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Tailoring Noble Metal-Free Ti@TiO₂ Photocatalyst for Boosting Photothermal Hydrogen Production

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10 **Keywords: photocatalysis, hydrogen, nanomaterials, titanium suboxide, sonohydrothermal**

11 **Abstract**

12 In this work, we provide new insights into the design of Ti@TiO₂ photocatalyst with enhanced
13 photothermal activity in the process of glycerol reforming. Ti@TiO₂ nanoparticles have been obtained
14 by sonohydrothermal treatment of titanium metal nanoparticles in pure water. Variation of
15 sonohydrothermal temperature allows controlling nanocrystalline TiO₂ shell on Ti⁰ surface. At
16 100<T<150°C formation of TiO₂ NPs occurs mostly by crystallization of Ti(IV) amorphous species
17 and oxidation of titanium suboxide Ti₃O presented at the surface of Ti⁰ nanoparticles. At T>150°C,
18 TiO₂ is also formed by oxidation of Ti⁰ with overheated water. Kinetic study highlights the importance
19 of TiO₂ nanocrystalline shell for H₂ generation. Electrochemical impedance spectroscopy points out
20 more efficient electron transfer for Ti@TiO₂ nanoparticles in correlation with photocatalytic data. The
21 apparent activation energy, E_a=(25-31)±5 kJ·mol⁻¹, assumes that photothermal effect arises from
22 diffusion of glycerol oxidation intermediates or from water dynamics at the surface of catalyst. Under
23 the heating, photocatalytic H₂ emission is observed even in pure water.

24 **INTRODUCTION**

25 Hydrogen is a clean fuel that, when consumed in a fuel cell, yields only water. Today, 95% of hydrogen
26 is produced from fossil fuels, such as natural gas and oil (Baykara, 2018). Conversion of solar energy
27 into hydrogen via photocatalytic splitting of water is an alternative sustainable process of paramount
28 interest for clean energy storage (Ma et al. 2014; Ghosh, 2018). In this view, preparation of stable and
29 nontoxic catalysts from non-precious elements showing high photocatalytic activity under solar light
30 irradiation is of great importance. Among a wide variety of catalysts, titanium oxide, TiO₂, has been
31 recognized as one of the most popular photocatalysts. However, TiO₂ can absorb only around 6% of
32 the sunlight, owing to a quite large bandgap of 3.2 eV for anatase phase (Ghosh, 2018). Another serious
33 bottleneck of TiO₂ is a rapid electron-hole recombination leading to the decrease in photocatalytic
34 activity. Therefore, tremendous efforts have been undertaken to narrow bandgap of TiO₂ and to
35 improve photogenerated charge separation. The recent advances in photocatalysis with TiO₂-based

36 materials pointed out several strategies of TiO₂ bandgap engineering: doping of TiO₂ with cations or
37 anions, codoping with cations and anions, self-doping of TiO₂ with Ti³⁺, and surface sensitization with
38 organic dyes or transition metal complexes (Ma et al. 2014). On the other hand, fabrication of TiO₂
39 heterojunctions with other semiconductors, anatase-rutile phase junctions, and TiO₂ loading with
40 cocatalysts, often noble metal nanoparticles, allows to minimize electron-hole recombination during
41 the photocatalytic process (Ghosh, 2018).

42 Design of catalyst morphology is another important strategy to reach maximal photocatalytic
43 activity. Core-shell nanoparticles have attracted a great deal of attention as promising photocatalysts
44 for hydrogen production due to the synergism between the cores and shells and/or new properties
45 providing by the interactions between the cores and shells (Gawande et al. 2015). Recently, we reported
46 strong photothermal effect in the process of photocatalytic hydrogen production from the aqueous
47 solutions of methanol and glycerol in the presence of noble metal-free Ti@TiO₂ core-shell
48 nanoparticles (NPs) (Nikitenko et al. 2015, Nikitenko et al. 2018). It is noteworthy that the combination
49 of photonic and thermal energy could be very beneficial for efficient solar energy harvesting (Ma et al.
50 2020). However, the mechanism of Ti@TiO₂ formation and the influence of TiO₂ nanocrystalline shell
51 on the photocatalytic performance have not been examined. In this work, we applied simultaneous
52 ultrasonic and hydrothermal treatment, called sonohydrothermal treatment (SHT), for the preparation
53 of Ti@TiO₂ NPs with controlled Ti/TiO₂ ratio. SHT is an emerging environmentally benign technique
54 effective for the synthesis of nanocrystalline materials with enhanced properties (Nikitenko et al. 2015,
55 Nikitenko et al. 2018, Cau et al. 2013). Glycerol reforming was used to evaluate the photothermal
56 performance of prepared Ti@TiO₂ NPs. Glycerol is a low-cost biomass derivative suitable for
57 hydrogen production (Shimura et al. 2011). Furthermore, quite high boiling point of glycerol (290°C)
58 allows to study the photothermal effect in a large temperature range. In addition, Ti@TiO₂ NPs have
59 been studied for the first time using electrochemical impedance spectroscopy (EIS). Combination of
60 characterization techniques and kinetic study provided new insights into the mechanism of hydrogen
61 formation and the origin of photothermal effect in studied system.

