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Copper-Modified Titania-Based Photocatalysts for the Efficient Hydrogen Production under UV and Visible Light from Aqueous Solutions of Glycerol

Anna Yu. Kurenkova 1, Anastasiya Yu. Yakovleva 1,2, Andrey A. Saraev 1, Evgeny Yu. Gerasimov 1, Ekaterina A. Kozlova 1,* and Vasily V. Kaichev 1

1 Federal Research Center, Boreskov Institute of Catalysis SB RAS, Lavrentieva Ave. 5, 630090 Novosibirsk, Russia
2 Department of Natural Science, Novosibirsk State University, Pirogova St. 1, 630090 Novosibirsk, Russia
* Correspondence: kozlova@catalysis.ru

Abstract: In this study, we have proposed titania-based photocatalysts modified with copper compounds for hydrogen evolution. Thermal pre-treatment of commercial TiO2 Degussa P25 (DTiO2) and Hombifine N (HTiO2) in the range from 600 to 800 ºC was carried out followed by the deposition of copper oxides (1–10 wt. % of Cu). The morphology and chemical state of synthesized photocatalysts were studied using X-ray diffraction, UV–Vis diffuse reflectance spectroscopy, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy, and XANES/EXAFS X-ray absorption spectroscopy. Photocatalytic activity was tested in the hydrogen evolution from aqueous solutions of glycerol under ultraviolet (λ = 381 nm) and visible (λ = 427 nm) light. The photocatalysts 2% CuO/DTiO2 T750 and 5% CuO/DTiO2 T700 showed the highest activity under UV irradiation (λ = 380 nm), with the rate of H2 evolution at the level of 2.5 mmol (H2) g−1 h−1. Under the visible light irradiation (λ = 427 nm), the highest activity of 0.6 mmol (H2) g−1 h−1 was achieved with the 5% CuO/DTiO2 T700 photocatalyst. The activity of these photocatalysts is 50% higher than that of the platinized 1% Pt/DTiO2 sample. Thus, it was shown for the first time that a simple heat treatment of a commercial titanium dioxide in combination with a deposition of non-noble metal particles led to a significant increase in the activity of photocatalysts and made it possible to obtain materials that were active in hydrogen production under visible light irradiation.

Keywords: photocatalysis; hydrogen evolution; titanium dioxide; anatase; rutile

1. Introduction

The use of hydrogen as an energy source makes it possible to solve many problems associated with environmental pollution. Currently, there are various industrial methods for producing hydrogen, such as steam reforming of natural gas, coal gasification, biomass processing, etc. [1]. Unfortunately, as a rule, these methods are energy-consuming and can be cost-effective only for large-scale production. Therefore, one of the promising methods of hydrogen production is the use of renewable energy sources, in particular its photocatalytic synthesis under the action of solar radiation. The photocatalytic production of hydrogen is also of interest because hydrogen can be produced from inexpensive raw materials: water and many organic compounds, e.g., ethanol, methanol, glycerol, sugars, or carboxylic acids [2].

The photocatalytic splitting of water using semiconductors as a photocatalyst was first described in 1972 [3], and this initiated the worldwide development of photocatalytic hydrogen production. However, photocatalytic water splitting is accompanied by the recombination of photogenerated charge carriers, which reduces the quantum efficiency of the process. An addition of various compounds as electron donors can hinder the recombination of electron–hole pairs formed in the photocatalytic process and makes it possible...
to obtain hydrogen without admixture of oxygen \([4,5]\). In addition, the use of organic compounds as the sacrificial agent is attractive from a practical point of view. Indeed, along with hydrogen production, it helps to solve important environmental problems associated with water purification from various organic pollutants \([6–9]\). Among the various organic substances used to produce hydrogen, glycerol is of particular interest \([10]\). Indeed, since glycerol is a by-product of the synthesis of biodiesel from vegetable oils, the growing production of biodiesel will induce an increase in the production of glycerol as well. Thus, the use of glycerol as an electron donor in photocatalytic systems can help reduce the cost of hydrogen production \([11,12]\).

The most common photocatalysts are semiconductors capable of absorbing light in the ultraviolet and visible regions. There are a number of different materials that can be used as the basis for photocatalysts for hydrogen production, and one of them is titanium dioxide \([13–17]\). This compound attracts special attention due to its stability under the action of light, availability, nontoxicity, and relatively low cost \([5]\). The band gap of TiO\(_2\) is 3.2 eV for the anatase phase and 3.0 eV for the rutile phase; therefore, TiO\(_2\) is photocatalytically active only under UV irradiation. Since UV radiation in sunlight constitutes only a small part (about 5%), it is necessary to increase the activity of TiO\(_2\) under visible light \([18]\). A common method here is to reduce the band gap. It can be achieved via several approaches, for example, by calcination of TiO\(_2\) at high temperatures and doping it with metals \([19–24]\). As a dopant, copper has attracted attention due to its high electron work function, which greatly improves the separation efficiency of photogenerated electrons and holes \([25–27]\). Copper oxides are promising cocatalysts in the processes under visible light irradiation, since both CuO and Cu\(_2\)O have a narrow band gap and absorb light in the visible region \([27,28]\).

