

## Article

# Influence of Pt Oxidation State on the Activity and Selectivity of g-C<sub>3</sub>N<sub>4</sub>-Based Photocatalysts in H<sub>2</sub> Evolution Reaction

Anna Yu. Kurenkova <sup>1</sup>, Andrey A. Saraev <sup>1,2,\*</sup>, Denis D. Mishchenko <sup>1,2</sup>, Evgeny Yu. Gerasimov <sup>1</sup>  
and Ekaterina A. Kozlova <sup>1</sup>

<sup>1</sup> Federal Research Center, Boreskov Institute of Catalysis SB RAS, Lavrentieva Ave. 5, 630090 Novosibirsk, Russia; kurenkova@catalysis.ru (A.Y.K.); q14999@yandex.ru (D.D.M.); gerasimov@catalysis.ru (E.Y.G.); kozlova@catalysis.ru (E.A.K.)

<sup>2</sup> Synchrotron Radiation Facility SKIF, Boreskov Institute of Catalysis SB RAS, Nikol'skiy Ave. 1, 630559 Kol'tsovo, Russia

\* Correspondence: asaraev@catalysis.ru

**Abstract:** Graphitic carbon nitride g-C<sub>3</sub>N<sub>4</sub> has been modified using platinum and platinum oxide (0.5–5 wt.%) and studied in photocatalytic H<sub>2</sub> evolution reactions with ethanol aqueous solution under visible light irradiation ( $\lambda = 409$  nm). An analysis of the by-products of the reaction (CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> etc.) was also carried out. The morphology, particle size distribution, and optical properties of the photocatalysts, and the chemical states of platinum cations were examined using various methods. The photocatalysts were investigated using a wide range of methods to clarify the morphology, particle size distribution, optical properties, and the chemical states of platinum cations. Factors affecting not only the activity, but also the selectivity of the photocatalyst in the target process of hydrogen production, have been established. The highest rate of H<sub>2</sub> evolution achieved over 0.5 wt.% Pt/g-C<sub>3</sub>N<sub>4</sub> photocatalyst is 0.6 mmol h<sup>−1</sup> g<sup>−1</sup> (selectivity 98.9%), which exceeds the activity of pristine g-C<sub>3</sub>N<sub>4</sub> by 250 times. Increasing the Pt or PtO content up to 5 wt.% leads to an increase in the rate of formation of by-products (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and CO<sub>2</sub>) and a decrease in the selectivity of H<sub>2</sub> evolution. The study also delves into the role of platinum and the mechanism of charge transfer in PtO/g-C<sub>3</sub>N<sub>4</sub> and Pt/g-C<sub>3</sub>N<sub>4</sub> photocatalysts due to light irradiation.

**Keywords:** photocatalysis; photocatalytic H<sub>2</sub> evolution; g-C<sub>3</sub>N<sub>4</sub>; platinum; visible light; ethanol



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## 1. Introduction

The development of alternative energy sources is attracting considerable attention due to the growing demand for energy carriers, as well as the negative impact of greenhouse gases on the climate [1,2]. Hydrogen is one of the most promising energy carriers owing to its high calorific value, wide distribution, and absence of toxic products during combustion [3]. However, traditional methods for producing hydrogen are based on the use of fossil fuels, in particular natural gas [4]. The development of alternative methods of hydrogen production, using only renewable energy sources, will allow the transition to «green» hydrogen [5].

One of the most promising methods is the photocatalytic hydrogen evolution from aqueous solutions on semiconductor materials, since this technology allows one to convert the energy of sunlight into the energy of chemical bonds. Under the action of light irradiation with a certain wavelength, photogenerated charge carriers are formed in the semiconductor—an electron and a hole—and then participate in redox reactions on the surface of the semiconductor, which in this case is a photocatalyst [6–9]. The first semiconductor material used as a photocatalyst was titanium dioxide, and photocatalysts based on it are still widely used today, despite the wide band gap of TiO<sub>2</sub> (3.0–3.2 eV). Significant progress has been made in the field of materials for photocatalytic hydrogen production. Among others, photocatalysts with high activity under the action of visible radiation have

been developed: metal organic frameworks [10–12], metal sulfides [13–18], metal-doped perovskite [19,20], and (oxy)nitrides of Ti and Ta [21–23]. However, sulfides and nitrides tend to undergo photocorrosion and decrease in activity during long-term photocatalytic tests. At the same time, the synthesis of MOFs or the doping of perovskites is not always attractive for practical applications due to the complexity and cost of their synthesis.