62 MATERIALS AND METHODS

63 *2.1. Catalyst preparation*

64 The commercially available titanium nanopowder (Nanostructured & Amorphous Materials, Inc. Ti,
65 99%) is an air-sensitive material and it was stored in the argon-filled glove box prior use. Stable
66 Ti@TiO₂ NPs were prepared by SHT treatment of Ti nanopowder in pure water (Milli-Q 18.2 MΩ·cm
67 at 25 °C). The SHT reactor is shown in **Supplementary Figure S1** and described previously (Nikitenko
68 et al. 2015; Nikitenko et al. 2018; Cau et al. 2013). In a typical experiment, 2 g of air passivated Ti
69 nanopowder was dispersed in 50 mL of water using ultrasonic bath, placed in SHT reactor and heated
70 at selected temperatures in the range of T = 100–214 °C (autogenic pressure P = 1.0–19.0 bar) under
71 simultaneous ultrasonic treatment (f = 20 kHz, P_{ac} = 17 W) for 3 hours. After cooling, the treated NPs
72 were recovered by centrifugation, washed with pure water and dried at room temperature under reduced
73 pressure.

74 *2.2. Catalyst characterization*

75 Powder X-Ray Diffraction (XRD) diagrams were recorded with the use of a Bruker D8 Advance X-
76 ray diffractometer equipped with a linear Lynx-eye detector (Cu Kα_{1,2} radiation, λ = 1.54184 Å). XRD
77 patterns were collected between 10° and 90° (θ-2θ mode) at room temperature, with a step size of Δ(2θ)
78 = 0.02° and a counting time of 1.8 s·step⁻¹. Quantitative phase analysis was performed by Rietveld

79 refinement with the phase detection limit about 5 % (León-Reina et al. 2016). High-resolution
80 transmission electron microscopic (HRTEM) and scanning transmission electron microscopic (STEM)
81 measurements coupled with EDX mapping (SDD Oxford detector) were performed using a Jeol
82 2200FS (200 kV) microscope. XPS analysis was achieved with an ESCALAB 250 Thermo Electron
83 device operated under ultra-high vacuum. The excitation source was a monochromatic source (Al-K α ,
84 $\epsilon = 1486.6$ eV) with a ca. 0.4 mm² X-ray spot. The pass energy was fixed at 20 eV. The photoelectron
85 spectra were calibrated using the Au 4f 7/2 (83.9 \pm 0.1 eV) and Cu 2p 3/2 (932.8 \pm 0.1 eV)
86 photoelectron lines. The XPS spectra were treated using AVANTAGE software. The binding energy
87 scale was established by referencing the adventitious C 1s peak at 284.8 eV. The reflectance spectra
88 were recorded in BaSO₄ pellets with a Shimadzu UV-3600 spectrophotometer. Thermogravimetric
89 analysis (TGA) was performed by means of TGA-DTA/DSC Setsys Evolution (Setaram
90 Instrumentation) device in air flow (900 °C, 10 °C·min⁻¹). The concentration of titanium species in
91 solution after photolysis was measured using SPECTRO ARCOS ICP-OES instrument (detection limit
92 \sim 0.1 ppm).