The purpose of this work was to develop a method for the synthesis of photocatalysts based on TiO\(_2\) and copper compounds for the photocatalytic production of hydrogen under UV and visible irradiation. Photocatalysts with the composition of CuO\(_x\)/TiO\(_2\) (Degussa P25) and CuO\(_x\)/TiO\(_2\) (Hombifine N) were synthesized by the deposition of a cocatalyst on the surface of TiO\(_2\), which was preliminarily calcined at different temperatures. The catalysts were tested in the photocatalytic production of hydrogen from aqueous solutions of glycerol. The effects of calcination temperature and cocatalyst deposition on the activity in the target process were determined.

2. Materials and Methods

2.1. Reagents

The CuO\(_x\)/TiO\(_2\) catalysts were synthesized using the following reagents: Cu(NO\(_3\))\(_2\)·3H\(_2\)O (Acros Organics, 98%+, Geel, Belgium), H\(_2\)PtCl\(_6\)·6H\(_2\)O (Aurat, Pt 37.8%+, Moscow, Russia), NaBH\(_4\) (Acros Organics, 98%+, Geel, Belgium), Na\(_2\)S (Acros Organics, 60%+, Geel, Belgium), TiO\(_2\) Degussa (Evonik) P25 (Evonik Industries, Essen, Germany), and TiO\(_2\) Hombifine N (Sachtleben Chemie, Duisburg, Germany). Photocatalytic experiments were carried out using analytical-grade glycerol (Reakhim, Moscow, Russia).

2.2. Pretreatment of TiO\(_2\) Samples

The TiO\(_2\) samples were obtained using titanium dioxides of commercial grades, Degussa P25 and Hombifine N. For calcination, 500 mg of TiO\(_2\) was placed in a crucible and kept in a muffle furnace at a constant temperature (600–850 °C in increments of 50 °C) for 3 h.

2.3. Synthesis of Photocatalysts CuO\(_x\)/TiO\(_2\) and Pt/TiO\(_2\)

To obtain the photocatalysts with 1, 2, 5, and 10 wt. % of copper, TiO\(_2\) samples (495, 490, 475, and 450 mg, respectively) were impregnated with a proper amount of 0.1 M solution of Cu(NO\(_3\))\(_2\) under constant stirring for 40 min, and then an excess of a fresh 0.1 mol solution of NaBH\(_4\) was added and stirred for 1 h. The resulting suspension was washed and centrifuged 5 times and then dried in air at 50 °C for 5 h. To prepare a
1 wt. % Pt/TiO$_2$ sample, a TiO$_2$ sample (495 mg) was impregnated with a 0.2 M solution of H$_2$PtCl$_6$ and then reduced with NaBH$_4$ and then washed and dried in the same way as for photocatalysts with deposited copper.

In the case of using Hombifine N, the synthesized samples contained 1 wt. % and 5 wt. % Cu. In the case of using Degussa P25, the samples contained 1, 2, and 5 wt. % Cu. The obtained photocatalysts were labeled as y% CuO$_x$/DTiO$_2$ T or y% CuO$_x$/HTiO$_2$ T, where y corresponds to the weight content of copper, and T is the temperature of TiO$_2$ calcination, DTiO$_2$ denotes TiO$_2$ Degussa P25, and HTiO$_2$ denotes TiO$_2$ Hombifine N. For example, the label 5% CuO$_x$/DTiO$_2$ T700 denotes a TiO$_2$ Degussa P25 sample calcined at 700 °C and modified with copper with a calculated content of 5 wt. %. We decided to indicate the mass percentage of copper, because it was difficult to determine the stoichiometric composition of CuOx and accordingly calculate the content of copper oxide.

2.4. Sample Testing Methods
2.4.1. Physical Methods

The synthesized samples were characterized by X-ray diffraction (XRD), low-temperature nitrogen adsorption, diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HR TEM), and XANES/EXAFS X-ray absorption spectroscopy.

The phase composition of the photocatalysts was determined by XRD with a Bruker D8 Advance diffractometer (Bruker AXS GmbH, Ettlingen, Germany) using monochromatized Cu Kα radiation with a wavelength of 1.5418 Å. The crystal size (CS) was estimated as the coherent scattering domain size using the Scherrer formula. The specific surface area (SSA) and pore volume of the catalysts were obtained by low-temperature N$_2$ adsorption–desorption (N$_2$ adsorption at 77 K) using an ASAP 2400 apparatus (ASAP Industries Manufacturing, Houma, LA, USA). Their optical properties were studied by the DRS method. Diffuse reflection spectra in UV and visible regions were obtained using a Shimadzu UV-2501 PC spectrophotometer (Shimadzu, Kyoto, Japan) with an ISR-240A diffuse reflection attachment.

The chemical composition of the catalyst surface was studied by XPS with a photoelectron spectrometer (SPECS Surface Nano Analysis GmbH, Berlin, Germany) using non-monochromatized Al Kα radiation (hυ = 1486.6 eV). The spectrometer was equipped with a PHOIBOS-150 hemispherical analyzer (SPECS Surface Nano Analysis GmbH, Berlin, Germany) and an XR-50 X-ray source with a double Al/Mg anode. The charging effect was corrected using the binding energy of the Ti2p$^{3/2}$ peak at 459.0 eV.