A promising semiconductor material of interest to researchers is graphitic carbon nitride  $g\text{-C}_3\text{N}_4$  due to its band structure, stability, and lack of toxicity [24,25]. The narrow band gap (2.7 eV) provides  $g\text{-C}_3\text{N}_4$  with activity under visible light irradiation, which makes up a significant part of the solar spectrum [26–28]. Another advantage of  $g\text{-C}_3\text{N}_4$  is the strongly negative position of the conduction band (−1.3 V vs. NHE), which provides the significant reduction potential of photogenerated electrons [29,30]. Thus, the band structure of  $g\text{-C}_3\text{N}_4$  is favorable for the effective occurrence of reduction reactions under visible light. In addition,  $g\text{-C}_3\text{N}_4$  can be produced in one step from available precursors such as melamine, urea, and other nitrogen-containing organic compounds.

However, pristine  $g\text{-C}_3\text{N}_4$  has low activity in photocatalytic reactions due to the high rate of recombination of photogenerated electrons and holes, as well as poor adsorption of reagents on the photocatalyst surface [31]. The  $g\text{-C}_3\text{N}_4$  performance in the photocatalytic  $\text{H}_2$  evolution reaction can be improved in several ways. The change of morphology, leading to the breakage of interlayer hydrogen bonds, allows the lifetime of photogenerated charge carriers [32] to increase. The increased surface area allows more reactant to adsorb, which also increases the reaction rate [33]. The coating of the semiconductor surface with  $g\text{-C}_3\text{N}_4$  quantum dots allows the shortening of the distance for electrons and holes to migrate to the surface, reducing the rate of charge recombination [34].

A widely used method for modifying  $g\text{-C}_3\text{N}_4$  is the deposition of particles of metals or their compounds on the surface of the photocatalyst. Due to the spatial separation of charges occurring at the interface between a semiconductor and a metal, or between two different semiconductors, the lifetime of photogenerated electrons and holes increases significantly [35,36]. Platinum and its compounds are most often used as such cocatalysts in photocatalytic hydrogen evolution reactions [37–43]. It is known that platinum in the metallic state is the most active cocatalyst due to the high Schottky barrier, formed in this case at the metal–semiconductor interface [44]. This phenomenon allows platinum particles to act as effective traps of electrons, significantly increasing their lifetime and, consequently, the rate of hydrogen production. However, in the case of  $\text{H}_2$  evolution from solutions of organic compounds, for example, alcohols, it is important to monitor not only the rate of  $\text{H}_2$  formation, but also the formation rate of oxidation products of organic substrates in the gas phase.

Nevertheless, the selectivity of the  $\text{H}_2$  evolution process from aqueous solutions of organic substances is rarely studied [45], and the effect of the state of platinum on the activity and selectivity of the process has not been studied at all. At the same time, the influence of the oxidation state of platinum on the rate of photocatalytic destruction of dyes, as well as the oxidation of methanol, phenol and formic acid, has been shown in the literature, which confirms the significant influence of the state of platinum on photocatalytic processes [46,47].

In the current work, we have presented for the first time the effect of the platinum valence state on the activity and selectivity of  $g\text{-C}_3\text{N}_4$ -based photocatalysts in  $\text{H}_2$ 's evolution from ethanol aqueous solution under light irradiation (409 nm), and, therefore, reveal the key factors that determine the activity and selectivity of photocatalysts based on  $g\text{-C}_3\text{N}_4$  modified with Pt and  $\text{PtO}_x$ . The novelty of the study is provided by the establishment of correlations between the platinum oxidation state and the selectivity of the target process—hydrogen evolution from aqueous ethanol solution. The possibility of controlling the selectivity for  $\text{H}_2$  evolution over  $g\text{-C}_3\text{N}_4$ -based photocatalysts by changing the platinum state has been shown for the first time.

## 2. Materials and Methods

### 2.1. Photocatalyst Synthesis

Melamine was chosen as a precursor for the synthesis of g-C<sub>3</sub>N<sub>4</sub>. A sample of melamine (Sigma-Aldrich, St. Louis, MO, USA, 99%) was placed in a crucible and then in an oven at 500 °C for 2 h with a heating rate of 10° per minute. The obtained yellow powder was ground in a mortar and modified via a platinum or platinum oxide deposition method.

