Selective Photocatalytic Reductions of Nitrobenzene Derivatives using $PbBiO_2X$ and Blue Light

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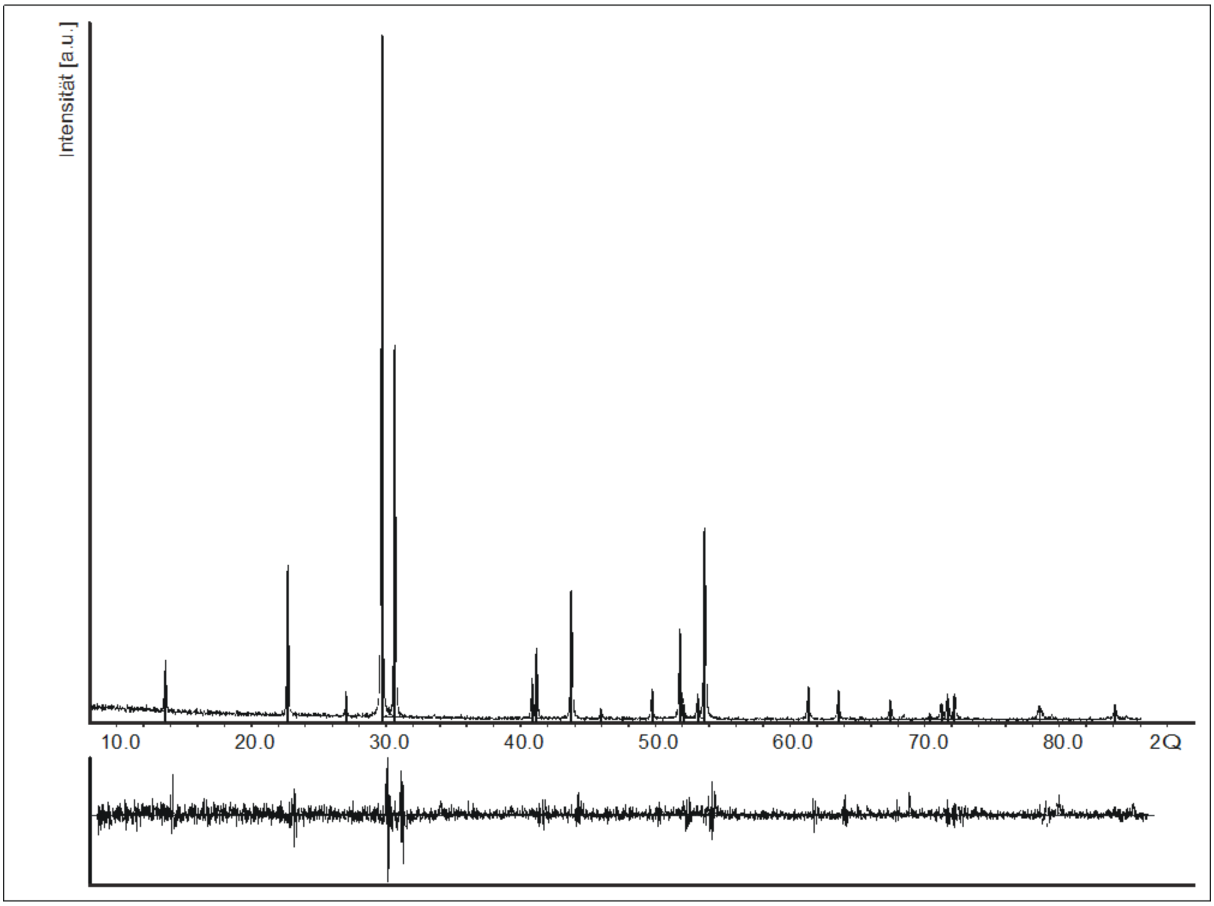
Supporting Information