The chemical state of copper in the bulk of the catalysts was studied using XANES X-ray absorption spectroscopy at the station of the Kurchatov Synchrotron Radiation Source (Moscow, Russia). The electron energy in the storage ring was 2.5 GeV at a beam current of 50–150 mA. To monochromatize synchrotron radiation, we used a silicon single crystal with (111) orientation in the form of a cut-out monoblock mounted on a goniometric head. The energy resolution achieved was ΔE/E = 2 × 10$^{-4}$. The X-ray absorption spectra of the catalysts were obtained in fluorescence geometry (a sample with 20% Cu was tested in the transmission mode). The X-ray beam intensity before and after passing through the sample was measured using ionization chambers equipped with Keithley 6487 digital picoameters.

The microstructure of the photocatalysts was studied by HRTEM using a ThemisZ electron microscope (Thermo Fisher Scientific, Waltham, MA, USA) at an accelerating voltage of 200 kV. The microscope was equipped with a SuperX energy-dispersive spectrometer and a spherical aberration corrector. The maximum resolution of the microscope was 0.06 nm. For the HR TEM analysis, the samples were ultrasonically dispersed onto perforated carbon substrates attached to aluminum grids.
2.4.2. Catalytic Tests

The photocatalytic activity of synthesized samples was determined using the setup shown in Figure 1. The setup consisted of a glass reactor with a quartz window ($S_{\text{window}} = 22 \text{ cm}^2$), an LED source of irradiation, and a magnetic stirrer.

![Figure 1](image-url)

**Figure 1.** (a) Spectra of LEDs with the wavelength at maximum intensity; (b) scheme of reaction set-up for photocatalytic study. 1—LED, 2—quartz window, 3—sampler, 4—reactor, 5—reaction mixture, 6—stir bar, 7—magnetic stirrer.

The reaction mixture consisted of a photocatalyst (50 mg) and a 2.8% aqueous solution of glycerol. The total volume of the suspension was 100 mL. Before the experiment, the reaction mixture was purged with Ar for 15 min to remove atmospheric oxygen. After the purge, either an LED-381 nm (for UV irradiation) or an LED-427 nm (for visible light irradiation) was turned on (Figure 1). Under irradiation of the photocatalyst, the reaction mixture evolved hydrogen. During the experiment, the gas phase (250 $\mu$L) was sampled with a gas syringe (Hamilton) every 15 min. The experiment lasted from 90 to 150 min, depending on the photocatalyst activity. The amount of hydrogen was determined using a Chromos GC-1000 chromatograph (Chromos, Moscow, Russia) with a thermal conductivity detector and with Ar as the carrier gas.

3. Results and Discussion

3.1. Physical Methods

3.1.1. XRD and BET Methods

The changes in the structure of TiO$_2$ during its calcination were studied by XRD. The X-ray diffraction patterns of the photocatalysts CuO$_x$/HTiO$_2$ with copper contents of 1 and 5 wt. % calcined at temperatures from 600 to 750 $^\circ$C are shown in Figure 2a. As can be seen, the patterns show only peaks due to the anatase phase with the addition of low-intensity peaks due to copper and copper oxides. Since there are no rutile peaks, it can be concluded that Hombifine N does not undergo any phase transformation at these calcination temperatures.

In contrast, the calcination of Degussa P25 leads to the phase transition of anatase to rutile. As seen from Table 1 and Figure 2b, the calcination of Degussa P25 at temperatures from 600 to 750 $^\circ$C leads to an increase in the rutile content, and starting from 800 $^\circ$C, the sample contains only the rutile phase. The textural characteristics of the Degussa P25 samples were determined using low-temperature nitrogen adsorption. As seen from Table 1, the specific surface area and pore volume of the uncalcined TiO$_2$ sample and the sample calcined at 600 $^\circ$C practically coincide, whereas the calcination at 700 $^\circ$C or 800 $^\circ$C leads to a significant decrease in the specific surface area and pore volume. Thus, the calcination of the commercial titanium dioxides at temperatures up to 600 $^\circ$C does not change the textural characteristics and phase composition of the samples.
Figure 2. XRD patterns of the samples based on (a) TiO$_2$ Hombifine N and (b) TiO$_2$ Degussa P25.

Table 1. Structural and textural characteristics of calcined Degussa P25 samples.

| No. | Sample     | Phase Composition, wt. % | CS, nm   | SSA, m$^2$ g$^{-1}$ | V, cm$^3$ g$^{-1}$ |
|-----|------------|--------------------------|----------|---------------------|-------------------|
| 1   | DTiO$_2$   | 85% (Anatase)/15% (Rutile) | 19/30    | 55                  | 0.48              |
| 2   | DTiO$_2$ 600 | 75% (Anatase)/25% (Rutile) | 21/40    | 55                  | 0.52              |
| 3   | DTiO$_2$ 650 | 68% (Anatase)/32% (Rutile) | 35/65    | 41                  | 0.16              |
| 4   | DTiO$_2$ 700 | 36% (Anatase)/63% (Rutile) | 45/85    | 19                  | 0.074             |
| 5   | DTiO$_2$ 750 | 5% (Anatase)/95% (Rutile)  | 62/>100  | 12                  | 0.046             |
| 6   | DTiO$_2$ 800 | 100% (Rutile)            | >100     | 10                  | 0.035             |
The XRD data imply that the thermal treatment of the photocatalysts based on Hombifine N could not lead to an increase in their photocatalytic activity (see below). The samples based on Degussa P25 were characterized in more detail.

