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NEUTRON-FLUENCE-DEPENDENT EVOLUTION OF DEFECT STATES IN NANOCRYSTALLINE TiO_2 PARTICLES

E.A. Huseynova

Institute of Biophysics, Ministry of Science and Education of the Republic of Azerbaijan, Baku, Azerbaijan
efsane.huseynova@yahoo.com

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Abstract: In this study, electron spin resonance spectroscopy was employed to investigate the modification of paramagnetic centers in TiO_2 nanoparticles after neutron irradiation. The initial and irradiated samples were compared over a broad magnetic-field range of 0–6000 G and in a selected resonance region of 3300–3700 G. The wide-field spectra reveal that neutron irradiation does not produce a completely new dominant resonance line over the whole magnetic-field range, but it strongly modifies the intensity, line shape, and baseline behavior of the main paramagnetic response. The enlarged resonance region demonstrates a systematic attenuation and redistribution of the Electron Spin Resonance (ESR) signal after neutron exposure, especially near the principal resonance feature around 3500–3550 G. These spectral changes are attributed to the restructuring of native defect states, electron trapping at irradiation-induced vacancies, and a possible contribution from neutron-transmutation-assisted vanadium-related centers formed through the activation of titanium isotopes. The results indicate that neutron irradiation modifies nanocrystalline TiO_2 not only through displacement-type defect generation but also through spin-center conversion processes that affect the detectable ESR response.

Keywords: TiO_2 particles, neutron irradiation, defect states, oxygen vacancies, radiation-induced defects, titanium dioxide.

1. Introduction

Titanium dioxide is one of the most extensively studied oxide semiconductors because of its chemical stability, wide band gap, photocatalytic activity, and relevance to energy, environmental, sensing, and radiation-related technologies [1–4]. Among its crystalline forms, anatase is particularly important due to its high surface activity and strong sensitivity to point defects [5–7]. When TiO_2 is reduced to the nanocrystalline scale, the large surface-to-volume ratio increases the contribution of surface defects, undercoordinated atoms, oxygen vacancies, trapped electrons, and localized paramagnetic centers. Therefore, nanocrystalline anatase serves not only a functional oxide material but also a useful model system for studying radiation-induced defect formation.

Neutron irradiation is fundamentally different from many other external modification methods. In addition to producing atomic displacement and defects, neutron exposure can activate specific isotopes and may cause nuclear transmutation [8–14]. In TiO_2, the oxygen sublattice and titanium sublattice can both be affected, although titanium-related reactions are generally expected to dominate because of the isotopic composition and neutron-capture probability of titanium. In particular, neutron capture by titanium isotopes can produce unstable intermediate nuclei that may subsequently decay into new atomic species. This process can introduce chemically different centers into the oxide lattice and influence the local electronic environment. Electron spin resonance (ESR) spectroscopy is highly suitable for detecting such changes because it directly probes unpaired electrons and paramagnetic defect states [15–20]. In irradiated oxides, ESR signals may originate from oxygen vacancies, Ti^{3+} centers, trapped electrons, surface radicals, vacancy-related complexes, or transmutation-related paramagnetic centers. The line shape, line width, and intensity of the ESR spectrum can therefore provide valuable information about defect evolution following neutron exposure. The present study provides a reinterpreted ESR-based analysis of neutron-irradiated nanocrystalline anatase TiO_2 using two spectral views: a broad magnetic-field spectrum and a magnified view of the main resonance region. Unlike a purely descriptive comparison of spectra, this article focuses on the dose-driven redistribution of paramagnetic centers and the possible coexistence of defect annihilation, electron trapping, vacancy formation, and transmutation-assisted spin-center modification.

