Control of TiO_{2-x} antioxidant behavior by a $Ti^{3+}(Ti^{2+})/Ti^{4+}$ ratio

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MOTIVATION

Recent developments in TiO_2-related photocatalysis have been linked to highly defective TiO_{2-x} nanoparticles (NPs). It has been demonstrated that high levels of oxygen vacancies and diverse defects, such as Ti^{3+} ions, can significantly improve TiO_{2-x} photocatalytic performance [1]. At the same time, some researchers have reported on a crucial role of the Ti^{3+}/Ti^{4+} ratio in the TiO_{2-x} structure on antioxidant properties of TiO_{2-x} surfaces and NPs [2]. Based on these findings, we hypothesize that changing the $Ti^{3+}(Ti^{2+})/Ti^{4+}$ ratio in the TiO_2 structure [3] we can modify its antioxidant behavior.

AIMS

In this study, two types of TiO_{2-x} NPs were synthesized using a modified method that involved varying the amount of nitric acid as a catalyst and peptizing agent. The TiO_{2-x} NPs were of uniform size (about 5 nm), but possessed different $Ti^{3+}(Ti^{2+})/Ti^{4+}$ ratios. The structure of the synthesized TiO_{2-x} NPs was characterized using TEM, XRD and XPS. Additionally, the antioxidant properties of the synthesized TiO_{2-x} NPs were assessed using the Total Antioxidant Capacity (TAC) test and specific organic probes for various Reactive Oxygen Species (ROS).

EXPERIMENTAL

Colloids of TiO_2 NPs were obtained by the sol-gel method in a water-butanol mixture using tetrabutyl orthotitanate $Ti(OC_4H_9)_4$ as a precursor. The synthesis procedure was the following. First, 12.5 mL of $Ti(OC_4H_9)_4$ was mixed with 2 mL of n-butanol. Then, obtained mixture was drip added to 75 mL of distilled deionized water, stirring vigorously. To obtain aqueous colloids of TiO_2 NPs with different $Ti^{3+}(Ti^{2+})/Ti^{4+}$ ratio, different amount of concentrated HNO_3 as a catalyst and peptizing agent was used. Namely, 530 µL (TiO_2 NPs#1) and 200 µL (TiO_2 NPs#2) of HNO_3 were added to the hydrolysis mixtures, within 10 min of $Ti(OC_4H_9)_4$ addition, still stirring vigorously. Then, the mixtures were stirred for 4 h at 80°C in a water bath. The colloids were cooled down to room temperature and diluted up to 100 ml with distilled deionized water. Final concentrations of TiO_2 NPs#1 and TiO_2 NPs#2 in aqueous colloids were 20 g/L.

Transmission electron microscopy (Tecnai G2 F20 TMP from FEI) was used to analyze NPs size and morphology. Crystal phase structure and composition of NPs were analyzed by X-ray powder diffraction analysis (XRD) using a Siem ens D500 X-ray diffractometer. Ti^{2+}, Ti^{3+} and Ti^{4+} sites in TiO_2 NPs#1 and TiO_2 NPs#2 were determined by X-ray photoelectron spectroscopy (XPS) using a JSPM-4610 XPS 2400 photoelectron spectrometer.

