



Magnetic Properties and Photocatalytic Activity of the TiO₂ Micropowders and Nanopowders Coated by Ni Nanoclusters

D. Japaridze¹ · D. Daraselia¹ · E. Chikvaidze¹ · T. Gogoladze¹ · M. Nadareishvili² · T. Gegechkori² · T. Zedginidze² · T. Petriashvili² · G. Mamniashvili² · A. Shengelaya^{1,2}

Received: 20 November 2018 / Accepted: 20 March 2019
© Springer Science+Business Media, LLC, part of Springer Nature 2019

Abstract

In this work, TiO₂ micropowders and nanopowders coated by Ni nanoclusters have been prepared by original electroless deposition method. The presence of Ni nanoclusters at the surface of TiO₂ grains was confirmed by measuring the temperature dependence of magnetization. Optical spectroscopy measurements showed significant increase of light absorption in Ni-coated TiO₂ nanopowders. Photocatalytic properties of TiO₂/Ni powder were studied with electron paramagnetic resonance spectroscopy as well. It was found that deposition of Ni nanoclusters on a mixture of anatase (76%) and rutile (14%) nanopowder provides best results and the optimal Ni deposition time was determined.

Keywords Titanium dioxide · Photocatalysis · Magnetic clusters

1 Introduction

Hydrogen is a very attractive clean energy source for the future. The use of hydrogen as an energy source has several advantages, such as good energy conversion effectiveness, ability to be produced from water with zero emission, and different storage options, to name just few. The product of hydrogen combustion is water and therefore produces no pollutants. The sun energy can split water into hydrogen and oxygen in presence of catalysts and this reaction is called photocatalysis. Photocatalytic water splitting using semiconducting catalysts has received much attention and is a subject of active research. The best known semiconductor photocatalyst is TiO₂ due to its properties, such as high photocatalytic activity, excellent incident photoelectric conversion efficiency, photostability, chemical stability, corrosion resistance, and nontoxicity [1–4].

The photocatalytic reaction proceeds as follows. Absorbed into TiO₂, which is a semiconductor and has an energy gap of 3.2 eV between the valence and conduction bands, a sunlight photon creates an electron-hole pair. Having reached the TiO₂ surface, the produced electron and holes interact with water molecules and cause their splitting into hydrogen and oxygen [5].

As mentioned above, the photocatalytic reaction occurs on the surface. Therefore, the photocatalysts are usually used in the form of powders in order to increase the surface area. However, in this case, there emerges another problem that on the surface of small particles, the annihilation of electron-hole pairs is very fast, and they have no time to participate in the reaction. The high recombination rate of photogenerated electron and hole pairs in TiO₂ leads to a low quantum yield and poor photocatalytic activity. To circumvent the fast electron-hole annihilation, clusters of various substances are deposited on the TiO₂ grain surface. The clusters capture electrons and holes and hinder their annihilation. This process is schematically illustrated in Fig. 1.

We are exploring ways to improve the photocatalytic properties of titanium dioxide through the coating of TiO₂ nanoparticles by various metal clusters. In this work, preparation and characterization of pure and Ni-coated TiO₂ nanoparticles is reported and their photocatalytic activity under UV-vis light is investigated.

✉ D. Japaridze
davit.japaridze@tsu.ge

¹ Ivane Javakhishvili Tbilisi State University, Chavchavadze ave. 1, 0179 Tbilisi, Georgia

² Andronikashvili Institute of Physics, Ivane Javakhishvili Tbilisi State University, Tamarashvili Str. 6, 0177 Tbilisi, Georgia

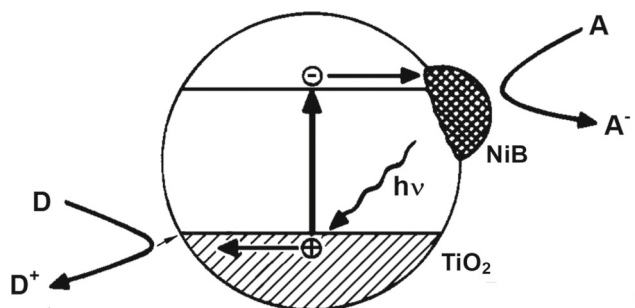


Fig. 1 Electron-hole pair production in cluster-deposited particles of TiO_2 powder under the effect of sunlight quanta and their interaction with surrounding molecules