93 *2.3. Electrochemical measurements*

94 Electrochemical Impedance Spectroscopy (EIS) was studied at dark conditions in the frequency range
95 from 0.1 Hz to 100 kHz with an AC amplitude 10 mV. The electrolytic cell was filled with 1 M KOH
96 and bubbled with Ar for 20 minutes prior the measurements. Silver / silver chloride (Ag/AgCl) and
97 platinum (Pt) were used as the reference electrode and counter electrode, respectively. The working
98 electrode was prepared by ultrasonic dispersion of the synthesized photocatalyst (5 mg) in the mixture
99 of 1 mL isopropanol (VWR, \geq 99.7%) and 40 μ L Nafion (Aldrich, 5 wt% lower aliphatic alcohols, 15-
100 20% water). Then 5 μ L of the photocatalyst suspension was deposited onto glassy carbon electrode.

101 *2.4. Photothermal hydrogen formation*

102 The photocatalytic study was performed in aqueous glycerol (99 % Sigma-Aldrich) solutions using a
103 thermostated gas-flow cell made from a borosilicate glass and adapted to mass spectrometric analysis
104 of the outlet gases. The image of the photocatalytic cell is shown in **Supplementary Figure S2**. In a
105 typical run, 7.8 mg of photocatalyst was ultrasonically dispersed in 65 mL of aqueous glycerol solution
106 and placed into the photoreactor. Photolysis was carried out using a white light of ASB-XE-175W
107 xenon lamp equipped with ozone blocking coatings. The lamp was placed at 8 cm away from the
108 reactor and the light power at this distance was measured by X1-1 Optometer (Gigahertz-Optik) using
109 UV-3710-4 (300-420 nm) and RW-3705-4 (400-1100 nm) calibrated detectors. The obtained values of
110 light power were equal to 8.9 W and 0.6 W for vis/NIR and UV spectral ranges respectively, which
111 provides the close spectral match to solar spectra. The solutions inside the reactor were stirred
112 continuously and the temperature was gradually increased up to 95 °C during photolysis. The Ar gas
113 flow through the reactor was kept constant at 58 mL·min⁻¹ and controlled by a volumetric flowmeter.
114 The gaseous products in the outlet gas were analyzed using a Thermo Scientific PRIMA BT mass
115 spectrometer. The H₂ formation rate was quantified using external calibration curves prepared with
116 standard gas mixtures in argon (Messer). The water vapors were trapped with molecular sieve (Sigma-
117 Aldrich, 5 Å) prior to mass spectrometric analysis.

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120

121 **RESULTS AND DISCUSSION**122 **3.1. Morphological and structural studies**

123 TEM images depicted in **Figure 1A** reveal a quasi-spherical morphology of air passivated Ti particles
 124 with an average size of around 30-150 nm without any crystals at the surface. On the other hand, EDX
 125 mapping (**Figure 2A**) indicates the presence of oxygen-enriched layer at the surface of air-passivated
 126 Ti particles. This layer with a thickness about 11 nm is also clearly distinguishable in the HRTEM
 127 image of Ti NPs particles in **Figure 1A**. Sono-hydrothermal treatment leads to the formation of
 128 nanocrystalline shell composed of 10-20 nm oxygen-enriched particles, however, formed core-shell
 129 particles preserve quasi-spherical morphology as it is displayed in **Figures 1B,C and 2B**. We noticed
 130 that at the SHT temperature of about 100 °C only few nanocrystals are formed, nevertheless their
 131 amounts increase with the increase of SHT temperature. The average particle size increases on ca. 5-
 132 10 % after the coating with TiO₂ compared to initial Ti particles.

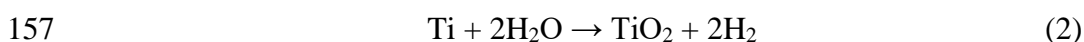
133 XRD diagram of air passivated Ti NPs in **Figure 3A** displays the patterns of metallic α -phase
 134 titanium (JCPDS 00-044-1294) with admixtures of tetragonal nonstoichiometric titanium hydride TiH_x
 135 ($x = 1.53 - 1.97$, JCPDS 01-079-6209) as it often observed in commercial titanium powders (Ageev et
 136 al. 1976). However, more thoughtful analysis of XRD data using Rietveld refinement revealed the
 137 presence of scarce Ti₃O suboxide with $P\bar{3}1c$ space group symmetry (Yamaguchi 1969). To the best of
 138 our knowledge, this is the first observation of Ti₃O phase at the nanoscale. It is worth noting that the
 139 XRD diagram of Ti NPs does not exhibit the presence of crystallized Ti(IV) oxides. The XRD data of
 140 the samples SHT treated at 164 °C and 214 °C clearly point out drop of Ti₃O content and formation of
 141 TiO₂ anatase (JCPDS 00-021-1272), which is in line with HRTEM observations (**Figure 1B**).