For the deposition of metallic platinum, the method of reduction of platinum ions with sodium borohydride was used. The required amount of 0.02 M aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> (Reakhim, Moscow, Russia, 98%) was added to a suspension of g-C<sub>3</sub>N<sub>4</sub> (300 mg) and stirred for 1 h; then, freshly prepared 0.1 M solution of NaBH<sub>4</sub> (Acros Organics, Geel, Belgium, 99%) was added and the resulting suspension was stirred for 1 h. The Pt/TiO<sub>2</sub> photocatalyst thus obtained was washed several times with distilled water and dried in air at 60 °C for 5 h.

For PtO deposition, 300 mg of g-C<sub>3</sub>N<sub>4</sub> was added to 20% ethanol aqueous solution in a photocatalytic reactor. Then, the reactor with the obtained suspension was purged with argon to remove oxygen for 30 min, and kept under a 380-nm LED (30 V, 1 A) for 3 h. The obtained powder was washed several times with distilled water and dried in air at 60 °C for 5 h.

The amount of deposited Pt or PtO on g-C<sub>3</sub>N<sub>4</sub> was 0.5, 2, and 5 wt.%.

### 2.2. Photocatalyst Characterization

The photocatalysts were characterized via X-ray diffraction (XRD), UV-vis spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy, and high-resolution transmission electron microscopy (HR TEM), including the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) technique.

The chemical state of cations and surface composition of the catalyst were studied via XPS using a photoelectron spectrometer (SPECS Surface Nano Analysis GmbH, Berlin, Germany) using non-monochromatized Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV). The spectrometer was equipped with a PHOIBOS-150 hemispherical analyzer and an XR-50 X-ray source with a double Al/Mg anode. The calibration of the binding energy scale was performed by setting the C 1s peak at 288.1 eV, which corresponded to carbon in the g-C<sub>3</sub>N<sub>4</sub>.

The chemical state of platinum in the bulk of the catalysts was studied via X-ray absorption spectroscopy at the EXAFS spectroscopy beamline of Siberian Synchrotron and Terahertz Radiation Center (SSTRC, Budker Institute of Nuclear Physics, Novosibirsk, Russia). The X-ray absorption near-edge structure (XANES) spectra of Pt L<sub>3</sub>-edge were recorded via transmission geometry. Energy calibration was performed using the first inflection point in the Pt L<sub>3</sub>-edge spectrum of Pt foil at 11,564 eV. The spectra were processed using standard procedures for subtracting the background and normalizing to the magnitude of the L<sub>3</sub>-absorption edge jump using the DEMETER 0.9.25 software package [48].

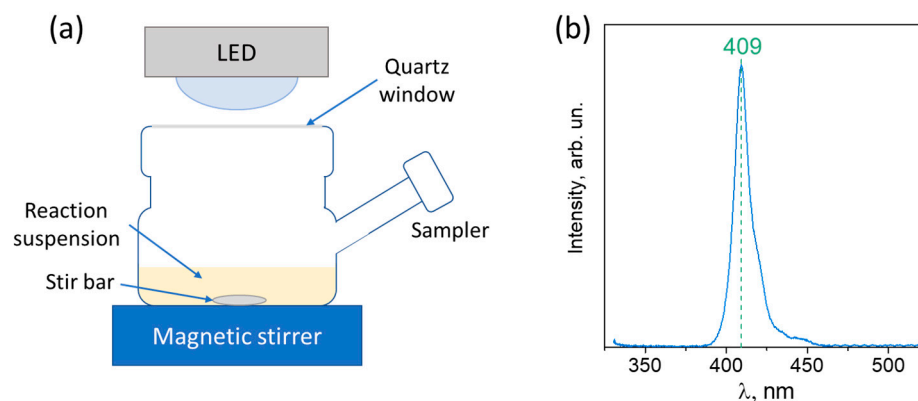
The morphology of the photocatalysts was studied via HR TEM using a ThemisZ electron microscope (Thermo Fisher Scientific, Waltham, MA, USA) at an accelerating voltage of 200 kV. The microscope was equipped with a SuperX energy-dispersive spectrometer and a spherical aberration corrector. The maximum 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.

The diffuse reflectance UV-vis spectra were measured using a UV-2501 PC spectrophotometer with an ISR-240A diffuse reflectance unit (Shimadzu, Kyoto, Japan).

The X-ray diffraction pattern was recorded using a D8 ADVANCE diffractometer equipped with a LYNXEYE linear detector (Bruker AXS GmbH, Karlsruhe, Germany). The diffraction patterns were obtained at room temperature in the 2 $\theta$  range from 10 to 70° with a step of 0.05° using Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å).