3.1.2. UV–Vis Spectroscopy

The optical properties of uncalcined Degussa P25 and Degussa P25 calcined at temperatures from 650 to 750 °C were studied by DRS. It is found that the calcination of this TiO$_2$ shifts the absorption edge to the longer waves due to an increase in the content of rutile (Figure 3a), which is consistent with the XRD data.

| No. | Sample | Phase Composition, wt. % | CS, nm | SSA, m$^2$g$^{-1}$ | V, cm$^3$g$^{-1}$ |
|-----|--------|--------------------------|--------|------------------|-----------------|
| 1   | DTiO$_2$ | 85% (Anatase)/15% (Rutile) | 19/30 | 55   | 0.48             |
| 2   | DTiO$_2$ | 75% (Anatase)/25% (Rutile) | 21/40 | 55   | 0.52             |
| 3   | DTiO$_2$ | 68% (Anatase)/32% (Rutile) | 35/65 | 41   | 0.16             |
| 4   | DTiO$_2$ | 36% (Anatase)/63% (Rutile) | 45/85 | 19   | 0.074            |
| 5   | DTiO$_2$ | 5% (Anatase)/95% (Rutile)  | 62/>100| 12   | 0.046            |
| 6   | DTiO$_2$ | 100% (Rutile)             | >100  | 10   | 0.035            |

Figure 3. (a,c) Diffuse reflectance spectra of photocatalysts and (b,d) Tauc plots with tangent to graph (dotted line).

To determine the band gap, the absorption spectra were plotted in the Tauc coordinates (Figure 3b). First, the adsorption coefficient $F(R)$ was found from the DRS data according to the Kubelka–Munk Equation (1):

$$ F(R) = \frac{(1 - R)^2}{2R}, \quad (1) $$

where $R$ is the reflection coefficient of the sample. Then, the absorption curves were plotted in the Tauc coordinates for allowed indirect transitions. According to the calculated data, the calcination leads to a decrease in the band gap from 3.14 eV (for the uncalcined sample) to ca. 3.0 eV for the samples calcined at temperatures from 650 to 750 °C.

In addition, the DRS method was used to study the samples with deposited cocatalysts. As seen from Figure 3c, the addition of cocatalysts also enhances the absorption in the
visible region. In the case of Cu-containing catalysts, this effect is a result of the formation of copper oxides [29] (see the XPS and XANES results below).

3.1.3. XPS and XANES Methods

The surface of the samples CuO_x/DTiO_2 was characterized using the XPS method (Figure 4). There were two series of the samples: a series 5% CuO_x/DTiO_2 T (where T = 600, 650, 700, and 750 °C) and a series y % CuO_x/DTiO_2 T750 (where y = 1, 2, 5, and 10 wt. %). With their use, we studied how the mass fraction of the copper cocatalyst and the temperature of the Degussa P25 pre-calcination affect the properties of the photocatalyst.

Figure 4. XPS spectra of Cu2p (a) 5% CuO_x/DTiO_2 T600–T750; (b) (1–10)% CuO_x/DTiO_2 T750.

The Cu2p3/2 spectra of the catalysts show two symmetric peaks at 933.0–933.6 eV and 934.8–935.4 eV, respectively. The spectra also contain two shake-up satellites, which are related to the peak at 934.8–935.4 eV. These data indicate that the peak at 934.8–935.4 eV and its satellites belong to copper in the Cu2+ state (presumably in the composition of CuO), while the peak at 933.0–933.6 eV corresponds to copper in the state Cu0 or Cu1+. It should be noted that the Cu2p3/2 binding energies of the Cu1+ and Cu0 states are close; thus, the unambiguous identification of these states using XPS is complicated. However, as seen from Table 2, the predominant state of copper in the samples is Cu2+.

Table 2. Surface contents of atoms for the analyzed photocatalysts according to XPS data.

| No. | Sample              | [Cu]/[Ti] | [O]/[Ti] | Cu2+, % |
|-----|---------------------|-----------|----------|---------|
| 1   | 5% CuO_x/DTiO_2 T600 | 0.26      | 4.8      | 85      |
| 2   | 5% CuO_x/DTiO_2 T650 | 0.14      | 3.3      | 52      |
| 3   | 5% CuO_x/DTiO_2 T700 | 0.22      | 3.2      | 51      |
| 4   | 5% CuO_x/DTiO_2 T750 | 0.24      | 3.4      | 60      |
| 5   | 1% CuO_x/DTiO_2 T750 | 0.17      | 3.1      | 63      |
| 6   | 2% CuO_x/DTiO_2 T750 | 0.25      | 3.2      | 64      |
| 7   | 10% CuO_x/DTiO_2 T750| 0.48      | 3.7      | 64      |
Unfortunately, the XPS method does not provide unambiguous information on the state of copper; moreover, under conditions of an XPS experiment, Cu$^{2+}$ can be reduced to Cu$^{1+}$ under X-ray radiation. Therefore, to clarify the state of copper in the samples, they were studied by XANES (Figure 5). We tested the samples prepared based on DTiO$_2$ pretreatment at 750 °C. As a result, it was shown that Cu$^{2+}$ in the samples was in the form of Cu(OH)$_2$ and CuO. With an increase in the amount of copper, the percentage of Cu$^{2+}$ decreases, and the percentage of Cu$^{1+}$ in the form of Cu$_2$O increases (Table 3). In addition, an increase in the amount of copper leads to the appearance of copper in the metallic state. Its amount gradually increases and achieves the maximum in the sample 5% CuO$_x$/DTiO$_2$ T700.