2. Experimental

Nanocrystalline anatase TiO_2 powder was used as the material under investigation. The nanoparticles had an average particle size of approximately 5 nm, a specific surface area of 480–650 m^2/g, and a true density of about 3.9 g/cm^3. The high specific surface area is important because surface-related paramagnetic centers can strongly influence the ESR response of oxide nanoparticles. The TiO_2 nanopowder was divided into several groups: an unirradiated control sample (c.s.) and neutron-irradiated samples exposed to different fluences. The irradiation was carried out in the TRIGA Mark II research reactor at the Jozef Stefan Institute, Ljubljana, Slovenia. The reactor operated at full power of 250 kW, and the samples were irradiated under a neutron flux of approximately 5.79×10^{12} $n/cm^2 \cdot s$. The applied neutron fluences were: 1.6×10^{15} n/cm^2, 8×10^{15} n/cm^2, 4×10^{16} n/cm^2 and 2×10^{17} n/cm^2. After irradiation and at appropriate decay period, ESR measurements were performed at room temperature using an X-band ESR spectrometer operating near 9.85 GHz. The spectra were recorded in two magnetic-field ranges. The first measurement range covered the broad interval from 0 to 6000 G and was used to observe the general spectral structure. The second measurement range focused on the principal resonance region between 3300 and 3700 G, allowing a more detailed comparison of the main ESR line shape before and after neutron irradiation.

3. Results and Discussion

Fig. 1 presents the ESR spectra of the control and neutron-irradiated nanocrystalline TiO_2 samples in the broad magnetic-field range from 0 to 6000 G. The spectra show that the dominant ESR response is concentrated near the central high-field region, while the remaining portions of the spectrum contain weaker broad components and baseline variations. The most intense resonance is observed around the main resonance region near 3500–3550 G. This signal is characteristic of paramagnetic centers with an effective g-factor close to that expected for electron-type centers in oxide matrices. In nanocrystalline TiO_2, such a signal can be associated with trapped electrons, Ti^{3+}-related states, oxygen-vacancy-associated centers, or surface-localized paramagnetic defects. Owing to the extremely small particle size and high specific surface area, both bulk and surface centers may contribute to the measured ESR signal.

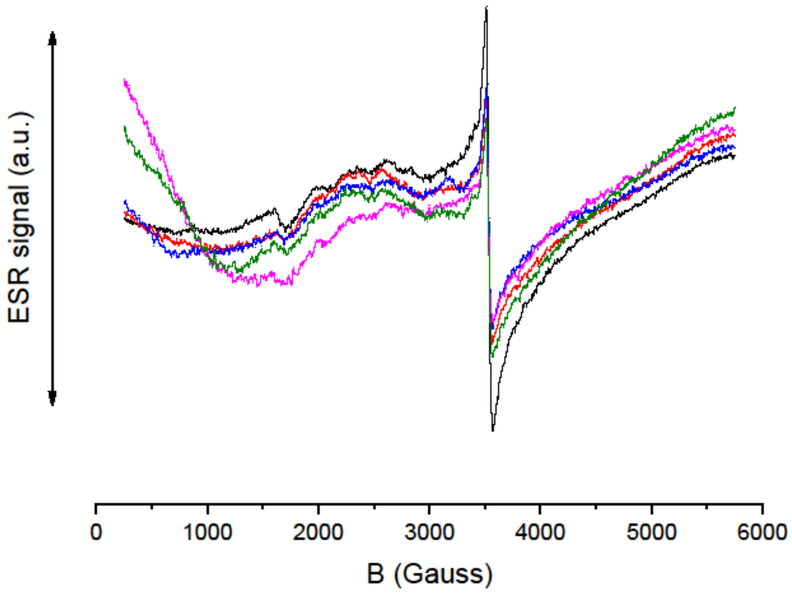

Fig. 1. Broad-field ESR spectra of initial and neutron-irradiated nanocrystalline TiO_2 particles recorded in the magnetic-field interval of 0–6000 G.