Content

1. Syntheses of Pb*Pn*O$_2$*X*



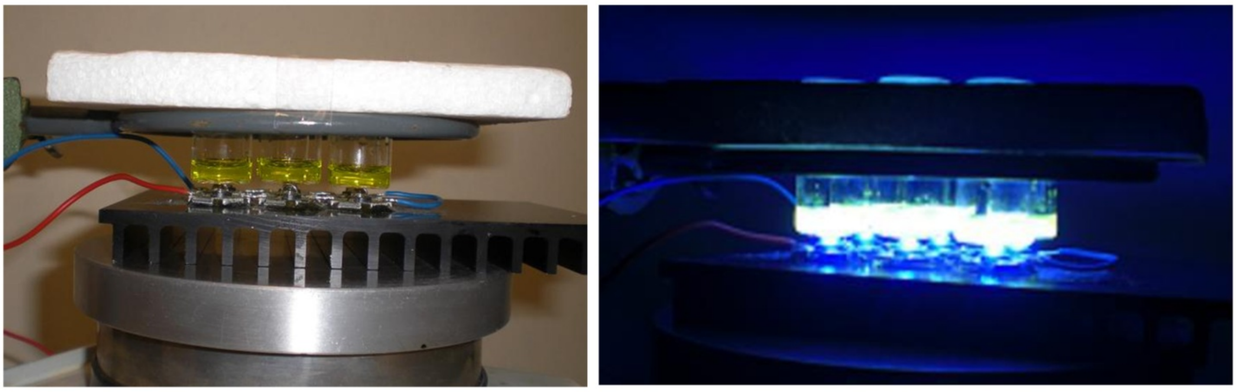
PbPnO$_2$$X$ (Pn = Bi^{3+}, Sb^{3+} and X = Cl$^-$, Br$^-$ and I$^-$) have been synthesized as described before.**Fehler! Textmarke nicht definiert.**

X-ray powder diffraction data were collected on a STOE Stadi P (Cu$K_{\alpha1}$, germanium monochromator). Cell constants were determined from powder patterns by least square refinement using the program package *WinX^{POW}*.

2. Photocatalytic Reductions

General

TEOA (300 mg, 2·10^{-3} mol), starting material (2·10^{-4} mol), PbPnO$_2$$X$ (50 mg) and 2.5 ml acetonitrile were placed in the reaction vial, sealed with a septum and cooled by liquid nitrogen. The mixture was allowed to warm up to room temperature under 50 mbar and flushed with nitrogen. This procedure was repeated once; afterwards the cell was irradiated under stirring for 24 h with the high power LED (440 nm, 3 Watts electrical power, 80 Lumen). For analysis, 500 µl of the reaction mixture were taken out directly by Eppendorf pipette and mixed with 500 µl of a standard (toluene). 1 µl of this solution was injected in the GC or GC/MS. The signals were integrated from the chromatogram.



Irradiation set-up. Each reaction vial is irradiated by one high power LED (80 Lumen, 440 nm emission).

Kinetic measurements

TEOA (300 mg, $2{\cdot}10^{-3}$ mol), nitrobenzene ($2{\cdot}10^{-4}$ mol), Pb*Pn*O_2*X* (50 mg) and 2.5 ml acetonitrile were placed in the reaction vial, sealed with a septum and cooled by liquid nitrogen. The mixture was allowed to warm up to room temperature under 50 mbar and flushed with nitrogen. This procedure was repeated once; afterwards the cell was irradiated under stirring for 24 h with the high power LED (440 nm, 3 Watts electrical power, 80 Lumen). For analysis, 20 µl of the reaction mixture were taken out directly by a Hamilton syringe and mixed with 20 µl of a standard (toluene). 1 µl of this solution was injected in the GC. The signals were integrated from the chromatogram.