2 Experimental

TiO_2 powder with grain size of ~ 200 nm was purchased from Sigma-Aldrich. TiO_2 nanopowder with mean grain of 25 nm was supplied by Degussa company. Nickel cluster-coated TiO_2 nanopowders were obtained by a novel technology of metallic cluster deposition on fine powders developed at the Andronikashvili Institute of Physics of Ivane Javakhishvili Tbilisi State University. The technology is electroless and inexpensive, it proceeds at low temperatures ($50\text{--}60^\circ\text{C}$), and hence does not lead to changes of the material to be coated nor of the material of clusters [6, 7]. According to this method, in order to obtain Ni nanopowder, the starting composition was as follows: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 30 g/l; $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ 40 g/l; ethylenediamine 5 g/l; NaOH 40 g/l, and regenerative NaBH_4 6 g/l. The excess amount of borohydride causes the solution to decay and metallic Ni precipitates in the solution. At the end of the process, the solution is transparent, which confirms the precipitation of the nickel from solution. The process runs at 60°C . To coat with Ni clusters, TiO_2 nanopowder was loaded into the previously prepared solution for chemical nickel plating without adding reducing agent. This mixture was processed with ultrasound of 40-W power during 20 min, and then was warmed up to 60°C under continuous stirring by a magnetic stirrer. As a next step, a reducing agent dissolved in 5–10 ml of distillate was added to this heated and homogeneous suspension. The process of nickel plating starts instantly and the start of the process is controlled by a stopwatch. The process of Ni coating can be stopped instantly at any moment of time by placing the suspension in a distillate with ice.

Magnetic properties of the Ni-coated TiO_2 nanopowders were measured by using vibrating sample magnetometer (VSM) (Cryogenic Limited, UK). The temperature dependence of magnetization in a zero field-cooled (ZFC) and field-cooled (FC) magnetic modes were measured in a magnetic field at 1000 Oe.

Optical absorption spectra of the distillate suspensions of the photocatalyst powders were measured. First, the light absorption of distilled water over the entire working spectral range was preliminarily studied. It appeared to be rather low.

However, in order to exclude the distortion of the absorption spectra of the powders under study as a result of the distillate effect, we recorded the absorption spectra of the powders dissolved in the distillate in reference to pure distillate. For this purpose, a cell with a solution of the powder under study was placed in one compartment of the 4-compartment spectrophotometer F-46 and an identical cell with pure distillate—in other compartment. To check the validity of the procedure, we prepared several similar reference aqueous suspensions of the same powder. Then their absorption curves were taken. The obtained spectra coincided very closely with the maximum difference of $\pm 5\%$.

EPR spectra were recorded by spectrometer EPR-V (Russia), with microwave frequency at 9.1 GHz and magnetic field modulation frequency at 100 KHz. Experiments were carried out with microwave power at 15 mW. The values of hyperfine splitting and g-factor were measured by means of EPR standard. As an EPR standard, the MgO doped with Mn^{2+} ions was used.

3 Results and Discussion

3.1 Magnetometry and Optical Spectroscopy Results

The results of magnetization measurements for two types of TiO_2/Ni nanopowders obtained as a result of TiO_2 nanopowder coating during 1 and 10 min are presented in Figs. 2 and 3.