A key observation from Fig. 1 is that neutron irradiation changes the relative spectral intensity and line shape without completely replacing the initial ESR pattern. This means that neutron exposure modifies the existing defect system rather than generating only one isolated new paramagnetic species. The spectra of the irradiated samples remain broadly similar in position, but their amplitudes and background behavior differ from the control sample. This indicates that irradiation affects the concentration, electronic environment, and interaction state of paramagnetic centers. The broad low-field part of the spectra also changes after irradiation. Although these features are weaker than the principal resonance line, they are important because they may reflect magnetically interacting centers, surface-related disorder, or defect clusters formed under neutron exposure. In nanocrystalline oxides, defect clustering is especially plausible because point defects created in the lattice can migrate over short distances and interact with surfaces, grain boundaries, or pre-existing structural imperfections.

The attenuation of the main signal with increasing neutron fluence can be interpreted as evidence for electron redistribution. Neutron irradiation can produce oxygen vacancies, titanium vacancies, interstitials, and trapped-charge states. Some of these defects may trap electrons that previously contributed to the initial ESR signal. As a result, the detectable free-electron-type resonance can decrease even while the total number of structural defects increases. Therefore, lower ESR intensity does not necessarily mean fewer radiation defects; rather, it may indicate conversion of ESR-active centers into less visible or differently broadened configurations.

Fig. 2 shows the magnified ESR spectra in the 3300–3700 G region. This selected interval is more informative for evaluating the main paramagnetic resonance because it removes most of the broad-field background and emphasizes the line-shape evolution around the principal resonance. The control sample (c.s.) exhibits the strongest and most developed resonance profile. After neutron irradiation, the signal intensity decreases and the resonance shape becomes more compressed. The irradiated spectra lie closer to each other than to the control spectrum, indicating that even the lower irradiation levels strongly affect the initial defect population. The highest fluence, 2×10^{17} n/cm^2, shows a clearly modified spectral response compared with the unirradiated state. The main resonance region contains two important features: the positive part of the derivative-like ESR signal before the resonance crossing and the negative part after the resonance maximum. The decrease in both components after irradiation suggests that the concentration or mobility of the original paramagnetic centers is reduced. This can occur if irradiation-induced vacancies and defect complexes act as electron traps. In this case, electrons become localized in environments where their ESR response is broadened, shifted, or partially suppressed.

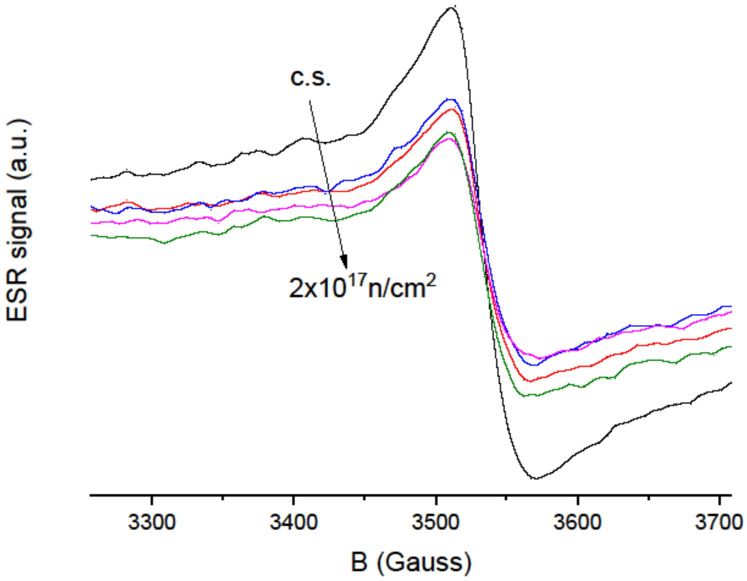

Fig. 2. Magnified ESR spectra of initial and neutron-irradiated nanocrystalline TiO_2 *particles in the selected magnetic-field range of 3300–3700 G.*