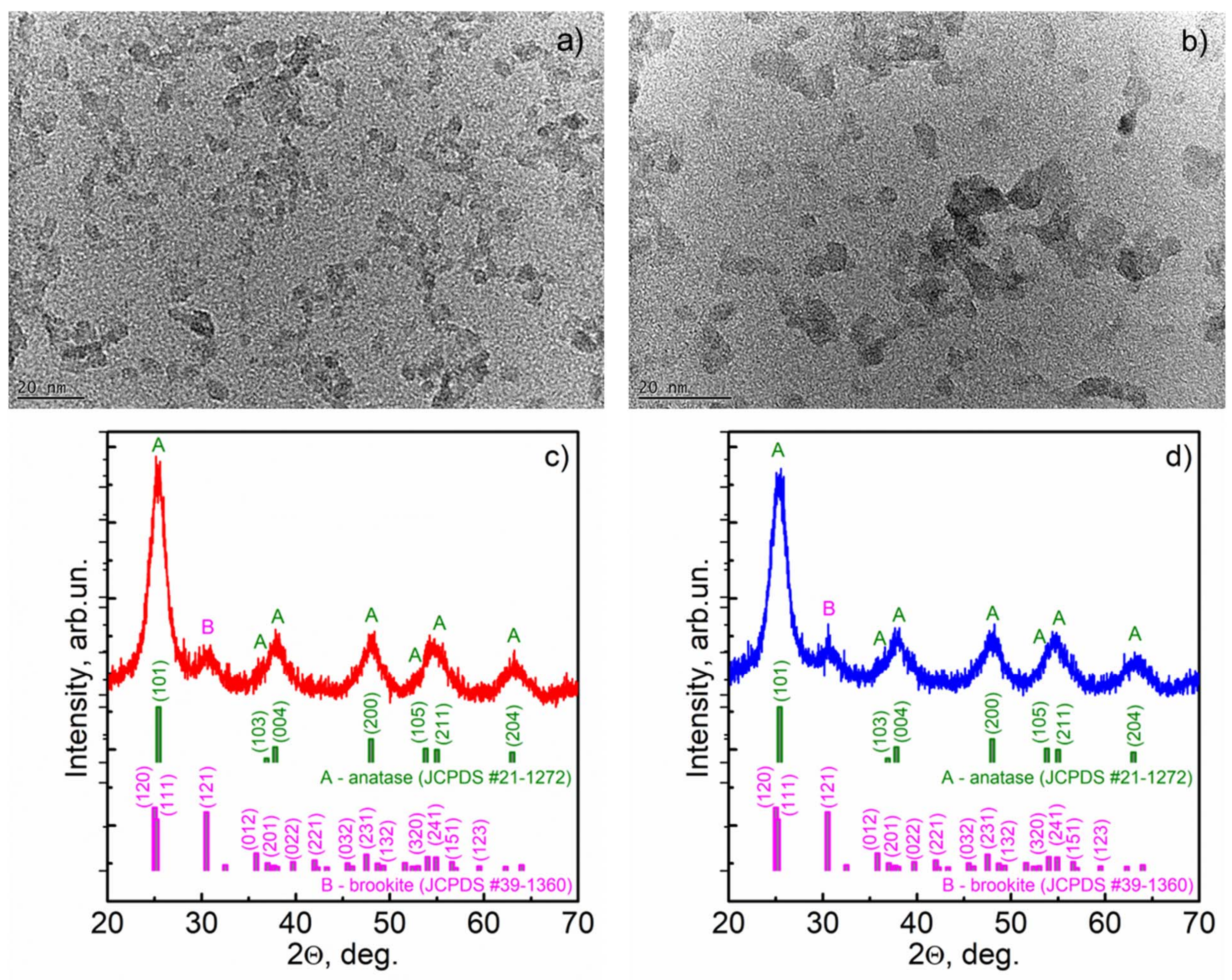

Fig. 1 TEM images (a, b) and XRD patterns (c, d) of TiO_2 NPs#1 (a, c) and TiO_2 NPs#2 (b ,d).