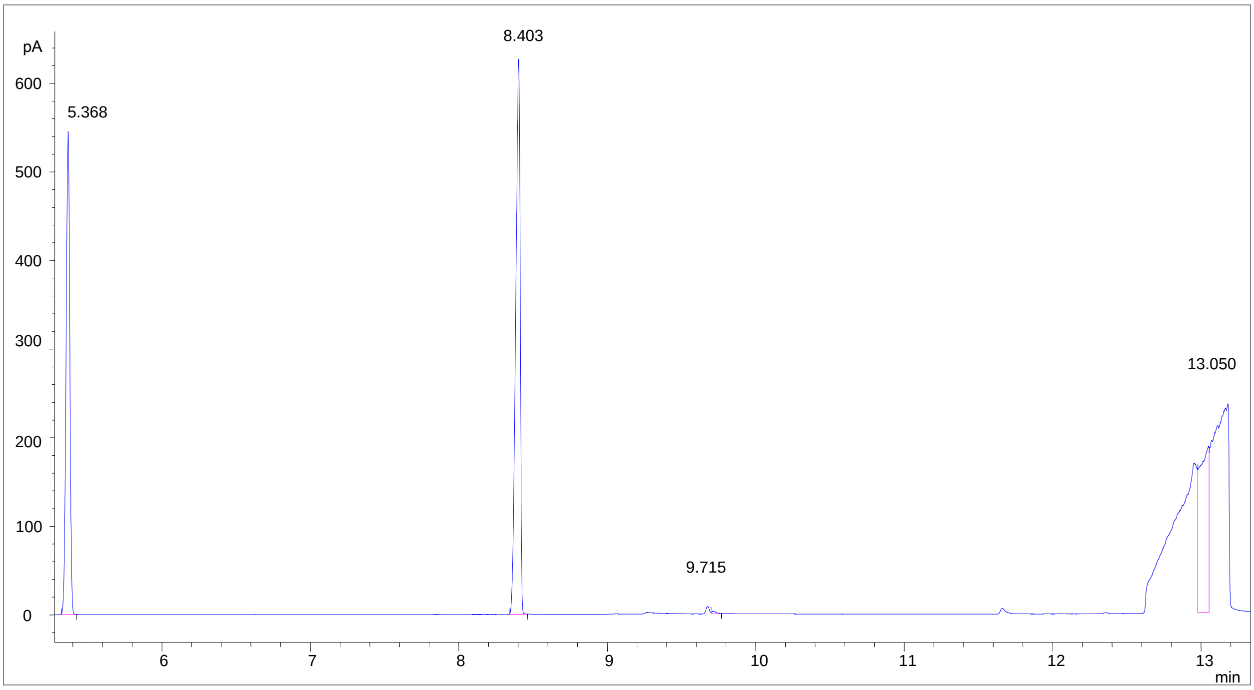
GC-Measurements

A GC 5890 Series II from Hewlett-Packard was used. Injection-temperature (splitinjection: 40:1 split) was at 50 °C, detection temperature was at 300 °C (FID). The column was a capillary column from J+W Scientific - DB-5MS / 30 m X 0.25m / 0.25 µm film. Helium was used as carrier gas with a flow of 1 mL/ min. Data acquisition and evaluation was done by using the software Agilent ChemStation Rev.A.06.03. (509).

GC-measurements were made and investigated while integrating the signals obtained. The GC oven temperature program adjustment was as follows:

The initial temperature was 40 °C. This was kept for 3 minute and then increased constantly at a rate of 15 °C/min for 16 minutes. The final temperature of 280 °C was kept for 5 minutes.

3. Exemplary gas-chromatographic analyses of photoreductions



GC chromatogram of photocatalysis with $PbBiO_2Br$ after 24 h irradiation: t = 5.368 min toluene, t = 8.403 min aniline, t = 9.715 min nitrobenzene, t = 13.05 min TEOA.