![Figure 5. XANES spectra of the K-absorption edge of Cu (a) (1–10)% CuO$_x$/DTiO$_2$ T750; (b) 5% CuO$_x$/DTiO$_2$ T650–T750 in comparison with the spectra of metallic copper, Cu$_2$O, CuO, and Cu(OH)$_2$.](image)

Table 3. Phase composition of the samples according to the results of the linear combination fitting of Cu K-edge XANES spectra.

| No. | Sample                  | Cu$^{2+}$, % | Cu$^{1+}$, % | Cu$^0$, % |
|-----|-------------------------|--------------|--------------|-----------|
| 1   | 1% CuO$_x$/DTiO$_2$ T750| 85           | 15           | –         |
| 2   | 2% CuO$_x$/DTiO$_2$ T750| 49           | 42           | 8         |
| 3   | 5% CuO$_x$/DTiO$_2$ T750| 27           | 59           | 13        |
| 4   | 10% CuO$_x$/DTiO$_2$ T750| 12           | 54           | 35        |

At the Cu K-edge, the sample 1% Cu/DTiO$_2$ T750 has a broad intense peak in the region of 8996.2 eV, which is characteristic of copper in the Cu$^{2+}$ state. This state can exist in the form of Cu(OH)$_2$, Cu(NO$_3$)$_2$, and CuO nanoparticles; thus, a comparison with the reference spectra in this case does not allow an unambiguous conclusion about the
state of copper in this sample [30–32]. The spectra of other samples show a shoulder at the absorption edge in the region of 8981.2–8981.9 eV, which is characteristic of bulk CuO, Cu2O, and metallic copper. With an increase in the amount of deposited copper, its oxidation state decreases from Cu2+ to Cu0.

The spectra of the 5 wt. % CuOx/DTiO2 samples obtained at different calcination temperatures are similar. However, upon closer examination, it can be noted that the increase in the calcination temperature from 650 to 750 °C leads to the sharpening of both the peak and the shoulder. A sharper shoulder at the absorption edge is characteristic of copper in the form of Cu2O, and its appearance indicates that higher calcination temperatures facilitate the formation of this oxide. To clarify the chemical composition of the samples, their Cu K-edge XANES spectra were fitted by a linear combination of reference spectra in the energy range from −20 to 30 eV relative to the absorption edge (Figure 6).

Table 3 presents the results of the linear combination fitting (LCF). As seen, the sample with 1% Cu contains approximately half of the copper in the Cu2+ state in the form of Cu(OH)2, while the rest of the copper is in the form of CuO and Cu2O. As the amount of copper in the samples increases, the percentage of Cu2+ decreases and Cu1+ increases, so that for the samples 5–10% CuOx/DTiO2 T750, the percentage of Cu1+ achieves 50–60%. The percentage of copper in the metallic state also increases and achieves the maximum in the sample 10% CuOx/DTiO2 T750. Analyzing the state of copper in the 5 wt. % Cu sample, one can see that an increase in calcination temperature leads to an increase in the percentage of Cu1+ and a decrease in the percentage of Cu2+ and metallic Cu.

### 3.1.4. HR TEM Method

The samples 5 wt. % CuOx/DTiO2 (without calcination) and 5 wt. % CuOx/DTiO2 T700 were studied by HRTEM in the dark field mode (Figure 6), which provides high contrast images with the bright regions corresponding to heavier atoms. As seen from Figure 7, the particle size of copper in the sample 5 wt. % CuOx/DTiO2 is in a wide range from 1.5 to 5 nm, whereas the deposition of copper on calcined TiO2 facilitates the formation of Cu particles with a size of 1–2 nm. It can also be seen (Figure 7c) that in the sample
5 wt. % CuOₓ/DTiO₂, copper forms surface agglomerates, whereas in the sample 5 wt. % CuOₓ/DTiO₂ T700, it is uniformly distributed over the surface (Figure 7d). Probably, the uniform distribution of copper is a result of the following effect: the calcination of DTiO₂ leads to the formation of various defects that act as fixation centers for copper particles, thus preventing their agglomeration. Figure S1 (scale 1 µm) shows that the calcination at 700 °C leads to a growth of titanium dioxide particles, which completely confirms the XRD data.

Figure 7. HAADF STEM micrographs of (a) CuOₓ/DTiO₂ and (b) CuOₓ/DTiO₂ T700; EDX mapping of (c) CuOₓ/DTiO₂ and (d) CuOₓ/DTiO₂ T700.

Thus, the entire set of physicochemical methods demonstrates that the preliminary calcination of DTiO₂ significantly affects not only its structural and textural properties but also the state of the cocatalyst: the calcination of DTiO₂ at temperatures above 600 °C leads to a shift of the absorption edge to longer wavelengths and provides the uniform deposition of the cocatalyst on the DTiO₂ surface.