142 High-resolution Ti 2p XPS spectra shown in **Figure 4** were fitted using binding energies
 143 published in the NIST database (Wagner et al. 2003). The XPS spectrum of air passivated Ti NPs
 144 revealed the presence of Ti⁰ and lower oxidation states of titanium at the particle surface in agreement
 145 with the XRD analysis revealed the presence of titanium suboxide in Ti NPs. In contrast to XRD data,
 146 the XPS spectrum of Ti NPs also exhibits a signal typical for TiO₂ (**Figure 4A**). This discrepancy could
 147 be assigned to the formation of amorphous hydrated titanium oxide TiO₂·xH₂O at the surface of
 148 metallic titanium. SHT treatment causes disappearance of Ti⁰, TiO, Ti_xO_y and Ti₂O₃ peaks from the
 149 XPS spectrum and the experimental XPS spectrum of Ti@TiO₂ NPs can be fitted perfectly well by
 150 defect-free TiO₂ spectrum indicating effective coating of metallic titanium core (**Figure 4B**).

151 **Table 1** summarizes the phase compositions of initial Ti particles and prepared materials
 152 obtained from the Rietveld refinement of powder XRD data. One can conclude that air passivated Ti
 153 NPs are stable during the SHT treatment until ca. 100 °C. Further heating until ca. 150 °C causes
 154 oxidation of Ti₃O to TiO₂:



156 At higher temperature, metallic titanium is also oxidized yielding TiO₂:



158 According to the XPS data anatase nanocrystals at the surface of Ti NPs also can be formed by
 159 crystallization of TiO₂·xH₂O species. It is worth noting that SHT oxidation of Ti NPs is more effective
 160 than hydrothermal heating without ultrasound (**Table 1**), which was attributed to better heat and mass-
 161 transfer in the case of SHT process due to the acoustic cavitation, *i.e.* formation, nonlinear oscillations,

162 and implosion of microbubbles formed in the hydrothermal water under the effect of ultrasonic waves
163 (Cau et al. 2013). Results of TGA analysis displayed in **Supplementary Figure S4** and **Table 2** point
164 out the increase of titanium metallic core thermal stability with the increase of SHT temperature, which
165 is explained by the formation of protective TiO₂ shell. It should also be emphasized that the
166 hydrothermal oxidation of micrometric titanium powder begins at much higher temperature of about
167 450 °C (Yoshimura et al. 1989), which is most likely related to the particle size effect.

168 **3.2. Light absorption and charge transfer**

169 All Ti-based materials studied in this work have intense black color indicating extended photoresponse
170 with nearly full solar spectrum. The solid state reflectance spectra of both Ti and Ti@TiO₂ NPs (**Figure**
171 **5**) exhibit a broad band spanning from UV to NIR spectral range, which was attributed to intraband
172 and interband transitions of metallic Ti (Gawande et al. 2015; Nikitenko et al. 2015). In addition, the
173 spectra of Ti@TiO₂ NPs reveal an absorption band centered at 220-350 nm typical for the bandgap
174 transition of crystallized TiO₂. Kubelka-Munk treatment of the spectral data using $(F(R)hv)^{1/2}$ vs E
175 function (López et al. 2012) shown in **Supplementary Figure S5** gives a bandgap energy value of
176 3.52 and 3.51 eV for SHT 164 °C and SHT 214 °C respectively, which is slightly greater than the
177 bandgap energy reported for commercial anatase TiO₂ powder ($E = 3.26$ eV) (López et al. 2012). This
178 difference may originate from the overlap of Ti⁰ interband/intraband transitions and TiO₂ bandgap in
179 the UV spectral range (**Figure 5**). Kubelka-Munk treatment could lead to the overestimated value of
180 the bandgap energy in this case.

