



### **1. X-ray diffraction (XRD)**

The XRD patterns of the samples were obtained by X-ray diffractometer (Bruker D8 ADVANCE) with an x-ray tube with a Cu anode as the primary x-ray beam source. The measured  $2\theta$  range between  $20^\circ$  and  $80^\circ$  was scanned in steps of  $0.04^\circ/2$  s. The accelerating voltage and applied current were 40 kV and 40mA, correspondingly. The crystalline phases were identified with reference to the PDF cards of the International Centre for Diffraction Data.

### **2. Photocatalytic – Liquid pollutant**

The photo catalytic evaluation of the modified TiO<sub>2</sub> powders has been realized by testing the photo catalytic degradation of an anionic azo dye, Methyl Orange (MO).

In each experiment 50 mg of the powder is mixed with 150 mL of an aqueous solution of the model pollutant (2 ppm). The mixture is stirred in the dark for 40 min and afterwards is being stirred and irradiated (Vis light) for 5 h. Aliquots are measured at intervals (Abs) and each measurement is expressed as the % removal of the model pollutant. For Visible radiation conditions, 4 parallel Daylight lamps (18 W each one) have been used and a UV cut off filter (UV cut off capability of 99 %).

### **3. Photocatalytic – Air pollutant**

Nitric oxide (NO) was chosen as representative airborne pollutant due to its potential health risks and ability to generate photochemical smog. The photocatalytic oxidation of NO by the prepared TiO<sub>2</sub> powders was investigated employing standard procedure based on ISO/DIS 22197-1 [45]. The samples were placed in a flow-type photoreactor where model air containing 1 ppm NO was issued. Flow rate of 3 L/min and relative humidity of 50% were retained during the experiment. Visible light illumination for 90min was applied. The concentrations of the NO, NO<sub>2</sub>, and NO<sub>x</sub> (NO<sub>x</sub>= NO + NO<sub>2</sub>) were monitored in dark and under illumination.

### **4. Scanning Electron Microscopy (SEM)**

The morphology of the powders was observed using scanning electron microscopy (SEM)( Zeiss EVO-MA10) equipped with an Oxford EDS analyzer, where the electron beam accelerating voltages used were between 4.3-7 kV with currents of the order of up to 10nA for EDX measurements and 450 pA for imaging. In order to improve the surface conductivity of the samples standard gold deposition was applied through vacuum evaporation.

### **5. Uv- Vis**

UV-Vis diffuse reflectance of the powders in the wavelength range 350–800nm as obtained using Agilent Carry 60 instrument. The measurements were performed using DRA Fibre Optic coupler (Harrick Agilent Barreline) in order to measure the energy gap of semiconductors.