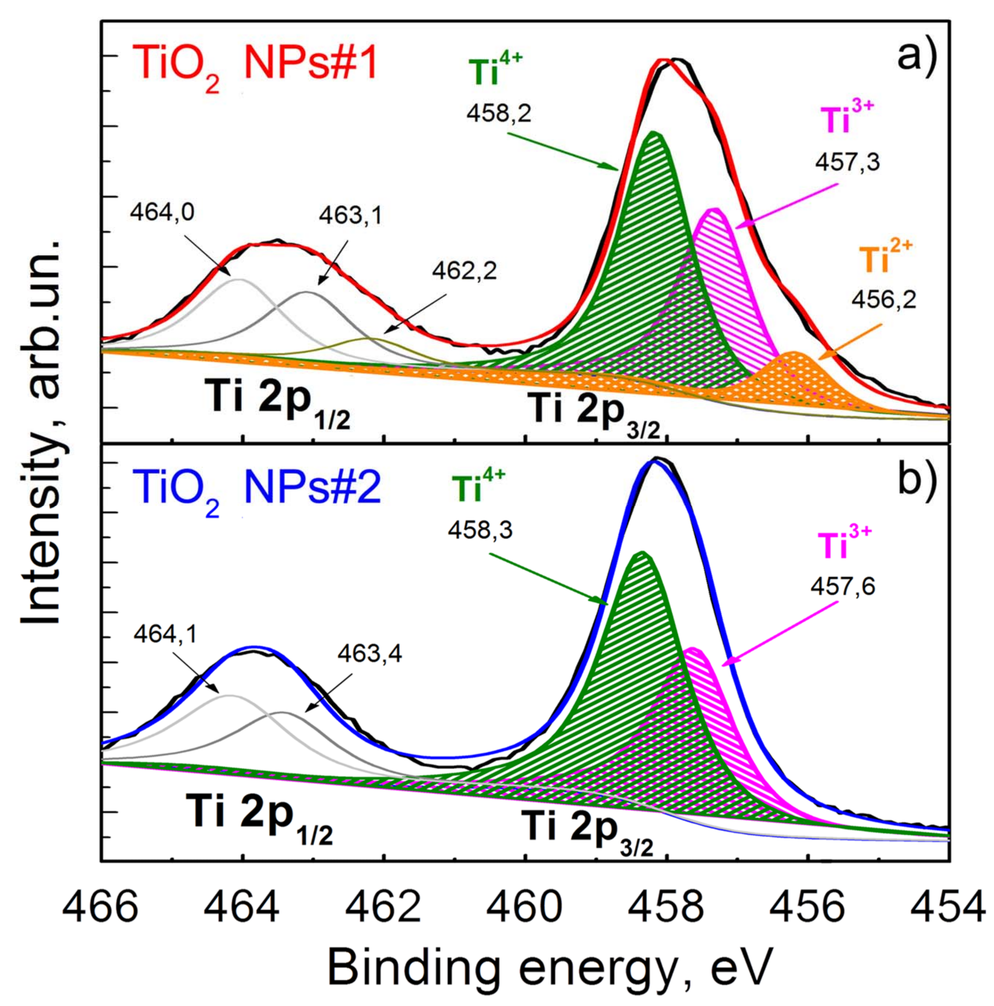

Fig. 2 XPS narrow scan of Ti2p (1/2, 23/2) core level with deconvolution results for TiO_2 NPs#1 (a) and TiO_2 NPs#2 (b) samples.

ROS SCAVENGING ACTIVITY

We have tested ROS scavenging activity for both types of TiO_2 NPs against hydroxyl radicals (·OH) formed during X-ray irradiation of water solutions by detecting spectroscopically using specific sensors - coumarin. Fig.3 shows that in the solutions containing TiO_2 NPs#1 and TiO_2 NPs#2, the concentration of ·OH radicals is remarkably less than in the control solution and the observed radical scavenging effect depends on NPs concentrations as well. Moreover, in the solutions containing TiO_2 NPs#1, ·OH scavenging is more effective. However, this difference decreases with decreasing the NPs concentration. This effect could be explained by the predomination of the reaction of neutralization of ·OH radicals with a participation of Ti^{2+} ions decreasing the total amount of available Ti^{2+} ions in the solution at smaller NPs concentrations.