The line shape of the irradiated spectra also suggests that neutron exposure produces a more heterogeneous defect environment. In an ideal single-center system, the ESR line would remain narrow and well-defined. Here, the broadening and intensity redistribution indicate overlapping contributions from several types of centers. These may include oxygen vacancy centers, titanium-related centers, surface trapped electrons, and transmutation-related vanadium-associated centers. A possible nuclear-transmutation pathway in TiO_2 is related to neutron capture by titanium isotopes. The reaction involving ^{50}Ti can lead to ^{51}Ti formation, followed by β-decay to ^{51}V. The resulting vanadium-related centers may interact with the oxygen sublattice and form local charge-compensation defects. Such centers can influence the ESR spectrum either directly, if they are paramagnetic, or indirectly, by changing the charge balance and defect chemistry of the anatase lattice. However, based only on the ESR spectra in Fig. 1 and Fig. 2, the contribution of vanadium-related centers should be treated as a plausible interpretation rather than as an isolated direct measurement. The observed spectral changes clearly demonstrate neutron-induced modification of paramagnetic states, but complementary methods such as gamma spectrometry, ICP-MS, XPS, or high-resolution EPR simulation would be necessary to quantify the exact concentration and oxidation state of transmuted vanadium.

The ESR behavior observed in Fig. 1 and Fig. 2 can be explained through a combined defect-evolution mechanism. Before irradiation, the nanocrystalline anatase contains native paramagnetic centers formed during synthesis, storage, and surface hydration/oxidation processes. These centers contribute to the initial ESR signal. After neutron irradiation, several processes occur simultaneously. First, elastic neutron interactions can displace atoms and form point defects. Second, ionization and recoil processes can redistribute trapped charges. Third, neutron capture by titanium isotopes can generate new nuclear products, including possible vanadium-related species. Fourth, the high surface area of 5 nm particles provides many sinks for mobile defects, allowing vacancy migration, surface trapping, and defect recombination. The observed decrease in the central ESR signal suggests that irradiation does not simply increase the number of ESR-active centers. Instead, it changes their electronic configuration. Some paramagnetic centers may be converted into diamagnetic states, while others become broadened due to magnetic interactions or local structural disorder. This explains why the irradiated spectra can show reduced main-line intensity even though the material has experienced additional radiation damage. The magnified spectra in Fig. 2 support this interpretation. The control sample has a stronger and more defined resonance, while irradiated samples show suppressed and redistributed intensity. This behavior is consistent with a transition from isolated native centers to a more complex defect network containing vacancy clusters, trapped electrons, and possible impurity-like transmutation centers.

The results demonstrate that neutron irradiation can be used as a tool for controlled modification of oxide nanoparticles. In nanocrystalline TiO_2, neutron exposure changes the ESR-visible defect structure and may promote the formation of intrinsic and transmutation-associated centers. Such modifications can influence photocatalytic activity, charge separation, electrical conductivity, and radiation tolerance. From an application perspective, this is important for two reasons. First, TiO_2-based materials may be used in radiation environments, where their defect stability must be understood. Second, neutron irradiation may serve as a non-conventional method for defect engineering and atomic-scale modification of nanomaterials. By controlling neutron fluence, it may be possible to tune the concentration and type of paramagnetic centers in TiO_2.

4. Conclusions

A new ESR-based analysis of neutron-irradiated nanocrystalline anatase TiO_2 has been presented using broad-field and magnified resonance spectra. The broad ESR spectra show that neutron irradiation modifies the general spin response of TiO_2 without producing a completely separate dominant resonance across the full magnetic-field range. The magnified spectra in the 3300–3700 G interval reveal a clear weakening and reshaping of the principal resonance line after irradiation. The spectral evolution is attributed to irradiation-induced restructuring of paramagnetic centers, electron trapping at newly formed vacancies, possible vacancy-complex formation, and potential contribution from titanium-to-vanadium transmutation processes. The decrease in ESR intensity is interpreted not as a simple reduction of radiation defects, but as a transformation of initially ESR-active centers into more complex, broadened, or electronically compensated defect states.