181 The electrochemical impedance spectroscopy (EIS) provides a valuable information about the
182 charge transfer and charge recombination processes at the interface of the catalysts and electrolytes
183 (Barsoukov et al. 2005). **Figure 6** shows the Nyquist plots and the proposed equivalent circuits of the
184 passivated Ti NPs and Ti@TiO₂ NPs obtained after SHT at 101 °C, 164 °C and 214 °C. The reduced
185 size of semicircles indicates a lower charge transfer resistance at the particle/electrolyte interface.
186 Surprisingly, Ti particles coated with TiO₂ nanocrystals exhibit more effective electron transfer than
187 air-passivated Ti NPs or Ti NPs treated at 101 °C with very low content of TiO₂ NPs at the Ti metal
188 surface. The resistances calculated for equivalent circuits are summarized in the **Table 3**. The R₁ refers
189 to the bulk resistance of electrodes and electrolytes, and R₂ represents the resistance at the interface of
190 the particles and electrolytes. A third resistance R₃ is only observed for Ti@TiO₂ NPs and is most
191 likely related to the second interface formed between TiO₂ nanoparticles from the shell and Ti⁰ core.
192 Interesting that R₃ increases with the temperature of SHT treatment, or, in other words, with the
193 increase of TiO₂ anatase content. High R₂ value (9.05 kΩ) for Ti⁰ NPs most probably is attributed to
194 the passivating layer at the metal surface leading to the hindering of charge transfer. Among Ti@TiO₂
195 NPs, the sample obtained at 214 °C displays the lowest R₂ value indicating the fastest charge transfer
196 rate for this material. This conclusion is in an agreement with an effective charge separation in
197 Ti@TiO₂ NPs recently demonstrated using photoluminescence spectroscopy (Nikitenko et al. 2018).

198 **3.3. Photocatalytic hydrogen production**

199 Typical hydrogen emission profiles and calculated H₂ yields for studied photocatalysts shown in
200 **Figure 7** highlight the crucial role of TiO₂ nanocrystalline shell in the reaction of photocatalytic
201 glycerol reforming. Kinetic data reveal a clear relationship between the temperature of SHT treatment,
202 or, in other words, between anatase content in Ti@TiO₂ NPs, and H₂ yield (**Figure 7B**). In addition,
203 photocatalytic activity correlates with EIS data exhibiting more effective charge transfer for SHT 214
204 °C NPs. The role of TiO₂ in the reaction mechanism can be understood in terms of the charge separation
205 between semiconducting TiO₂ shell and metallic Ti⁰ core. The optical spectra (**Figure 5**) show that the

206 incident light of the Xe lamp in UV/vis/NIR spectral range is mainly absorbed by Ti⁰ core. In
207 nonplasmonic metal, such as titanium, electron-hole pairs can be created by interband transitions via
208 nonradiative Landau damping mechanism (Kale et al. 2014). However, in a highly conducting, metallic
209 material, the electron-hole recombination would be extremely rapid in the absence of hole and/or
210 electron scavengers. Therefore, one might suggest that in Ti@TiO₂ core-shell NPs TiO₂ provides
211 effective charge separation, what was confirmed by fluorescence spectroscopy in previous study
212 (Nikitenko et al. 2018). In addition, TiO₂ can absorb at least part of the UV incident light followed by
213 electron-hole pairs generation in semiconducting particle. In this case, charge separation would be
214 provided by electron migration to Ti⁰ core, as it occurs in TiO₂ photocatalyst loaded with noble metal
215 nanoparticles (Ma et al. 2014, Ghosh 2018).