4. Determination of the Flat Band Potential according to Roy

50 mg of a sample were ultrasonicated for 15 min in an aqueous 0.1 mol/L solution of KNO_3. Further, 1 drop of concentrated HNO3 was added to this dispersion. Subsequent, 10 mg of methylviologen, a dicationic salt with a pH-independent redox-potential, were added to the mixture. The dispersion was stirred under nitrogen-atmosphere to avoid quenching of the photochemical reaction due to oxygen. A platinum electrode, an Ag/AgCl-reference-electrode and a pH-meter was attached to determine the dispersion’s potential and pH-value, respectively. In a next step, this setup was irradiated with a 150 W Xe arc light source for 60 min. After this time, pH and potential were recorded. Then, the pH was increased by adding NaOH at various concentrations drop wise. The changes in pH and potential were recorded

subsequently after the equilibrium-state was reached. The obtained experimental data were used to derive the flat band potentials according to ref.[1]

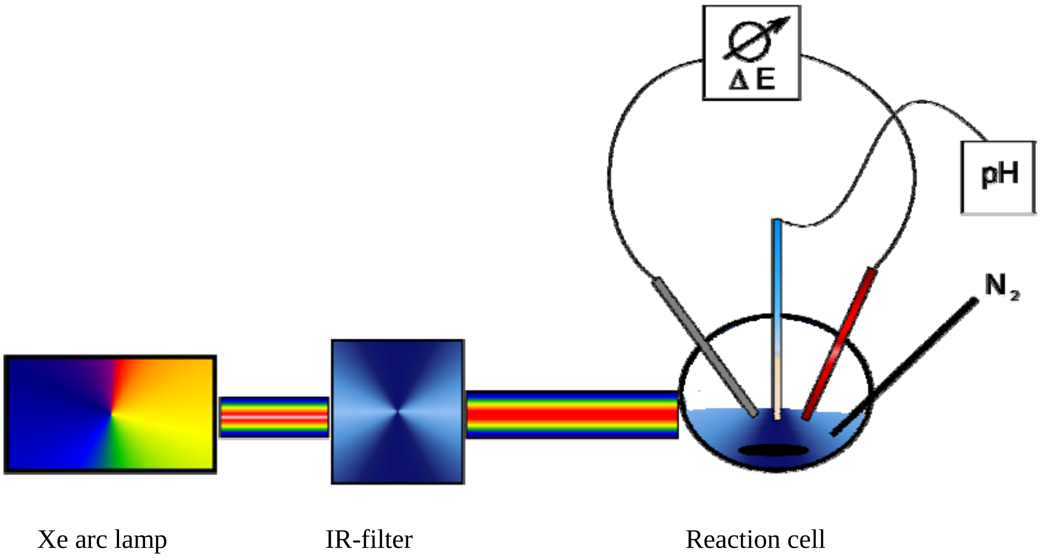


Fig. 1: Schematic setup for the measurement of the flat band potential by using a Xe arc light source; a separate IR-filter is required.

