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Peroxo-niobium oxyhydroxides sensitized TiO₂ crystals

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MATERIALS AND METHODS**-Materials synthesis**

Amorphous niobium oxyhydroxide/TiO₂ composites were prepared by slow dropping of a 1 mol L⁻¹ NaOH solution in a 500 mL Teflon beaker containing 100 mL of a 0.26 mol L⁻¹ NH₄NbO[(C₂O₄)(H₂O)](H₂O)_n solution, kindly donated by Companhia Brasileira de Metalurgia e Mineração (CBMM, Araxá, Minas Gerais, Brazil), and 3 g of TiO₂ (Merck®) at 70°C with vigorous stirring. The obtained solids were washed with deionized water until a neutral pH. This sample was named NbTi.

The NbTi sample was treated with hydrogen peroxide to produce peroxo-niobium oxyhydroxides on the TiO₂ surface. Briefly, the niobium oxyhydroxide/TiO₂ composite previously synthesized was treated with 8 mL of an aqueous hydrogen peroxide (50 %, v/v) solution and 100 mL of water for 2 min. After this contact time, the solid was washed with deionized water and dried in an oven for 12 h at 60°C. This sample was named NbTi//H₂O₂.

-Materials characterization

UV-Vis spectroscopy with diffuse reflectance geometry was carried out on a Cary 5E spectrometer from 200 to 800 nm. Teflon powder was used as reference material (100% transmission), and the Kubelka-Munk equation was used to manipulate all data. X-ray diffraction (XRD) was carried out on a Philips PW 1840 instrument using Cu radiation ($\lambda = 1.54118 \text{ \AA}$) at a 10/min scanning rate. Scanning electron microscopy (SEM) was carried out on a JEOL analyzer coupled to an Oxford (EDS/INCA 350) energy dispersive X-ray analyzer.

Photocatalytic tests

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Eighty milliliters of a 10 mg L⁻¹ methylene blue solution at pH 6.0 was mixed with 60 mg of the catalyst and irradiated with a 300 W Xe lamp equipped with a 400 nm cut-off filter to cut off the UV light. The photocatalytic reactions were monitored by UV–Vis spectroscopy (Shimadzu-UV-1601 PC) at 665 nm with circulating water through a temperature-controlled bath kept at 25 ± 1 °C.

Studies by ESI-MS

In an attempt to identify the intermediates of oxidation, methylene blue dye degradation was also monitored by positive ion mode ESI-MS on an Agilent MS-ion trap mass spectrometer. The reaction samples were analyzed by introducing aliquots into the ESI source with a syringe pump at a flow rate of 5 mL min⁻¹. The spectra were obtained as an average of 50 scans of 0.2 s each. Typical ESI conditions were as follows: heated capillary temperature of 150°C; sheath gas (N₂) at a flow rate of 20 units (4 L min⁻¹); spray voltage of 4 kV; capillary voltage of 25 V; and a tube lens offset voltage of 25 V.

Detection of reactive species

The evaluation the reactive species formed during the photocatalytic degradation of MB was based on the use of different scavenger molecules (isopropanol, ammonium oxalate and benzoquinone) introduced to the reaction medium prior to the addition of the photocatalysts. The dosage of these scavengers was 10 mM.