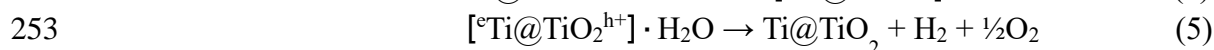
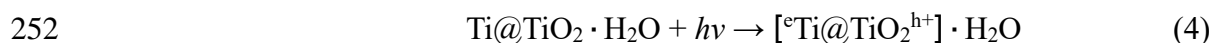
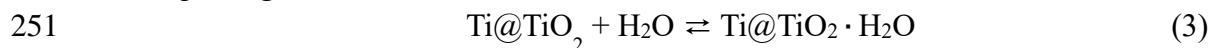
216 Furthermore, photocatalytic process with Ti@TiO₂ NPs exhibits strong photothermal effect in
217 an agreement with our previous results (Nikitenko et al. 2018). **Figure 7b** demonstrates that the yield
218 of H₂ increases in ca. 4 times when the bulk temperature increases from 37 °C to 95 °C. On the other
219 hand, in dark conditions formation of H₂ is not observed even at 95 °C indicating the photonic origin
220 of studied process. Kinetics of H₂ formation obeys an Arrhenius law (**Supplementary Figure S6**) and
221 the calculated apparent activation energy, E_{act}, for found to be equal to 31±5 and 25±5 kJ·mol⁻¹ for
222 SHT 164 °C and SHT 214 °C respectively. It is worth noting that these values are much lower than
223 the typical activation energy of chemical bonds and has been previously assigned to the diffusion of
224 intermediates at the catalyst surface (Nikitenko et al. 2018). Alternatively, the temperature dependence
225 of photocatalytic reactions can be also related to the dynamics of water adsorbed at the surface of the
226 catalyst (E_{act} = 16-21 kJ·mol⁻¹, Parrino et al. 2017).

227 **Figure 8** shows the influence of glycerol concentration on H₂ formation with the most active
228 SHT 214 °C Ti@TiO₂ photocatalyst. The yield of H₂ increases with the glycerol concentration and
229 then levels off at [Glycerol] ≥ 0.5 M in an agreement with Langmuir-type function indicating that the
230 mechanism of photocatalytic process involves glycerol adsorption at the active sites of the catalyst.
231 Similar behavior has been reported for photocatalytic glycerol reforming over Pt/TiO₂ (Jiang et al.
232 2015) and NiO/TiO₂ (Fujita et al. 2016) NPs. On the other hand, kinetics with Ti@TiO₂ NPs reveals
233 H₂ emission even from pure water at elevated temperature (**Supplementary Figure S7**). This
234 observation is largely in agreement with the above conclusion that both water and glycerol can
235 contribute to the observed photothermal effect.

236 Mass spectrometric measurements indicate the absence of CO₂ emissions (**Supplementary**
237 **Figure S8**) during the photothermal process with glycerol in consonance with our previous study
238 (Nikitenko et al. 2018). It is worth noting that photocatalytic glycerol reforming in the presence of
239 nanocrystalline P25 TiO₂ (83% of anatase and 17 % of rutile) leads to CO₂ and CO formation (Liu et
240 al. 2014), which implies a certain difference in reaction mechanisms with Ti@TiO₂ and TiO₂
241 photocatalysts. We found that in studied system H₂ formation is accompanied by acidification of
242 photolyte from pH=6 to pH=4 in a ca. 3 h of photolysis indicating formation of some acidic products
243 without decarboxylation. It has recently been suggested that glycerol is oxidized to glyceric acid in the
244 studied process (Nikitenko et al. 2018). In addition, it is known that the wet catalytic oxidation of
245 glycerol can also lead to the formation of other carboxylic acids without decarboxylation, such as
246 tartronic acid, mesoaxalic acid, and hydroxypyruvic acid (Worz et al. 2009).

247 On the basis of the above data, it can be concluded that the mechanism of H₂ formation in
248 studied system involves two reaction pathways illustrated in **Figure 9**: splitting of water molecules
249 (equations 3-5 presuming four-electron process) and glycerol reforming (equations 6-12):

250 *H₂O splitting:*

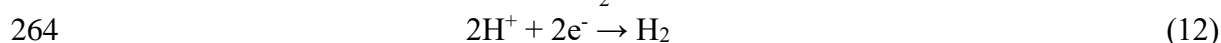
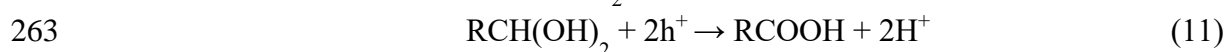
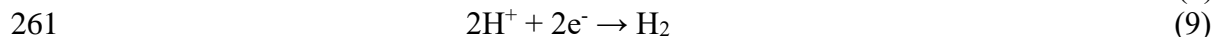
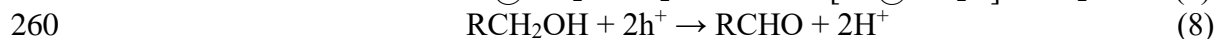
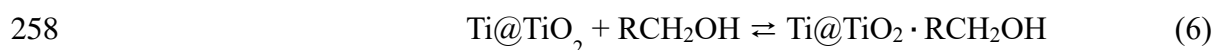