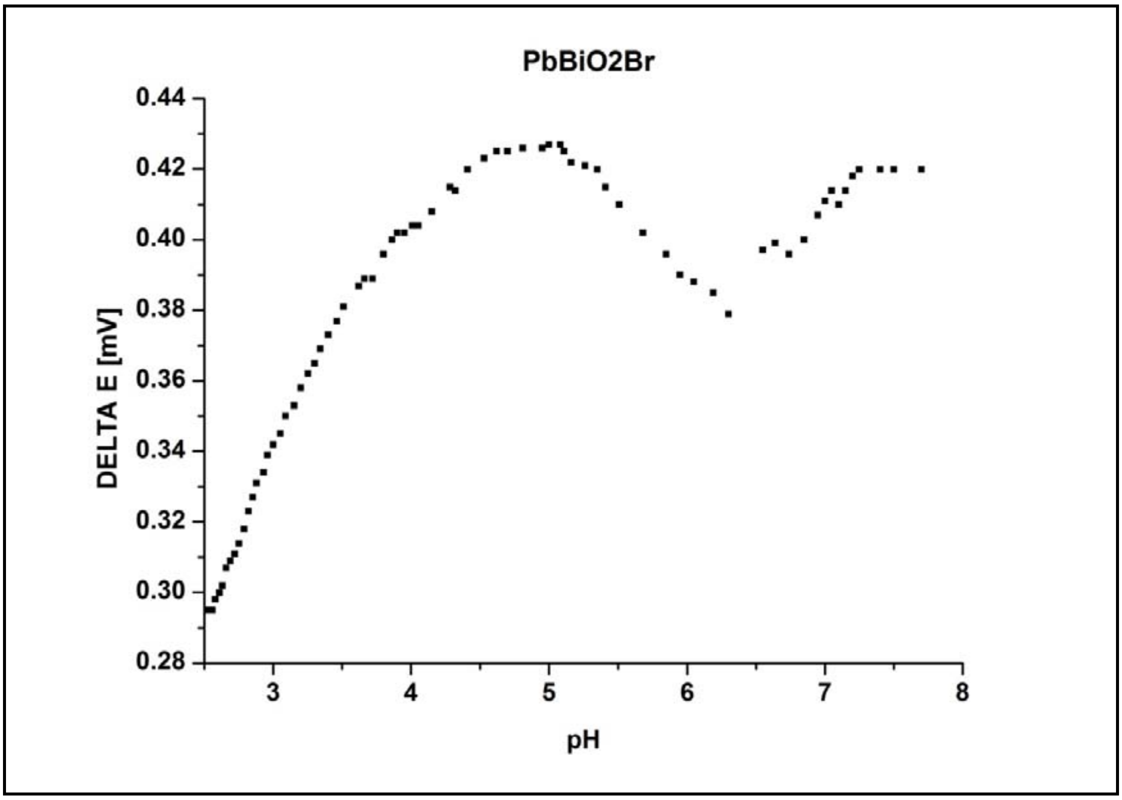


Fig. 2a: Titration curve of $PbBiO_2Br$ under the conditions mentioned above.

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[1] (a) A. M. Roy, G. C. De, N. Sasmal, S. S. Bhattacharyya, *Int. J. Hydrogen Energy* **1995**, *20*, 627. (b) O. L. Stroyuk, O. Y. Rayevska, A. V. Kozytskiy, S. Y. Kuchmiy, *J. Photochem. Photobiol. A: Chemistry* **2010**, *210*, 209.