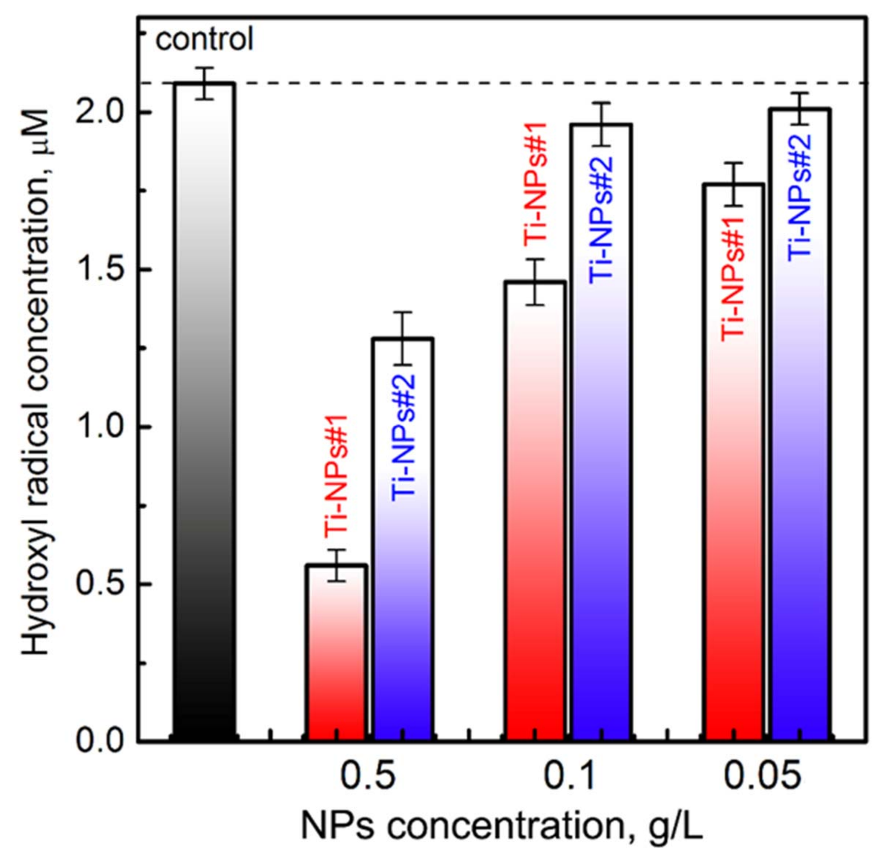

Fig. 3 Scavenging of ·OH radicals formed during radiolysis of water solutions (pH=7.4) containing TiO_2 NPs#1 or TiO_2 NPs#2 of different concentrations. X-ray irradiation during 15 min (radiation dose is 0.21 Gy). Error bars given as Standard Error of the Mean.

TAC ACTIVITY

TAC activity was estimated quantitatively by colorimentric method on a TECAN GENios microplate reader using test kit (Sigma Aldrich, cat. No MAK334) according to the manufacturer's instructions. The TAC results showed that both samples of TiO_2 NPs#1 and TiO_2 NPs#2 exhibited antioxidant activity. However, in the case of TiO_2 NPs#1, the TAC concentration is slightly higher, which can be explained by the greater defectiveness of its structure, namely, includes 8% of Ti^{2+} according to XPS data.