3.2. Kinetic Experiments
3.2.1. Activity of Photocatalysts under UV Irradiation

In these experiments, we studied how the kinetics and rate of photocatalytic hydrogen evolution depend on the amount of cocatalyst and the temperature of TiO₂ calcination (Figure 8).
As seen, in the series of HTiO₂ samples, the photocatalyst with 5 wt. % CuOₓ on uncalcined TiO₂ has the highest activity: the hydrogen evolution rate over it achieves 1.0 ± 0.1 mmol (H₂) g⁻¹ h⁻¹ (Figure 8a). In contrast, the catalysts based on calcined HTiO₂ show much lower activity (about 0.2–0.4 mmol (H₂) g⁻¹ h⁻¹). As noted above, the calcination of Hombifine N does not lead to the conversion of anatase to rutile, and as a result, the photocatalytic activity of the calcined samples is lower due to a decrease in their specific surface area and increase in crystallite size. The higher activity of the samples with the higher content of cocatalyst is caused by an increase in the efficiency of charge separation due to the transfer of photogenerated electrons between TiO₂ and copper compounds.

For the series of CuOₓ/DTiO₂ samples, the rates of hydrogen formation are significantly higher than in the previous case. At that, the reaction rate increases with an increase in the calcination temperature (Figure 8b). In contrast to the previous series, the calcination of TiO₂ at temperatures of 700–750 °C provides a significant increase in the activity of photocatalysts, while the further increase in the calcination temperature to 800 °C leads to the formation of less active photocatalysts. Indeed, the rate of hydrogen evolution over the uncalcined sample is 0.5 mmol (H₂) g⁻¹ h⁻¹, whereas the most active samples (2 wt. % CuOₓ/DTiO₂ T750 and 5 wt. % CuOₓ/DTiO₂ T700) provide the rates of 2.5 and 2.4 mmol (H₂) g⁻¹ h⁻¹, respectively. It should be noted that these rates, obtained under UV irradiation, are among the highest published for TiO₂-based systems (Table 4).

As shown in Section 3.1.3, the calcination of DTiO₂ leads to an increase in the amount of rutile and to a decrease in the sample surface area. Thus, based on the results of kinetic experiments, it can be concluded that, for the photocatalytic production of H₂, a decrease in the band gap of the photocatalyst is of crucial importance.
Table 4. Activity of photocatalysts based on TiO$_2$ in the formation of H$_2$ from aqueous solutions of alcohols.

| Photocatalyst       | Modification Method                              | Electron Donor | Radiation Source                        | $W$, $\mu$mol (H$_2$) g$^{-1}$ h$^{-1}$ | AQE, % | Ref |
|---------------------|--------------------------------------------------|----------------|-----------------------------------------|----------------------------------------|--------|-----|
| Fe/TiO$_2$          | Doping with metal atoms and deposition of metals | 10% Ethanol    | Xenon lamp, 500 W ($\lambda > 400$ nm)  | 248                                    | 0.1    | [22]|
| Ni/TiO$_2$          |                                                  |                |                                         | 205                                    |        |     |
| Ag/TiO$_2$          |                                                  |                |                                         | 265                                    |        |     |
| Fe-Ni/TiO$_2$       |                                                  |                |                                         | 348                                    |        |     |
| Fe/Ag/TiO$_2$       |                                                  |                |                                         | 512                                    |        |     |
| Ni/Ag/TiO$_2$       |                                                  |                |                                         | 336                                    |        |     |
| Fe-Ni/Ag/TiO$_2$    |                                                  |                |                                         | 793                                    | 0.2    |     |
| Cr-N@TiO$_2$        | Doping with non-metal atoms and metal cations    | 10% Glycerol   | Medium pressure mercury lamp, 450 W    | 126                                    |        | [24]|
| Co-N@TiO$_2$        |                                                  |                |                                         | 313                                    |        |     |
| Ni-N@TiO$_2$        |                                                  |                |                                         | 506                                    |        |     |
| Cu-N@TiO$_2$        |                                                  |                |                                         | 1615                                   |        |     |
| 1.5% Au@TiO$_2$     | Vacuum-assisted-impregnation route               | 25% Methanol   | Xenon lamp, 100 mW cm$^{-1}$ ($\lambda > 400$ nm) | 482                                    | 0.1    | [33]|
| 1.5% Au/TiO$_2$     | Vacuum-assisted-impregnation route               | 25% Methanol   | Xenon lamp, 100 mW cm$^{-1}$ ($\lambda > 400$ nm) | 223                                    |        |     |
| CuO$_x$ /TiO$_2$    | Surface deposition of metals                     | 0.5% Glycerol  | LED source, 30 W ($\lambda = 380$ nm)   | 550                                    |        | [12]|
| Pt/TiO$_2$          |                                                  |                |                                         | 1350                                   | -      |     |
| 80% Cu$_2$O/TiO$_2$ | Microemulsion method                             | 20% Methanol   | Xenon lamp                              | 215                                    |        |     |
| 60% Cu$_2$O/TiO$_2$ |                                                  |                |                                         | 892                                    |        |     |
| 40% Cu$_2$O/TiO$_2$ |                                                  |                |                                         | 1242                                   |        |     |
| 30% Cu$_2$O/TiO$_2$ |                                                  |                |                                         | 1388                                   |        | [34]|
| 20% Cu$_2$O/TiO$_2$ |                                                  |                |                                         | 1345                                   |        |     |
| TiO$_2$             |                                                  |                |                                         | 28                                     |        |     |
| Cu$_2$O             |                                                  |                |                                         | 3                                      |        |     |
| 2% Cu/TiO$_2$       | Impregnation reduction                            | 25% Methanol   | Xenon lamp                              | 5000                                   |        | [35]|
| 2% Ni/TiO$_2$       |                                                  |                |                                         | 2300                                   |        |     |
| 2% Co/TiO$_2$       |                                                  |                |                                         | 2250                                   |        |     |
| 2% Zn/TiO$_2$       |                                                  |                |                                         | 200                                    |        |     |
| 2% Cu/TiO$_2$       |                                                  |                |                                         | 220                                    |        |     |
| 2% Ni/TiO$_2$       |                                                  |                |                                         | 10                                     |        |     |
| 2% Co/TiO$_2$       |                                                  |                |                                         | 20                                     |        |     |
| 2% Zn/TiO$_2$       |                                                  |                |                                         | 11                                     |        |     |