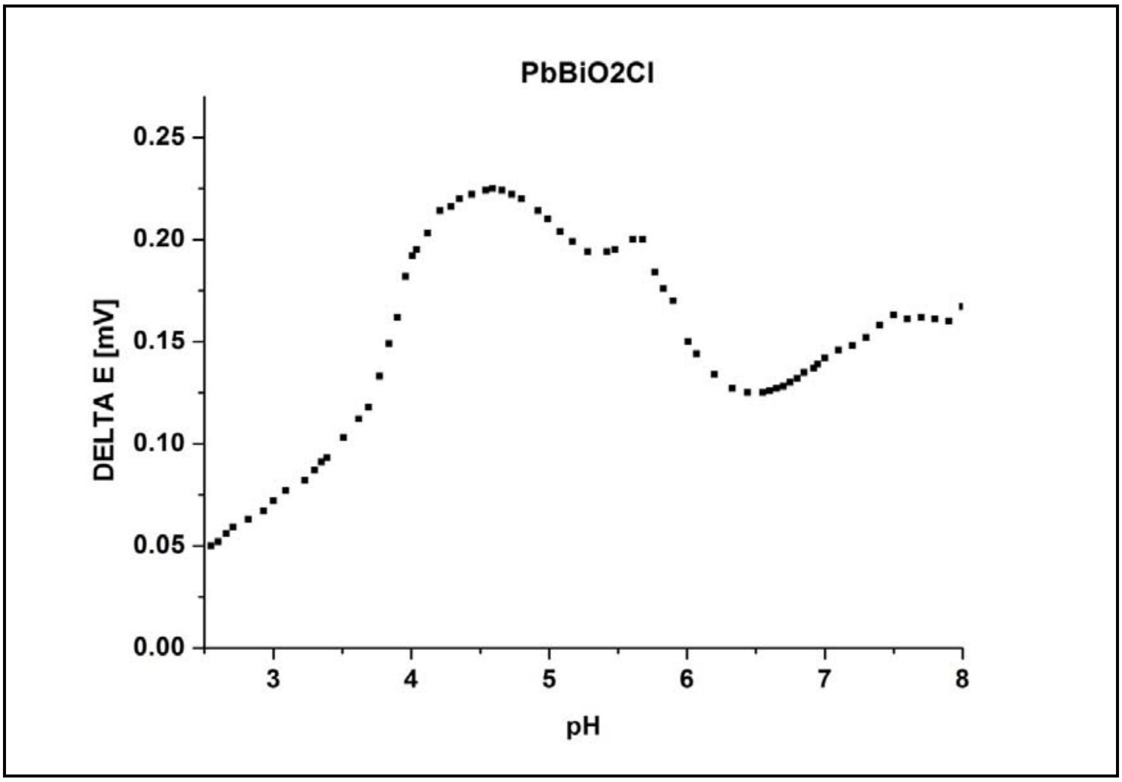


Fig. 2b: Titration curve of $PbBiO_2Cl$ under the conditions mentioned above.