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ЭВОЛЮЦИЯ ДЕФЕКТНЫХ СОСТОЯНИЙ В НАНОКРИСТАЛЛИЧЕСКИХ ЧАСТИЦАХ TiO_2 В ЗАВИСИМОСТИ ОТ ФЛЮЕНСА НЕЙТРОНОВ

Э.А. Гусейнова

Резюме: В данном исследовании для изучения модификации парамагнитных центров в наночастицах TiO_2 после нейтронного облучения была использована спектроскопия электронного парамагнитного резонанса. Исходные и облучённые образцы были сопоставлены в широком диапазоне магнитных полей 0–6000 Гс, а также в выделенной резонансной области 3300–3700 Гс. Анализ спектров, полученных в широком диапазоне магнитных полей, показал, что нейтронное облучение не приводит к появлению новой доминирующей резонансной линии во всём исследованном диапазоне, однако существенно изменяет интенсивность, форму линии и характер базовой линии основного парамагнитного отклика. Более детальное рассмотрение резонансной области выявило систематическое ослабление и перераспределение сигнала электронного парамагнитного резонанса (ЭПР) после воздействия нейтронов, особенно вблизи основной резонансной линии в области 3500–3550 Гс. Наблюдаемые спектральные изменения обусловлены перестройкой собственных дефектных состояний, локализацией электронов на вакансиях, индуцированных облучением, а также возможным вкладом ванадиевых центров, формирующихся в результате нейтронной трансмутации при активации изотопов титана. Полученные результаты свидетельствуют о том, что нейтронное облучение модифицирует нанокристаллический TiO_2 не только за счёт образования дефектов смещения, но и посредством процессов преобразования спиновых центров, оказывающих влияние на регистрируемый ЭПР-отклик.

Ключевые слова: частицы TiO_2; нейтронное облучение; дефектные состояния; кислородные вакансии; радиационно-индуцированные дефекты; диоксид титана.

NANOKRİSTALLİK TiO_2 HİSSƏCİKLƏRİNDƏ DEFEKTLƏRİN NEYTRON AXININDAN ASILI OLARAQ FORMALAŞMASI

Ə.Ə. Hüseynova

Xülasə: Bu tədqiqatda, neytron şüalandırılmasından sonra TiO_2 nanozərrəciklərinin paramaqnit mərkəzlərində baş verən dəyişiklikləri araşdırmaq üçün elektron spin rezonansı spektroskopiyasından istifadə edilmişdir. Başlanğıc və şüalanmış nümunələr 0–6000 G maqnit sahəsi diapazonunda və 3300–3700 G rezonans bölgəsində müqayisə edilmişdir. Geniş sahəli spektrlər göstərir ki, neytron şüalanması bütün maqnit sahəsi diapazonunda tamamilə yeni dominant rezonans xətti yaratmır, lakin əsas paramaqnit siqnalın intensivliyini, xətt formasını və baza xəttinin davranışını güclü şəkildə dəyişdirir. Genişləndirilmiş rezonans bölgəsi göstərir ki, xüsusilə təxminən 3500–3550 G ətrafındakı əsas rezonans xüsusiyyəti yaxınlığında neytron təsirindən sonra Elektron Spin Rezonansı (ESR) siqnalında sistematik zəifləmə və yenidən paylanma baş verir. Bu spektral dəyişikliklər yerli defektlərin yenidən qurulması, şüalanma nəticəsində yaranan vakansiyalarda elektronların tutulması və titan izotoplarının aktivləşməsi yolu ilə neytron transmutasiyası ilə əlaqəli vanadium mərkəzlərinin mümkün rolu ilə əlaqəlidir. Nəticələr göstərir ki, neytron şüalanması nanokristallik TiO_2-ni təkcə yerdəyişmə tipli defektlərin yaranması vasitəsilə deyil, həm də aşkar edilə bilən ESR cavabına təsir edən spin-mərkəz çevrilmə prosesləri vasitəsilə dəyişdirir.

Açar sözlər: TiO_2 hissəcikləri; neytron şüalanması; defektlər; oksigen vakansiyaları; şüalanma nəticəsində defektlər; titan dioksid.