3.2.2. Activity of Photocatalysts under Visible Light Irradiation

As noted, a significant part of the solar spectrum is represented by visible light. Therefore, it was of interest to study the activity of the synthesized catalysts under visible light irradiation (Figure 9).

The activities of all the photocatalysts are summarized in Table 5. As seen, the photocatalysts based on HTiO$_2$ are inactive under visible light. The activity of photocatalysts based on DTiO$_2$, as in the case of UV irradiation, significantly increases after calcination. The maximum activity of 0.6 ± 0.06 mmol (H$_2$) g$^{-1}$ h$^{-1}$ was achieved with the photocatalyst 5 wt. % CuO$_x$/DTiO$_2$ 700, as well as in the case of UV irradiation (Figure 8), while the activity of the uncalcined sample 1% CuO$_x$/DTiO$_2$ was close to zero, the same as for all samples calcined at 600. Note that the photocatalysts 5 wt. % CuO$_x$/DTiO$_2$ 700 demonstrate the activity that exceeds the activity of 1% Pt/DTiO$_2$ by 50%. Moreover, the obtained activity exceeds that for similar systems described in the literature (Table 4).
Figure 9. Rates of H₂ evolution over CuOₓ/DTiO₂. Conditions: m(cat.) = 50 mg, V = 100 mL, C₀(glycerol) = 0.38 M, λ = 427 nm.

The activities of all the photocatalysts are summarized in Table 5. As seen, the photocatalysts based on HTiO₂ are inactive under visible light. The activity of photocatalysts based on DTiO₂, as in the case of UV irradiation, significantly increases after calcination. The maximum activity of 0.6 ± 0.06 mmol (H₂) g⁻¹ h⁻¹ was achieved with the photocatalyst 5 wt. % CuOₓ/DTiO₂ 700, as well as in the case of UV irradiation (Figure 8), while the activity of the uncalcined sample 1% CuOₓ/DTiO₂ was close to zero, the same as for all samples calcined at 600. Note that the photocatalysts 5 wt. % CuOₓ/DTiO₂ 700 demonstrate the activity that exceeds the activity of 1% Pt/DTiO₂ by 50%. Moreover, the obtained activity exceeds that for similar systems described in the literature (Table 4).

Table 5. Activity of synthesized photocatalysts.

| No. | Sample                          | Catalytic Activity, mmol (H₂) g⁻¹ h⁻¹ | 381 nm | 427 nm |
|-----|---------------------------------|--------------------------------------|--------|--------|
|     |                                 |                                       |        |        |
| 1   | 1% CuOₓ/DTiO₂                   | 0.5 ± 0.05                           | 0      |        |
| 2   | 1% CuOₓ/DTiO₂ T600              | 0.6 ± 0.06                           |        | -      |
| 3   | 1% CuOₓ/DTiO₂ T650              | 1.0 ± 0.1                            | 0.2 ± 0.02|   |
| 4   | 1% CuOₓ/DTiO₂ T700              | 1.0 ± 0.1                            | 0.5 ± 0.05|   |
| 5   | 1% CuOₓ/DTiO₂ T750              | 1.3 ± 0.1                            | 0.5 ± 0.05|   |
| 6   | 2% CuOₓ/DTiO₂ T600              | 0.7 ± 0.07                           |        | —      |
| 7   | 2% CuOₓ/DTiO₂ T650              | 1.4 ± 0.1                            | 0.3 ± 0.03|   |
| 8   | 2% CuOₓ/DTiO₂ T700              | 2.0 ± 0.1                            | 0.5 ± 0.05|   |
| 9   | 2% CuOₓ/DTiO₂ T750              | 2.5 ± 0.25                           | 0.5 ± 0.05|   |
| 10  | 5% CuOₓ/DTiO₂ T600              | 0.6 ± 0.06                           |        | —      |
| 11  | 5% CuOₓ/DTiO₂ T650              | 1.6 ± 0.2                            | 0.1 ± 0.01|   |
| 12  | 5% CuOₓ/DTiO₂ T700              | 2.4 ± 0.2                            | 0.6 ± 0.06|   |
| 13  | 5% CuOₓ/DTiO₂ T750              | 2.2 ± 0.2                            | 0.4 ± 0.04|   |
| 14  | 10% CuOₓ/DTiO₂ T700             | 1.4 ± 0.1                            |        | —      |
| 15  | 10% CuOₓ/DTiO₂ T750             | 1.0 ± 0.1                            |        | —      |
| 16  | 5% CuOₓ/HTiO₂ T600              | 0.4 ± 0.04                           | —      | —      |
| 17  | 5% CuOₓ/HTiO₂ T650              | 0.4 ± 0.04                           | —      | —      |
| 18  | 5% CuOₓ/HTiO₂ T700              | 0.1 ± 0.01                           | —      | —      |
| 19  | 5% CuOₓ/HTiO₂ T750              | 0.2 ± 0.02                           | —      | —      |
| 20  | 1% CuOₓ/HTiO₂ T650              | 0.3 ± 0.03                           | —      | —      |
| 21  | 1% CuOₓ/HTiO₂ T700              | 0.2 ± 0.02                           | —      | —      |
| 22  | 1% CuOₓ/HTiO₂ T750              | 0.2 ± 0.02                           | —      | —      |