### 2.3. Photocatalytic Activity Test

The activity of photocatalysts was tested in  $H_2$  evolution reactions in a batch reactor using ethanol as a substrate (Figure 1a). The reactor with an aqueous suspension ( $V = 50$  mL) containing 20% ethanol aqueous solution and 30 mg of photocatalyst was ultrasonicated for 10 min and then purged with argon for 30 min to remove oxygen. After that, the suspension was irradiated with an LED with a maximum intensity at a wavelength of 409 nm (power density  $70 \text{ mW} \cdot \text{cm}^{-2}$ ) through a quartz window ( $S = 21 \text{ cm}^2$ ). The emission spectrum of the diode is shown in Figure 1b.



**Figure 1.** (a) Scheme of reactor for photocatalytic study; (b) spectrum of LED with the wavelength at maximum intensity.

The gas probe was analyzed with a gas chromatograph “GH-1000” (Chromos, Moscow, Russia) equipped with a flame ionization detector and thermal conductivity detector to identify the products of C1-C2 and  $H_2$ , respectively. Argon was used as a carrier gas. The hydrogen formation rate was determined using a linear fitting of the dependence of the hydrogen amount on time (a 60 min interval was used).

The selectivity of  $H_2$  evolution was defined as

$$S(H_2) = \frac{n(H_2)}{n(CO_2) + n(CO) + n(CH_4) + n(C_2H_4) + n(C_2H_6) + n(H_2)} \times 100\% \quad (1)$$

where  $n$  is amount of compound,  $\mu\text{mol}$ .

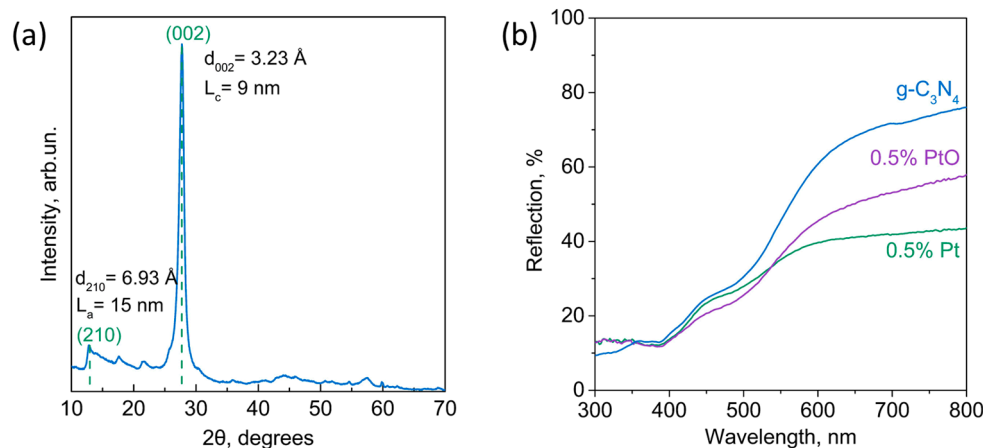
## 3. Results and Discussion

In this work, a series of Pt/g- $C_3N_4$  and PtO/g- $C_3N_4$  photocatalysts with different mass contents of cocatalyst (Pt, PtO) were synthesized. The structure of g- $C_3N_4$  obtained from melamine was examined via XRD. Due to the low content (0.5%) and small particle size, the state of the metal platinum and platinum oxide cocatalysts was investigated using XPS and XANES methods. The activity of photocatalysts was studied in the reaction of  $H_2$  production from an aqueous solution of ethanol under visible light irradiation (409 nm). In addition, an analysis of reaction by-products ( $CO$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ) in the gas phase was carried out to estimate the selectivity of the target process of  $H_2$  evolution.

### 3.1. Photocatalyst Characterization

The synthesized g- $C_3N_4$  was characterized via X-ray diffraction to confirm the structure of the obtained material (Figure 2a). One can see in the diffraction pattern of g- $C_3N_4$  two main peaks at  $\approx 12.8^\circ$  and  $\approx 27.7^\circ$ , corresponding to intraplanar and interplanar distances of g- $C_3N_4$ , respectively. Based on the presence of additional peaks at  $\approx 17.7^\circ$  and  $\approx 21.7^\circ$ , the structure was indexed in the orthorhombic  $P2_12_12$  cell. Interplanar distances  $d_{002} = 3.23 \text{ \AA}$  and  $d_{210} = 6.93 \text{ \AA}$  are in accordance with the literature data [49,50]. The 5% Pt/g- $C_3N_4$  and 5% PtO/g- $C_3N_4$  photocatalysts were also characterized via XRD (Figure S1). The formation of platinum metal particles was confirmed for the photocatalyst prepared via

the chemical reduction method. No peaks related to platinum or its oxide are observed in the XRD of the photocatalyst 5% PtO/g-C<sub>3</sub>N<sub>4</sub>, confirming the partial reduction of platinum ions. It is known that platinum oxide is generally poorly crystallized and hardly seen via XRD [51,52].