RESULTS AND DISCUSSION

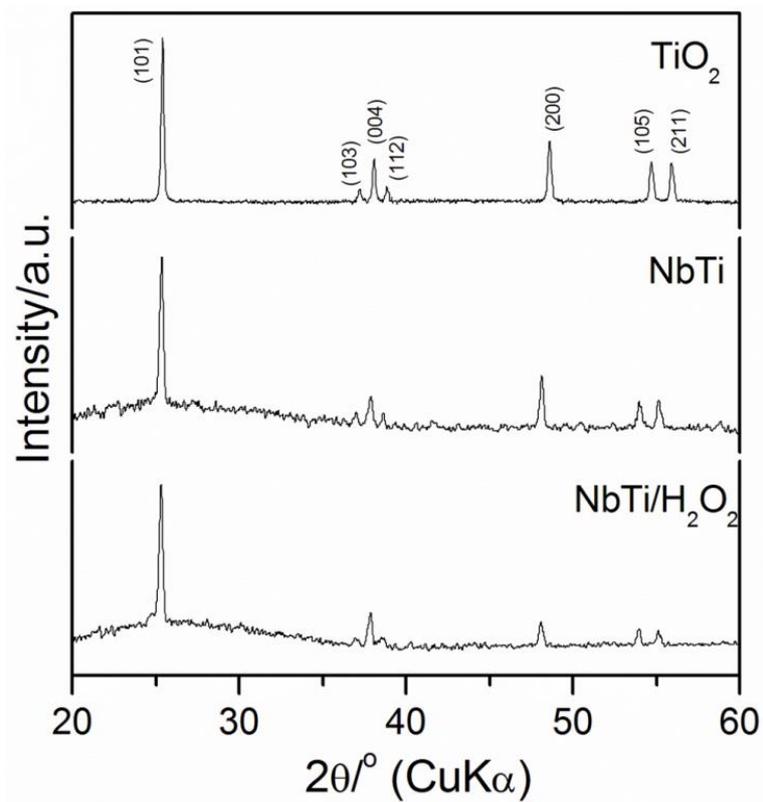


Fig. S1. Powder XRD patterns for the TiO₂, NbTi, and NbTi//H₂O₂ samples.

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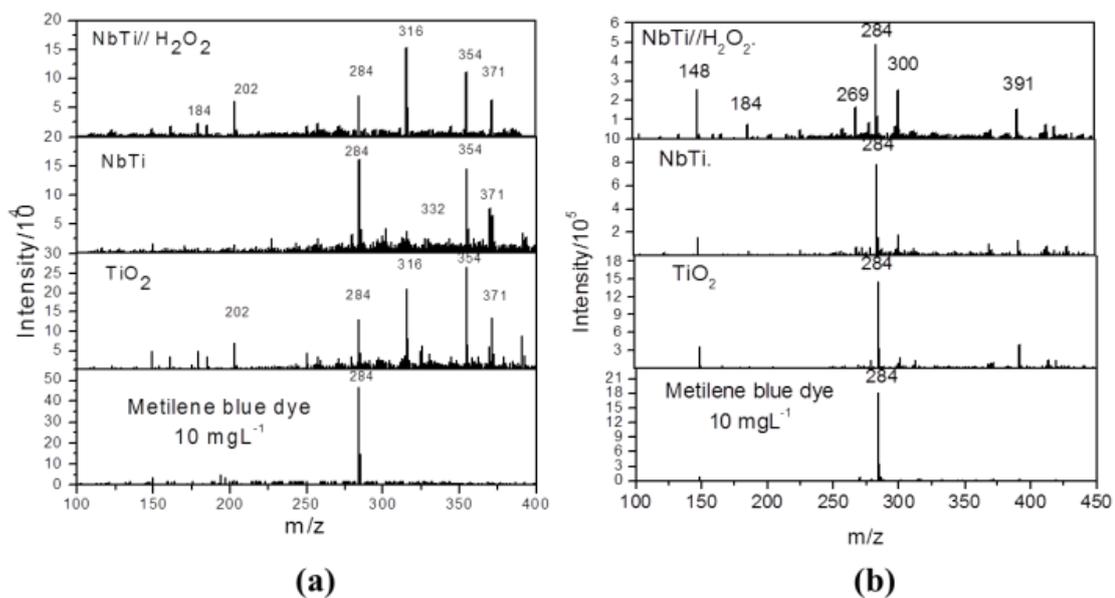


Fig. S2. ESI mass spectra in positive ion mode for the oxidation of methylene blue dye in water by the catalysts of interest, after 60 min (a) under UV or (b) Xe lamp.