254

255

256 *Glycerol reforming:*

257



265

266 where RCOOH in the equation (11) could represent a mixture of mentioned above carboxylic acids. It
 267 is worth mentioning that the direct water splitting is practically observable at the sufficiently high
 268 temperature only. In general, higher yield of hydrogen for glycerol compared to water was attributed
 269 to more effective hole scavenging by glycerol than by water (Jiang et al. 2015, Tang et al. 2008). The
 270 link between surface charge carrier dynamics and photocatalytic activity of Ti@TiO₂ NPs is in line
 271 with this conclusion.

272 Finally, the stability of Ti@TiO₂ photocatalysts at studied conditions was tested using HRTEM
 273 and ICP-OES techniques. Modification of the particle's morphology was not detected by HRTEM after
 274 photothermal experiments as shown in **Supplementary Figure S9**. ICP-OES analysis has been
 275 performed with SPECTRO ARCOS instrument (detection limit of titanium was ca. 0.1 ppm). Particles
 276 of catalyst have been removed from the reaction mixture by filtration through 0.2 μm PTFE filter prior
 277 analysis. The ICP-OES analysis after 8 hours of photocatalytic experiments in hot 0.5M glycerol
 278 solutions revealed a leak of about 0.09 % and 0.29 % of titanium for SHT 214 °C and SHT 164 °C
 279 Ti@TiO₂ NPs respectively.

280

281 CONCLUSIONS

282 In summary, this work provides some new insights into the structure and thermally-assisted
 283 photocatalytic properties of Ti⁰ and Ti@TiO₂ nanoparticles. Rietveld refinement of XRD data revealed
 284 the presence of scarce titanium suboxide Ti₃O with a $P\bar{3}1c$ space group symmetry in raw α-Ti⁰ NPs.
 285 According to STEM/EDX study this species is situated at the surface of Ti⁰ NPs. Formation of the
 286 species with lower oxidation states of titanium was also observed by XPS spectroscopy. Our results
 287 confirm previous conclusion (Kornilov et al. 1970) about Ti₃O stability at room temperature.
 288 Sonohydrothermal synthesis allows to control nanocrystalline TiO₂ shell in Ti@TiO₂ NPs using pure
 289 water as a solvent. Mechanism of TiO₂ shell formation depends on the SHT temperature: in the
 290 temperature range 100-150 °C TiO₂ is formed mainly by the oxidation of Ti₃O, and oxidation of Ti⁰ to
 291 TiO₂ occurs at higher temperature. Coating of titanium metal nanoparticles with anatase nanocrystals

292 provides their better stability to oxidation and strong photothermal effect of hydrogen production from
293 aqueous glycerol solutions. In a hot water, photocatalytic formation of hydrogen is observed even
294 without glycerol. However, the yield of hydrogen in the presence of glycerol is higher than that in pure
295 water, which can be related to more effective scavenging of photogenerated holes with glycerol.
296 Glycerol reforming leading to hydrogen production is not accompanied by CO₂ emission in studied
297 system. The acidification of the photolyte solution implies that glycerol is oxidized to some acidic
298 products, most probably, to the mixture of organic acids derived from glycerol. The apparent activation
299 energy $E_{\text{act}} = (25-31) \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$ of studied process is much lower than the typical activation energy
300 of chemical bonds indicating that the origin of the photothermal effect is related to the diffusion of
301 intermediates arise from glycerol or from the dynamics of water adsorbed at the surface of the catalyst.

302 DATA AVAILABILITY STATEMENT

303 The original contributions presented in the study are included in the article/supplementary materials,
304 further inquiries can be directed to the corresponding author/s.

305 AUTHOR CONTRIBUTIONS

306 All authors contributed to this work. S. I. N. and S. R. conceived the study, S. I. N., S. R., T. C., and
307 S. E. H. prepared the manuscript, T. C. and S. E. H. prepared the samples and performed their
308 characterization, S. E. H. and S. I. N. performed photocatalytic experiments, A. A. N. and S. E. H.
309 performed electrochemical study. All authors approved the submitted version.

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394 TABLES

395 **Table 1.** Variation of Ti NPs composition with the temperature of SHT treatment obtained by Rietveld
 396 refinement of XRD patterns. Time of treatment was equal to 3 h.