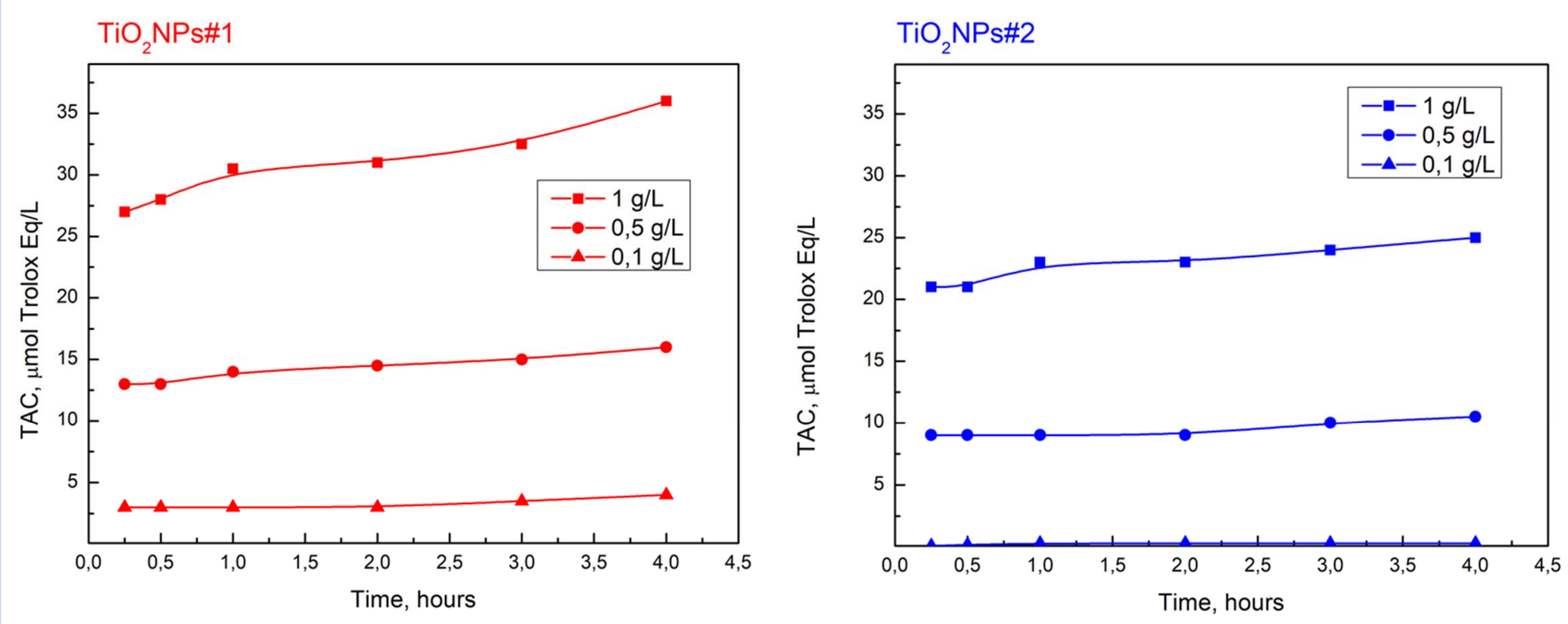

Fig. 4 Antioxidant activity of TiO_2 NPs and in water.

CONCLUSIONS

- √ Synthesized TiO_2 NPs#1 and TiO_2 NPs#2 samples are crystallites with a predominantly anatase phase and the same size of 5.0-6.0 nm.
- √ Simultaneously, TiO_2 NPs#1 and TiO_2 NPs#2 reveal the different amount of titatium ions in lower oxidation states: 38% of Ti^{3+} and 8% of Ti^{2+} ions in TiO_{2-x}NPs#1 and 37% of Ti^{3+} ions in TiO_{2-x}NPs#2.
- √ The results this investigation demonstrated that TiO_2 NPs with a higher $Ti^{3+}(Ti^{2+})/Ti^{4+}$ ratio exhibited greater antioxidant activity, specifically in the scavenging of ROS.

REFERENTS

1. Li D. et al. Thermal coupled photoconductivity as a tool to understand the photothermal catalytic reduction of CO2. // Chin. J. Catal. 41(2020): 154.
2. Suzuki R. et al. Reactive oxygen species inhibited by titanium oxide coatings // J. Biomed. Mater. Res. A. 66 (2003): 396.
3. Seminko V.V. et al. Effect of TiO2-x nanoparticle defect structure on hydroxyl radical scavenging activity under X-ray irradiation. // Colloids Surf. A. 651(2022): 129734.

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