Cu/TiO₂ (Degussa P25)

Cu/TiO₂ (Hombifine N)
Therefore, the highest activity both under UV irradiation and visible light is shown by the sample 5 wt. % CuO$_x$/DTiO$_2$ 700. This fact can be explained by the optimal combination of the following factors:

- An increase in the absorption of the photocatalyst due to the shift in the absorption edge of DTiO$_2$ and the deposition of copper compounds as a cocatalyst;
- The optimal ratio of anatase and rutile phases for the formation of heterojunctions;
- The size of DTiO$_2$ particles after calcination at 700 °C does not increase as much as after calcination at higher temperatures;
- Deposition of Cu/CuO$_x$ on the surface of calcined DTiO$_2$ leads to a uniform distribution of small cocatalyst particles;
- The presence of copper in the composition of various compounds (Cu, Cu$_2$O, Cu(OH)$_2$) facilitates the formation of a complex set of photogenerated charge heterojunctions, which significantly increases the electron lifetime and process efficiency.

Thus, when light reaches the photocatalyst, an electron–hole pair is generated both on titanium dioxide and on copper compounds. The presence of copper in various states significantly increases the absorption of light by the photocatalyst in the visible region [35]. Depending on the mutual arrangement of copper particles, copper oxides, and titanium dioxide, various types of heterojunctions can be formed [36]. If metallic copper is located between the particles of titanium dioxide and copper oxide, the charge transfer Z-scheme is realized, and proton reduction occurs on the particles of Cu$_2$O. Electrons in the conduction band of Cu$_2$O have a significant reduction potential, which greatly accelerates the rate of photocatalytic hydrogen production [37].

4. Conclusions

Thus, a series of photocatalysts based on TiO$_2$ of commercial grades, Hombifine N (HTiO$_2$) and Degussa P25 (DTiO$_2$), modified with copper compounds such as Cu, Cu$_2$O, CuO, and Cu(OH)$_2$ was synthesized and characterized by a set of physicochemical methods. It has been shown that the calcination of DTiO$_2$ at temperatures above 600 °C leads to a significant increase in the amount of the rutile phase in the photocatalyst, a shift in the absorption edge, and a uniform distribution of cocatalyst particles on the TiO$_2$ surface. The calcination of Hombifine N does not lead to the transformation of anatase to rutile. It has been shown that an increase in the amount of rutile and the addition of copper in the Cu$^{2+}$ oxidation state increase the absorption of DTiO$_2$ photocatalysts in the visible region and accordingly provide their high activity under visible light irradiation.

The samples 2% CuO$_x$/DTiO$_2$ T750 and 5% CuO$_x$/DTiO$_2$ T700 showed the maximum activity under UV irradiation (380 nm) in obtaining hydrogen from aqueous solutions of glycerol, with the rate of H$_2$ evolution at the level of 2.5 mmol (H$_2$) g$^{-1}$ h$^{-1}$. Under the visible light irradiation (427 nm), the highest activity of 0.6 mmol (H$_2$) g$^{-1}$ h$^{-1}$ was achieved with the 5% CuO$_x$/DTiO$_2$ T700 photocatalyst. The activity of these photocatalysts is 50% higher than that of the platinized 1% Pt/DTiO$_2$ sample. The pre-calcination of Hombifine N does not lead to the enhancement of photocatalyst activity due to the absence of phase transformation. It has been shown that the presence of CuO increases the activity of the photocatalysts to the greatest extent, and the reduction of Cu$^{2+}$ to the Cu$^+$ or Cu$^0$ states leads to a slowdown of the H$_2$ evolution.

In general, it can be concluded that a simple heat treatment of a commercial titanium dioxide in combination with a deposition of non-noble metal particles (e.g., copper) leads to a significant increase in the activity of photocatalysts and makes it possible to obtain materials that are active in the formation of hydrogen under visible light irradiation.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12183106/s1, Figure S1: HAADF STEM micrographs of (a) CuO$_x$/DTiO$_2$ and (b) CuO$_x$/DTiO$_2$ T700.
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