Sample	mol.% ($\pm 5\%$)		
	Ti	Ti ₃ O	TiO ₂ anatase
Air passivated Ti*	86	14	--
SHT 101 °C	88	12	--
HT 150 °C **	88	5	7
SHT 164 °C	≥ 80.5	≤ 1.5	18
SHT 214 °C	≥ 62	≤ 3	35

397 *The admixture of TiH_x and amorphous TiO₂·xH₂O species were not
 398 taken into account. **HT stands for hydrothermal treatment without
 399 ultrasound. XRD and TEM data for these NPs are shown in
 400 **Supplementary Figure S3.**

401

402 **Table 2.** Thermal stability of Ti and Ti@TiO₂ NPs obtained from TGA analysis. T_{ox} indicates the
 403 beginning of metallic titanium core oxidation calculated as it shown in Supplementary Figure S4.

Sample	Air passivated Ti	SHT/101 °C	SHT/164 °C	SHT 214 °C
T _{ox} ± 10 °C	230	240	263	304

404

405 **Table 3.** EIS parameters for Ti and Ti@TiO₂ NPs.

Samples	R ₁ (Ω)	R ₂ (Ω)	R ₃ (k Ω)
Ti@TiO ₂ SHT 214 °C	59.95	7.96	5.44
Ti@TiO ₂ SHT 164 °C	48.63	22.85	7.67
Ti@TiO ₂ SHT 101 °C	42.06	34.03	9.12
Air passivated Ti NPs	49.84	9.05 (k Ω)	not been observed

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410 **FIGURE CAPTIONS**

411 **Figure 1.** Typical TEM images of initial Ti particles (**A**), SHT-treated particles in water at 101 °C (**B**)
412 and >150 °C (**C**). The distance of 0.35 nm corresponds to (101) plane of TiO₂ anatase.

413 **Figure 2.** STEM/EDX mapping of air passivated Ti⁰ NPs (**A**) and SHT-treated at 164 °C Ti@TiO₂
414 NPs (**B**), green dots – Ti, red dots - O.

415 **Figure 3.** XRD patterns of the initial Ti NPs and Ti@TiO₂ NPs treated at different temperatures under
416 SHT conditions (**A**). Zoom of the figure (**A**) in 39-41 2θ° range indicating the decrease in Ti₃O content
417 with increasing of SHT temperature (**B**). Example of Rietveld fit of the XRD diagram for Ti NPs in
418 39-41 2θ° range indicating the presence of Ti₃O phase (**C**), red line – Ti₃O, black line – α-Ti.

419 **Figure 4.** Fitted Ti 2p high-resolution XPS spectra of air-passivated Ti⁰ (**A**) and SHT/214 °C Ti@TiO₂
420 (**B**) NPs. Red line indicates experimental spectrum.

421 **Figure 5.** Solid-state reflectance spectra of Ti⁰ NPs before and after sonohydrothermal treatment at
422 different temperatures. The spectrum of Ti particles SHT treated at 101 °C is very similar to the
423 spectrum of air-passivated Ti⁰ particles reported recently (Nikitenko et al. 2015).

424 **Figure 6.** Nyquist plots for Ti⁰ NPs and Ti@TiO₂ NPs and the equivalent circuit for Ti⁰ (**A**) and
425 Ti@TiO₂ (**B**).

426
427 **Figure 7.** Typical hydrogen emission profiles with catalysts obtained at 101 °C, 164 °C and 214 °C
428 SHT temperatures in solutions of 0.5 M glycerol under Xe-lamp white light and Ar flow (**A**), and H₂
429 yields in 0.5 M glycerol solutions and pure water for SHT-214°C catalyst (**B**). The uncertainty for H₂
430 yields was estimated about 10-15 %.

431

432 **Figure 8.** Plot of the H₂ formation yields against glycerol concentrations over SHT 214 °C Ti@TiO₂
433 photocatalyst at 53 °C and 87 °C.

434

435 **Figure 9.** Graphical sketch of suggested mechanism of H₂ photocatalytic formation in the presence of
436 Ti@TiO₂ core-shell nanoparticles.

437 **Conflict of Interest:** The authors declare that the research was conducted in the absence of any
438 commercial or financial relationships that