Characteristic features of the magnetization data in Figs. 2 and 3 are the peaks on the ZFC magnetic moment temperature dependences. Such a peak is known to be

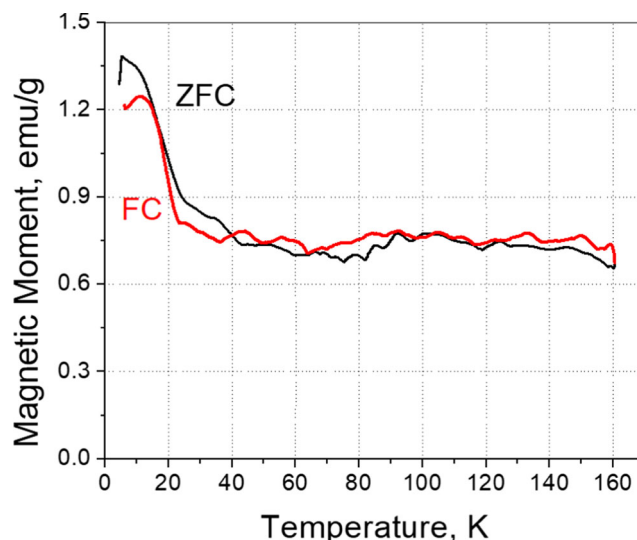


Fig. 2 Temperature dependence of zero field-cooled (ZFC) and field-cooled (FC) magnetic moments of anatase TiO_2 nanopowder coated by Ni clusters with the deposition time of 1 min in applied magnetic field at 1000 Oe

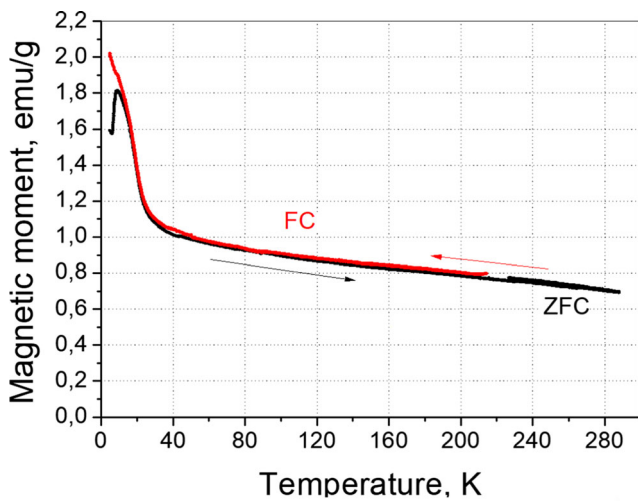


Fig. 3 Temperature dependence of zero field-cooled (ZFC) and field-cooled (FC) magnetic moments of anatase TiO_2 nanopowder coated by Ni clusters with the deposition time of 10 min in applied magnetic field at 1000 Oe

characteristic for the superparamagnetic particles and correspond to the so-called blocking temperature T_B , which characterizes the magnetic anisotropy energy of the particles [8]. Therefore, we conclude that obtained TiO_2 nanoparticles coated with Ni become superparamagnetic due to the presence of Ni clusters on the surface of TiO_2 . From the position of the ZFC peaks at 1000 Oe, the blocking temperatures T_B are about 6 and 9 K, for 1-min and 10-min coated samples, respectively. The size of Ni nanoparticles can be estimated from the observed blocking temperatures [9]. By taking $T_B = 6$ K and 9 K, we obtained the mean diameter of Ni clusters 7 nm and 8 nm for 1-min and 10-min coated samples, respectively.

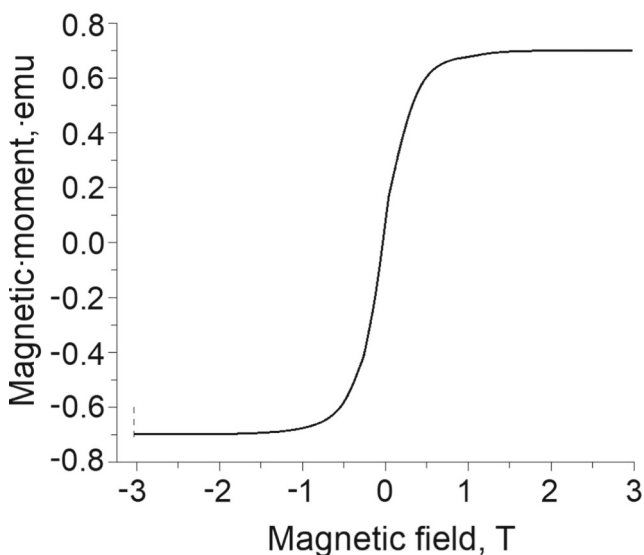


Fig. 4 M - H dependence of anatase TiO_2 nanopowder coated by Ni clusters measured at 260 K