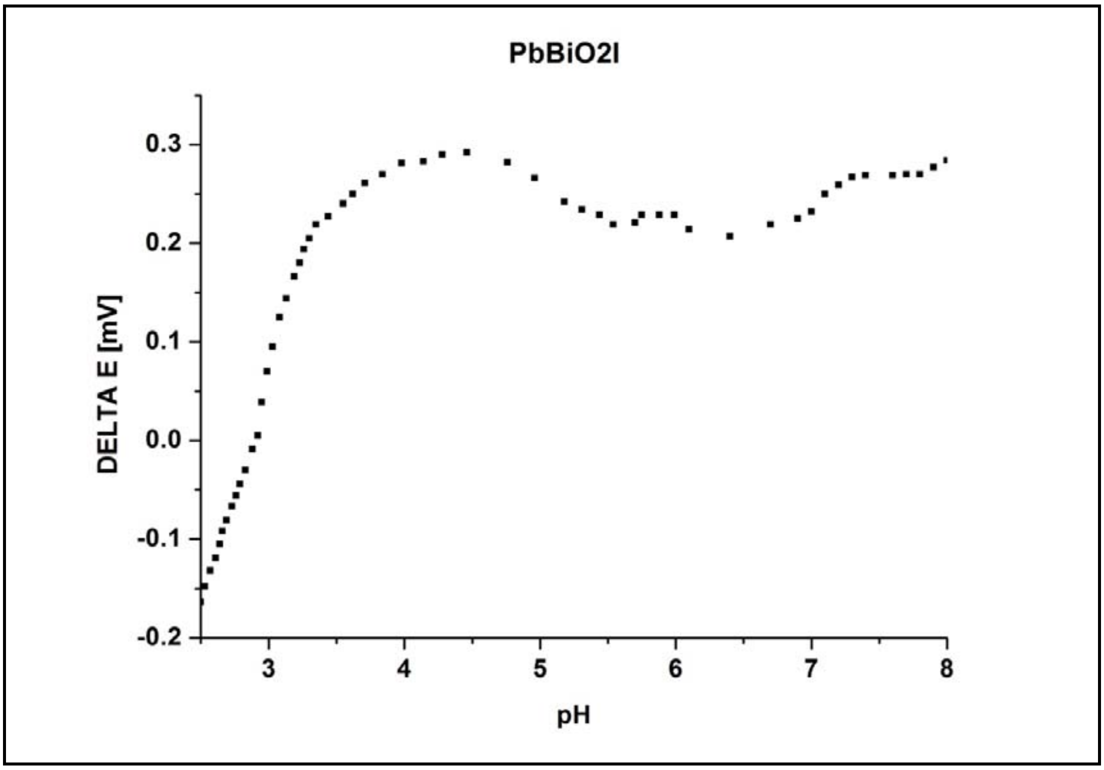
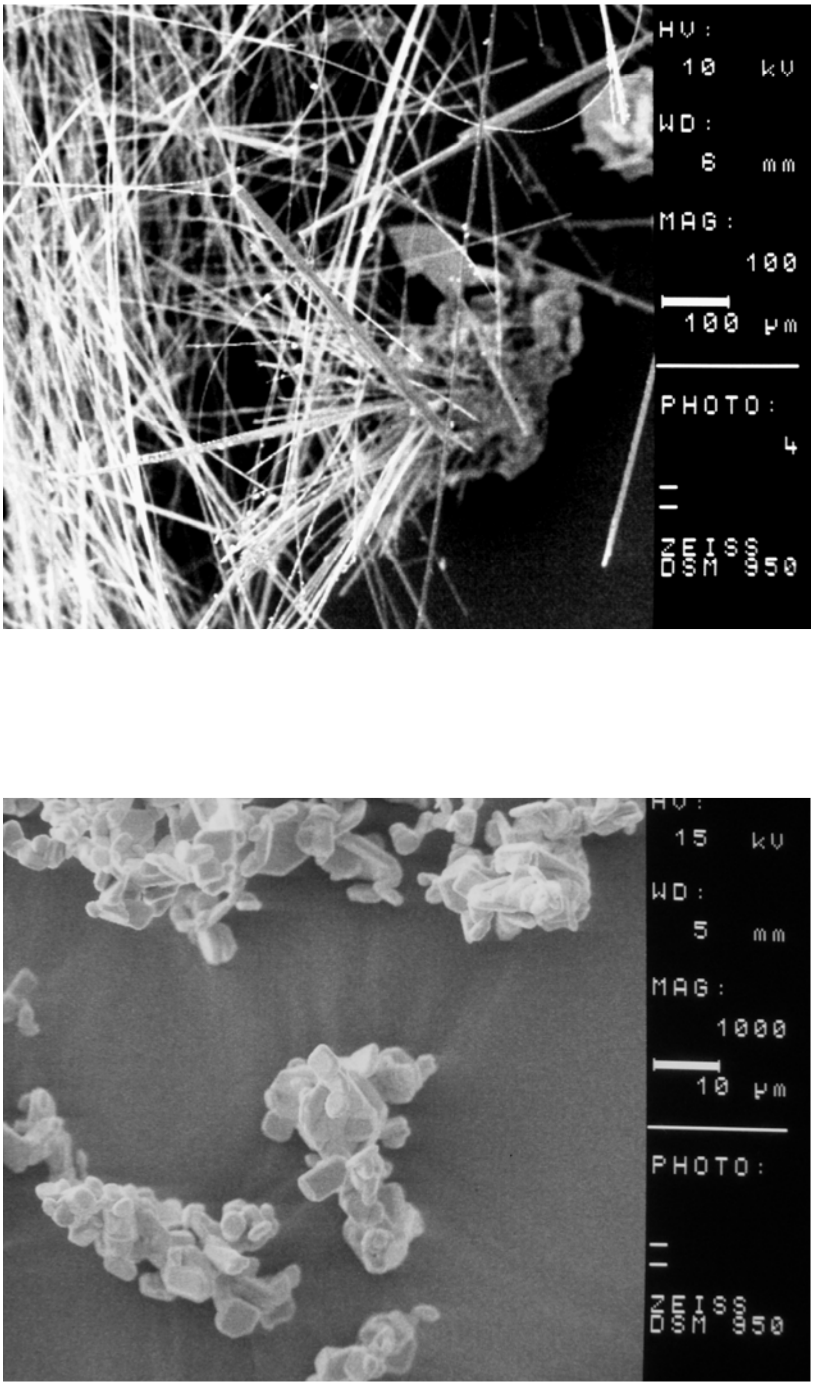


Fig. 2c: Titration curve of $PbBiO_2I$ under the conditions mentioned above.

5. SEM photographs of a) $PbBiO_2I$ showing the crystallographic *c* axis as needle axis and b) platelets of $PbBiO_2Br$ showing the *c* axis perpendicular to the (001) surface.



a)

b)