**Figure 2.** (a) XRD pattern of synthesized g-C<sub>3</sub>N<sub>4</sub>,  $L_a$ —average crystallite size in the plane of the layer calculated using the Scherrer equation;  $L_c$ —average crystallite size in the direction perpendicular to the layer calculated using the Scherrer equation; (b) diffuse reflectance spectra of g-C<sub>3</sub>N<sub>4</sub>, 0.5% Pt/g-C<sub>3</sub>N<sub>4</sub>, and 0.5% PtO/g-C<sub>3</sub>N<sub>4</sub>.

The diffuse reflectance spectra are presented in Figure 2b. One can see that the platinum deposition leads to an increase in light absorption beyond the 450 nm region. The increase in light absorbance is due to the surface plasmon resonance of Pt nanoparticles. The shift in the absorption edge leads to a broadening of the action spectrum of the photocatalyst to the visible light. The obtained band gap value of g-C<sub>3</sub>N<sub>4</sub> (2.7 eV) agrees well with the literature data (Figure S2).

To confirm the formation of metallic platinum or PtO nanoparticles, we applied a combination of surface- and volume-sensitive methods—XPS and XANES spectroscopy. The Pt 4f core-level spectra of 0.5% Pt/g-C<sub>3</sub>N<sub>4</sub>, and 0.5% PtO/g-C<sub>3</sub>N<sub>4</sub> are presented at Figure 3a. One can see that the Pt4f core-level spectrum of 0.5% Pt/g-C<sub>3</sub>N<sub>4</sub> could be well fitted by one Pt 4f<sub>7/2</sub>-Pt 4f<sub>5/2</sub> doublet with a Pt 4f<sub>7/2</sub>-binding energy of 70.7 eV. In the case of 0.5% PtO/g-C<sub>3</sub>N<sub>4</sub>, the Pt4f core-level spectrum of 0.5% Pt/g-C<sub>3</sub>N<sub>4</sub> is fitted by one Pt 4f<sub>7/2</sub>-Pt 4f<sub>5/2</sub> doublet with a Pt 4f<sub>7/2</sub>-binding energy of 72.9 eV. According to the literature data, the peak at 70.7 eV could be attributed to the platinum in the metallic state, and the peak at the higher binding energy (72.9 eV) to the platinum in the oxidized state, Pt<sup>2+</sup> in PtO [40,53–55]. The surface atomic ratios [Pt]/[C<sub>3</sub>N<sub>4</sub>] for 0.5% Pt/g-C<sub>3</sub>N<sub>4</sub> and 0.5% PtO/g-C<sub>3</sub>N<sub>4</sub> are equal to 0.002 and 0.005 (Table 1). The observed difference in the surface ratios could be due to the formation of larger metallic platinum nanoparticles more than the deposition of PtO nanoparticles, which will be further confirmed via TEM.

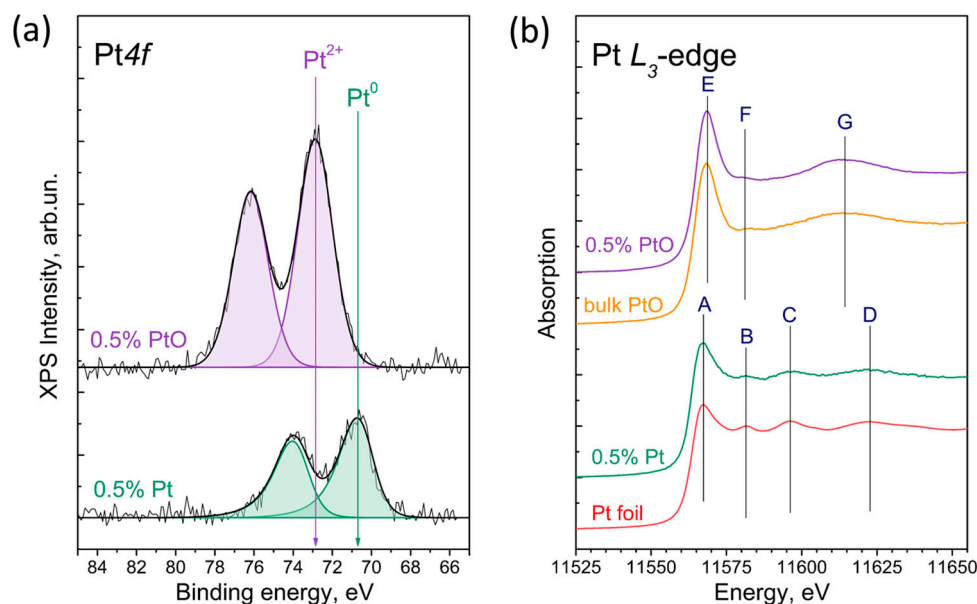
**Table 1.** Results of XPS study of the cocatalyst in 0.5% Pt/g-C<sub>3</sub>N<sub>4</sub> and 0.5% PtO/g-C<sub>3</sub>N<sub>4</sub>.