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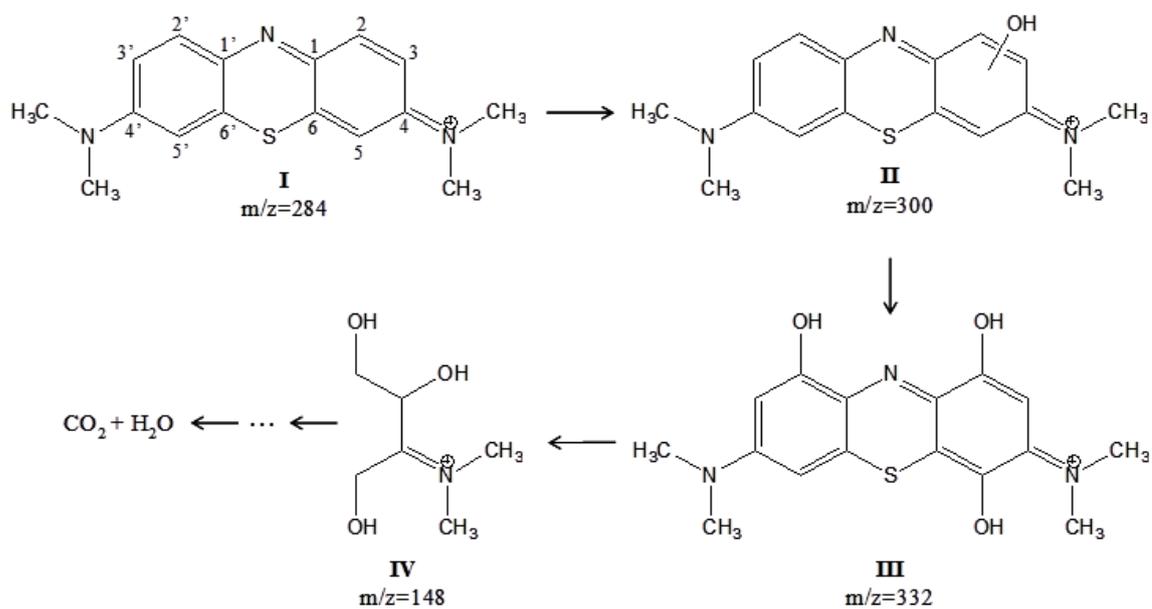


Fig. S3. Proposed structure intermediates after the photocatalytic reaction.

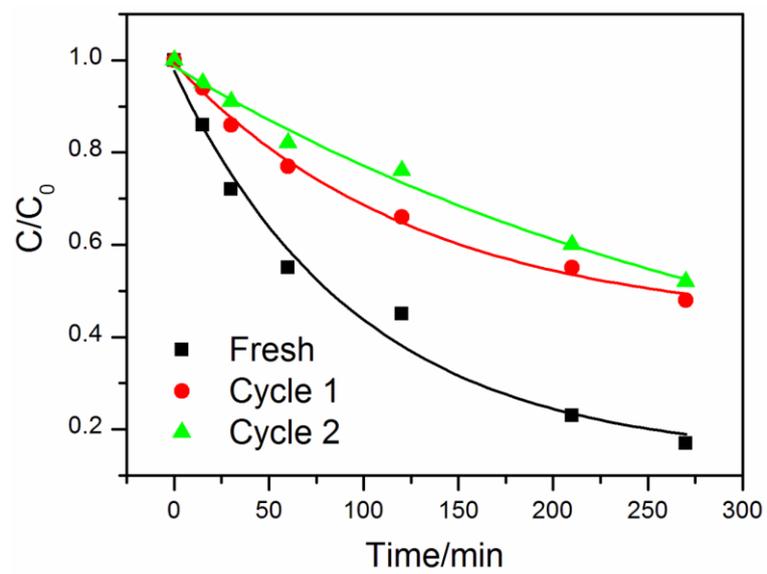


Fig. S4. Photocatalytic tests of reuse of the sample NbTi/H₂O₂.

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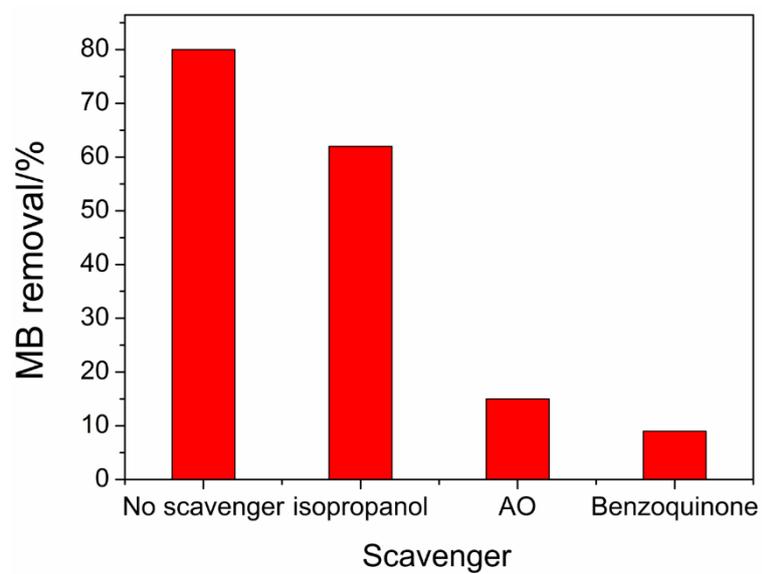


Fig. S5. Photodegradation of MB in the presence of different scavengers. AO = ammonium oxalate.