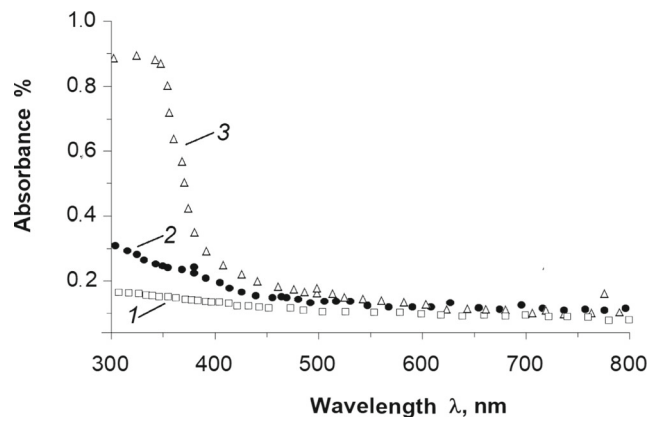


Fig. 5 Optical absorption spectra of TiO_2 powders before and after coating with Ni clusters. 1- TiO_2 (rutile) powder before coating with Ni clusters. 2- TiO_2 (anatase) powder before coating with Ni clusters. 3- TiO_2 (anatase) powder after coating with Ni clusters

The superparamagnetic behavior of TiO_2/Ni nanopowder is also confirmed by the absence of hysteresis in measured magnetic moment versus applied magnetic field M - H dependence shown in Fig. 4.

In order to characterize light absorption of the obtained TiO_2/Ni nanopowders, we took as starting materials two modifications of the TiO_2 , anatase, and rutile, with the grains ~ 200 nm in size. Their identical suspensions were prepared in distillate and optical absorption spectra were recorded over the wavelength range from 300 to 700 nm. Then, we deposited Ni clusters on the powders under study and measured again their absorption spectra over the same wavelength range. In Fig. 5, results of these experiments are shown. Points 1 correspond to the absorption spectrum of rutile modification of the TiO_2 powder before deposition of clusters. We observed that for this material optical absorption practically does not change after Ni clusters deposition and it is omitted. Points 2 correspond to the absorption spectrum of anatase modification of

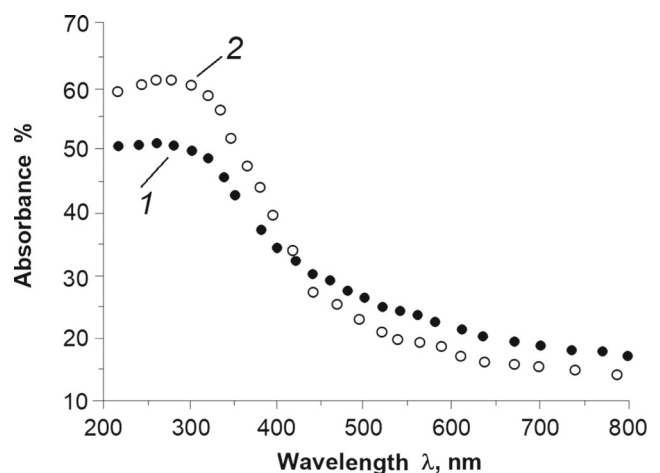
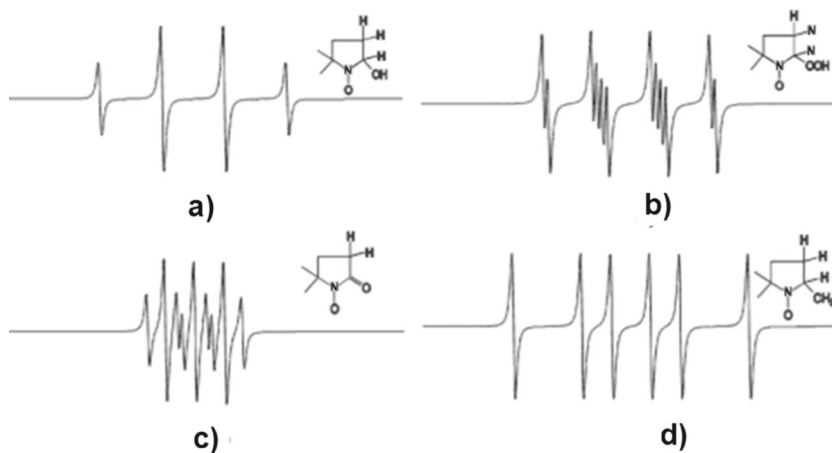