| Photocatalyst                            | [Pt]/[C <sub>3</sub> N <sub>4</sub> ] | Pt4f Binding Energy, eV | Pt <sup>0</sup> , % |
|------------------------------------------|---------------------------------------|-------------------------|---------------------|
| 0.5% Pt/g-C <sub>3</sub> N <sub>4</sub>  | 0.002                                 | 70.7                    | 100                 |
| 0.5% PtO/g-C <sub>3</sub> N <sub>4</sub> | 0.005                                 | 72.9                    | 0                   |

As mentioned above, an X-ray absorption spectroscopy allowed us to clarify the volume chemical state of the platinum nanoparticles deposited on g-C<sub>3</sub>N<sub>4</sub>. The XANES spectra of the Pt L<sub>3</sub>-edges of the 0.5%Pt/g-C<sub>3</sub>N<sub>4</sub> and 0.5% PtO/g-C<sub>3</sub>N<sub>4</sub> are presented in Figure 3b. It can be seen that the XANES spectra of the Pt L<sub>3</sub>-edge of 0.5%Pt/g-C<sub>3</sub>N<sub>4</sub> differs from that of 0.5% PtO/g-C<sub>3</sub>N<sub>4</sub>, but has features (peaks A-D) similar to those of



platinum in the metallic state (Pt foil). Thus, the XPS and XAS studies establish that in the case of 0.5%Pt/g-C<sub>3</sub>N<sub>4</sub>, the platinum nanoparticles are metallic and do not have a core-shell structure. At the same time, the spectrum of the Pt L<sub>3</sub>-edge of 0.5% PtO/g-C<sub>3</sub>N<sub>4</sub> is similar to that of platinum oxide PtO; both have the peaks E, F, and G. In the case of 0.5% PtO/g-C<sub>3</sub>N<sub>4</sub>, the XPS and XAS confirm that the platinum nanoparticles are completely oxidized and also do not have a core-level structure.

