. The degradation curves of photocatalytic oxidation of 10 ppm MO under UV-A are presented in Fig S3.

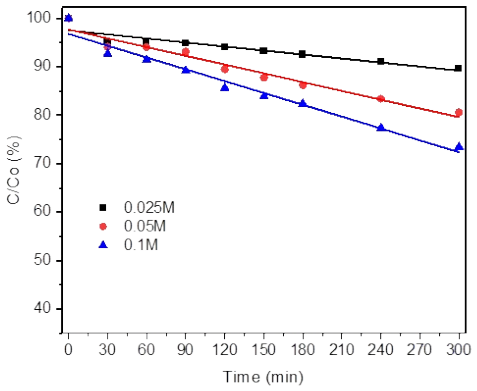

Fig S3 Degradation curves of methyl orange (MO) oxidation under UV-A irradiation on Bi_2O_3 films prepared from different molar concentration of precursor

It was observed that a higher molarity of the precursor solution led to higher photocatalytic activity. The degradation efficiency after 5 h under UV-A increased from 10% to 27% with the increase in precursor molarity from 0.025 to 0.1 M. However, further increase of molarity to 0.2 M resulted in incomplete solubility of bismuth (III) acetate in the solvent, which means that the concentration of acetic acid in solvent should be increased. Thus, the precursor concentration of 0.1 M was fixed for further experiments.

The effect of deposition temperature on the optical properties of Bi_2O_3 films

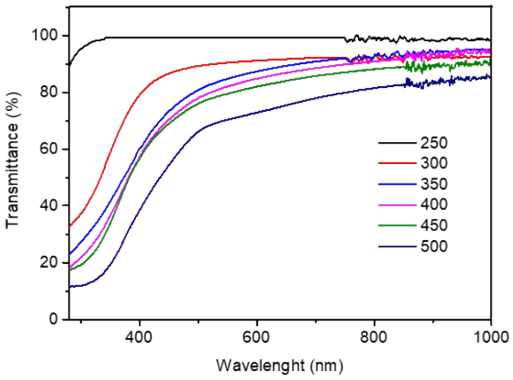

Fig S4 Total transmittance spectra of as-deposited Bi_2O_3 thin films prepared at different deposition temperatures

The effect of visible light on MO oxidation on Bi_2O_3 films

The photocatalytic activity of the samples deposited at 300-450 °C and deposited at 300 °C with further annealed at 350-400 °C was studied under VIS light. The degradation on 10 ppm MO on Bi_2O_3 films is presented in Fig S5.

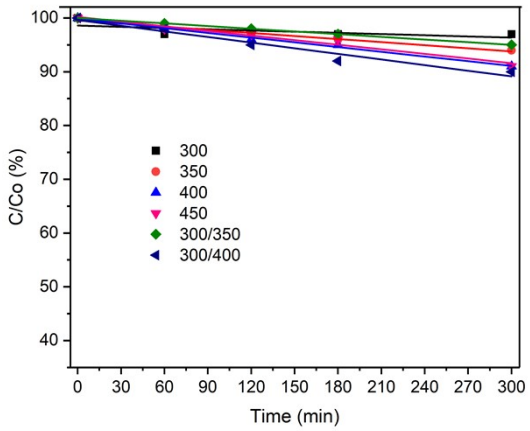

Fig S5 Degradation curves of methyl orange (MO) oxidation under VIS irradiation on Bi_2O_3 films prepared at different deposition and annealing temperatures

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