Fig. 6 Optical absorption spectra of Degussa P25 TiO_2 nanopowders before and after coating with Ni clusters. 1-P25 TiO_2 nanopowder before coating with Ni clusters. 2-P25 TiO_2 nanopowder after coating with Ni clusters

Fig. 7 EPR spectra from DMPO adducts resulted from the DMPO spin trap attached to the following radicals: (a) OH radical; (b) OOH radical; (c) oxygen radical; (d) methyl radical



the TiO_2 powder before deposition of clusters. After deposition of Ni clusters on TiO_2 powder with anatase structure, a strong increase of optical absorption was observed below about 600 nm as shown by points 3 in Fig. 5.

We also studied the effect of Ni clusters deposition on TiO_2 P25 nanopowders with mean grain size 25 nm produced by Degussa. This TiO_2 nanopowder contains 76% of anatase phase and 14% of rutile phase. Figure 6 shows optical absorption spectra of Degussa TiO_2 P25 nanopowders before and after coating with Ni clusters. As can be seen from Fig. 6, the optical absorption increases as a result of Ni clusters' deposition on TiO_2 P25 nanopowder below 400 nm.

3.2 EPR Study of Photocatalytic Activity of TiO_2/Ni Nanopowders

We applied electron paramagnetic resonance (EPR) spectroscopy to study the photocatalytic activity of TiO_2/Ni nanopowders [10]. EPR is a very sensitive microscopic technique to measure absorption of the microwaves by the paramagnetic species placed in an external magnetic field. Such kind of paramagnetic species are as follows: transition metal ions, triplet molecules, and free radicals, particles that consist of one or more of unpaired electrons. EPR allows not only to detect free radicals representing the products of photocatalytic

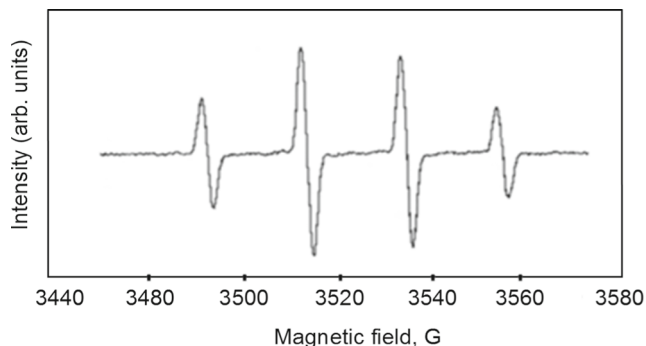


Fig. 8 EPR spectrum of the mixture $\text{TiO}_2 + \text{DMPO} + \text{H}_2\text{O}_2 + \text{buffer}$ irradiated by UV light during 2 min

activity, but also to study and describe their chemical nature, which enables us to determine the photocatalytic efficiency of the samples under study.