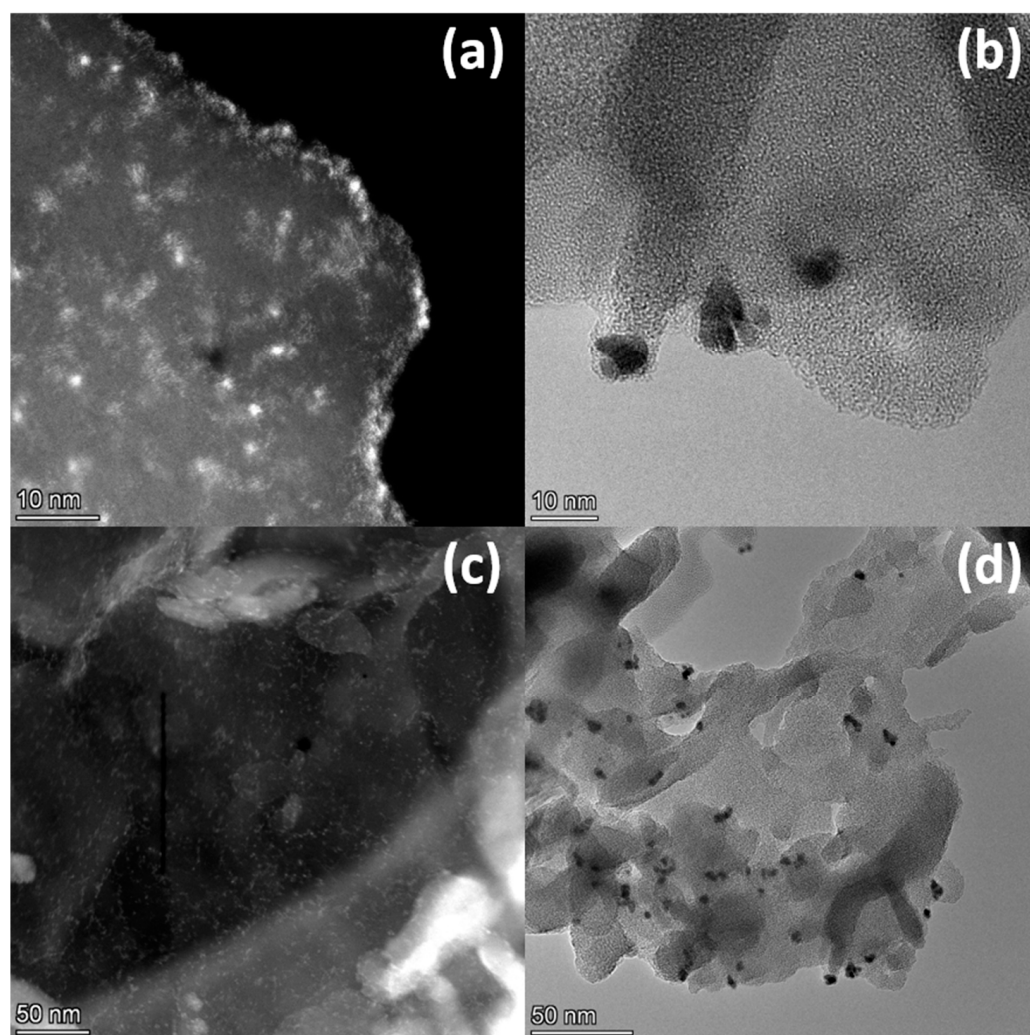


**Figure 3.** Pt 4f core-level spectra (a) and XANES Pt L<sub>3</sub>-edge spectra (b) of 0.5%Pt/g-C<sub>3</sub>N<sub>4</sub>, as well as XANES Pt L<sub>3</sub>-edge spectra of references (Pt foil and PtO). The Pt 4f core-level spectrum is normalized to the integral intensity of the C1s core-level peak, which corresponded to the spectrum of g-C<sub>3</sub>N<sub>4</sub>.

A study of the optical properties of photocatalysts showed that the deposition of both Pt and PtO leads to an increase in absorption in the visible region, which contributes to an increase in the rate of photocatalytic reactions under the visible light irradiation ( $\lambda > 380$  nm). It should be noted that after the modification of g-C<sub>3</sub>N<sub>4</sub> with cocatalysts, there is no shift in the absorption edge of the samples obtained, since the structure of g-C<sub>3</sub>N<sub>4</sub> does not change after the deposition of Pt or PtO (Figure 2b).

The morphology of the photocatalysts was studied via TEM (Figure 4). In the case of the PtO/g-C<sub>3</sub>N<sub>4</sub> photocatalyst, small single cocatalyst particles of size 1–2 nm are evenly distributed over the g-C<sub>3</sub>N<sub>4</sub> surface (Figure 4a,c). When platinum is deposited in the metallic state, platinum agglomerates of about 10 nm in size, consisting of smaller particles, can be observed (Figure 4b,d). This observation agrees well with the results of the XPS study of different surface [Pt]/[C<sub>3</sub>N<sub>4</sub>] ratios.

Thus, the methods used allow us to clarify the key features of the synthesized photocatalysts, which makes it possible to find the correlation between structure and photocatalytic properties. In summary, it can be concluded that photoreduction of Pt<sup>+4</sup> under UV light results in a uniform deposition of fine platinum oxide particles onto the g-C<sub>3</sub>N<sub>4</sub> surface. When platinum is reduced with a solution of NaBH<sub>4</sub>, Pt<sup>+4</sup> is completely reduced to the metallic state; however, the cocatalyst particles in this case are distributed unevenly, and form aggregates on the surface of the g-C<sub>3</sub>N<sub>4</sub>.