Usually free radicals, which are created during chemical reactions, such as atomic hydrogen, and superoxide oxygen radicals, have extremely short lifetimes. Their detection and investigation at room temperature are possible only by using the so-called spin trapping. The spin trap is a chemically synthesized molecule adducted to free radicals. The complex obtained as a result of capture of the free radical, the so-called adduct, is also a free radical. It has a much longer lifetime, which makes it possible to detect it with EPR and to study at room temperature. By measuring the EPR spectra of adducts attached to various radicals, we can reveal the chemical nature of the free radical and investigate its kinetics and formation energy.

One of the popular spin traps is 5,5-dimethyl-1-pyrroline N-oxide (DMPO). Examples of EPR spectra of the adducts obtained by trapping different radicals by DMPO are shown in Fig. 7.

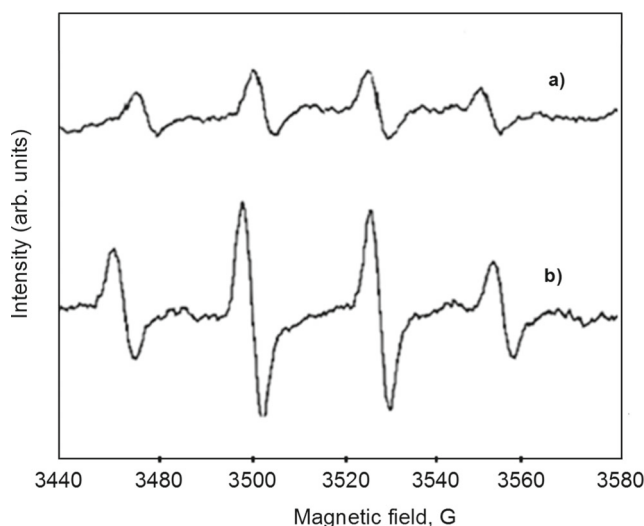


Fig. 9 EPR spectra of the mixtures irradiated by UV light during 2 min: (a) $\text{TiO}_2 + \text{DMPO} + \text{buffer}$ (pH 7.2); (b) $\text{TiO}_2\text{-P25} + \text{DMPO} + \text{buffer}$ (pH 7.2)

It is known that, in the presence of iron sulfate together with hydrogen peroxide in solution, the transfer of the electron from the ferrous iron ion onto the hydrogen peroxide surface takes place. As a result, hydrogen peroxide decomposes into a hydroxyl ion and a hydroxyl radical (Fenton's reaction). EPR signal of the hydroxyl radical generated by the DMPO spin trap with the ratio of hyperfine components 1:2:2:1 and spin-Hamiltonian parameters $a_N = 14.9$ and $a_H = 14.9$ is shown in Fig. 7a [11]. This method of obtaining the hydroxyl radical is

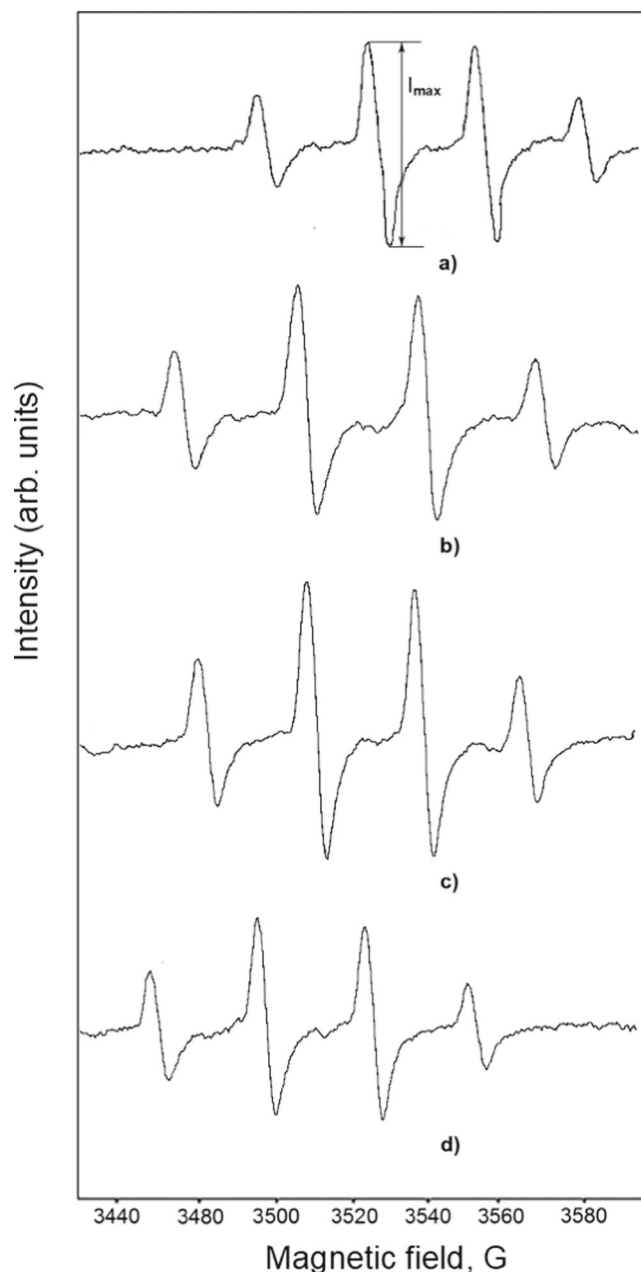


Fig. 10 EPR spectra of the mixtures irradiated by UV light during 2 min: (a) TiO_2 -P25 + DMPO + buffer (pH 7.2); (b) TiO_2/Ni -P25 + DMPO + buffer, deposition time $\tau = 15$ s; (c) TiO_2/Ni -P25 + DMPO + buffer, deposition time $\tau = 20$ s; (d) TiO_2/Ni -P25 + DMPO + buffer, deposition time $\tau = 25$ s

often used to measure the antioxidant activity of various compounds. In this work, we used TiO_2 instead of iron sulfate as an electron donor. By irradiating TiO_2 with ultraviolet (UV) light, we obtained the adduct spectrum 1:2:2:1 shown in Fig. 8. This means that the hydroxyl radical was attached to the spin trap, and the UV-irradiated TiO_2 was the electron donor.

At the next stage of the experiment, we excluded hydrogen peroxide from reactive substances. The reactive substances included TiO_2 (anatase)—DMPO—phosphate buffer (pH 7.2). This mixture was irradiated by UV light during 2 min. We obtained the spectrum similar to the one presented in Fig. 8, but with lower intensity (see Fig. 9a). When we used TiO_2 Degussa P25 (anatase 86%/rutile 14%), the spectrum intensity increased 3-fold as shown in Fig. 9b). This demonstrates the superior photocatalytic activity of Degussa P25 TiO_2 nanopowder compared to conventional TiO_2 powder.

Subsequent experiments involved the measurements of the photocatalytic activity of TiO_2 -P25 nanopowders coated with Ni during different deposition times and their comparison with the activity of TiO_2 -P25 nanopowders without Ni coating. Corresponding EPR spectra are presented in Fig. 10. It was found that the EPR signal amplitude is increasing in Ni-coated samples. However, as can be seen in Fig. 10, this increase depends on Ni coating time.

In Fig. 11, relative change of EPR signal intensity $\Delta I_{\text{rel}}(\%)$ $= \frac{I(\tau) - I(0)}{I(0)} \cdot 100\%$ in TiO_2/Ni -P25 + DMPO + buffer samples as a function of Ni deposition time is plotted. It shows that the EPR signal amplitude increases in Ni-coated nanopowders and the maximum intensity is obtained in a sample with a Ni deposition time 20 s. In this sample, EPR intensity is about 33% larger as compared to the sample without Ni coating. Therefore, one can conclude that the optimal Ni deposition time is 20 s. Obtained EPR spectra and their analysis show

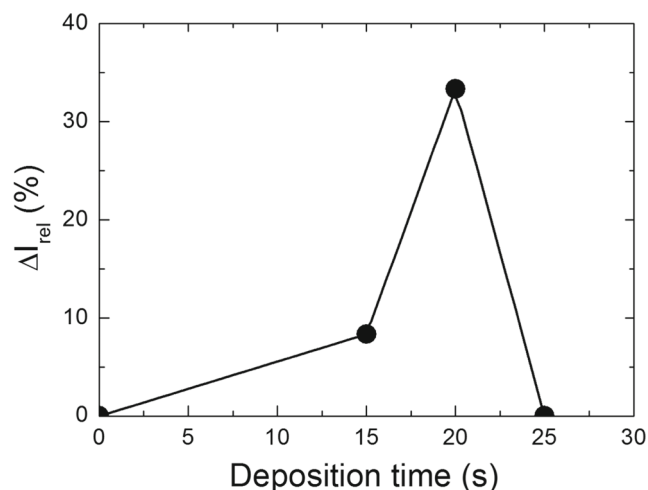


Fig. 11 Relative change of EPR signal intensity in TiO_2/Ni -P25 + DMPO + buffer samples as a function of Ni deposition time

that coating with Ni nanoclusters leads to substantial improvement of photocatalytic activity of TiO₂-P25 nanopowder in the UV light wavelength interval in agreement with the optical measurements.

4 Summary and Conclusions

In summary, TiO₂ powders coated with Ni nanoclusters with increased light absorption and enhanced photocatalytic activity were synthesized for the first time via an original facile electroless method. Magnetization measurements demonstrated the superparamagnetic behavior of obtained TiO₂/Ni powders. This confirms that indeed nanosized Ni clusters are deposited on the surface of TiO₂ grains. Optical spectroscopy measurements showed significant increase of light absorption in Ni-coated TiO₂ powders. Photocatalytic properties of TiO₂ powder were studied with EPR spectroscopy by using DMPO spin trap to detect hydroxyl radicals produced during UV irradiation. It was found that deposition of Ni nanoclusters on a TiO₂-P25 nanopowder provides best results and the optimal Ni deposition time was determined to be 20 s. The facile and fast method presented in the present work can be generally applied to coat different materials with transition metal nanoclusters to develop efficient sunlight-driven photocatalysts.

Funding This work was financially supported by the Shota Rustaveli National Science Foundation of Georgia under grant no. 216860.

References

1. Kaneko, M., Okura, I.: Photocatalysis science and technology, p. 29. Kodansha Springer, Tokyo (2002)
2. Panayotov, D.A., DeSario, P.A., Pietron, J.J., Brintlinger, T.H., Szymczak, L.C., Rolison, D.R., Morris, J.R.: *J. Phys. Chem. C*. **117**, 15035 (2013)
3. Navarro, R.M., Del Valle, F., de la Mano, J.V., Álvarez-Galván, M.C., Fierro, J.L.G.: *Adv. Chem. Eng.* **36**, 111 (2009)
4. Kudo, A., Miseki, Y.: *Chem. Soc. Rev.* **37**, 253 (2009)
5. Linsebigler, A.L., Lu, G., Yates Jr., J.T.: *Chem. Rev.* **95**, 735 (1995)
6. Khoperia, T.N., Zedginidze, T.I., Gegechkori, T.O.: *ECS Trans.* **25**, 97 (2010)
7. Khoperia, T., Mamniashvili, G., Nadareishvili, M., Zedginidze, T.: *ECS Trans.* **35**, 17 (2011)
8. Papaefthymiou, G.C.: *Nano Today*. **4**, 437 (2009)
9. Ay, F., Aktaş, B., Khaibullin, R.I., Nuzhdin, V.I., Rameev, B.Z.: *J. Magn. Magn. Mater.* **375**, 129 (2015)
10. Hurum, D.C., Agrios, A.G., Gray, K.A., Rajh, T., Thurnauer, M.C.: *J. Phys. Chem. B*. **107**, 4545 (2003)
11. Gunter, M.R., Tschirret-Guth, R.A., Witkowska, H.E., Fann, C.Y., Barr, R.D., Ortiz de Montellano, P.R., Mason, P.R.: *Biochem. J.* **330**, 1293 (1997)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.