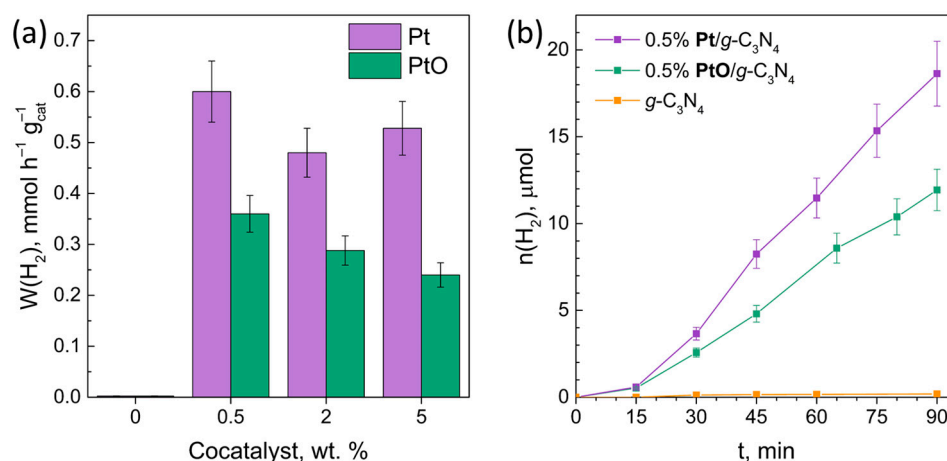


**Figure 4.** (a,c) HAADF STEM images of 0.5% PtO<sub>x</sub>/g-C<sub>3</sub>N<sub>4</sub> and (b,d) HR TEM images of 0.5% Pt/g-C<sub>3</sub>N<sub>4</sub>.

### 3.2. Photocatalytic Activity

The activity of the synthesized photocatalysts was studied in the reaction of H<sub>2</sub>'s evolution from ethanol aqueous solutions under visible light irradiation. For all the photocatalysts tested, the main reaction product is H<sub>2</sub>. The highest rate of H<sub>2</sub> evolution was achieved over the 0.5% Pt/g-C<sub>3</sub>N<sub>4</sub> catalyst, and reached 0.6 mmol h<sup>−1</sup> g<sub>cat</sub><sup>−1</sup>, which exceeds the activity of unmodified g-C<sub>3</sub>N<sub>4</sub> by 250 times. Among the photocatalysts containing platinum in the oxidized state, 0.5% PtO/g-C<sub>3</sub>N<sub>4</sub> showed the maximum activity in the H<sub>2</sub> evolution reaction, with rate of H<sub>2</sub> evolution of 0.36 mmol h<sup>−1</sup> g<sub>cat</sub><sup>−1</sup> (Figure 5a,b). It should be noted that an increase in the content of the cocatalyst in both the case of metallic and oxidized platinum does not lead to an increase in the rate of H<sub>2</sub> formation. This effect may be caused by the weak adsorption of ethanol on the surface of g-C<sub>3</sub>N<sub>4</sub>, which limits the rate of hydrogen evolution in the case of composite photocatalysts.

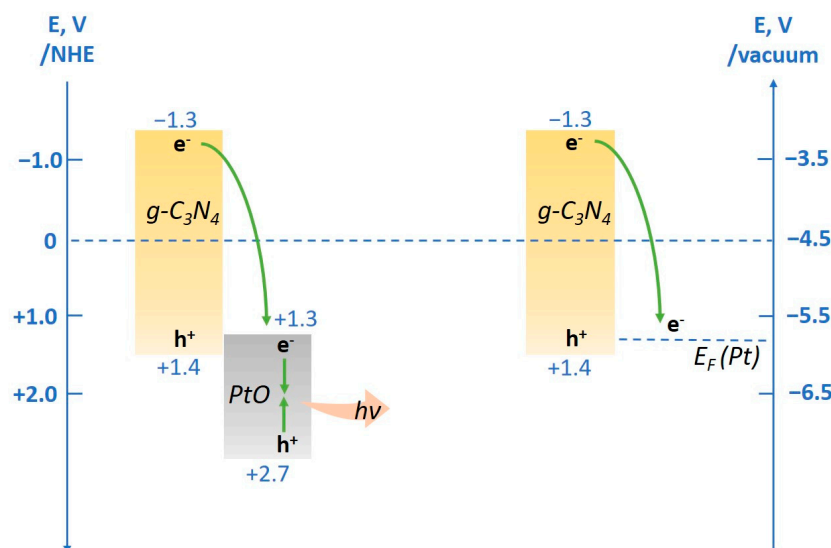
The higher activity of the platinum cocatalyst compared to platinum oxide is caused by differences in the energy structure of these compounds. Both during the deposition of platinum and platinum oxide on the surface of g-C<sub>3</sub>N<sub>4</sub>, heterojunctions arise at the interface between the two phases; a photogenerated electron migrates from the g-C<sub>3</sub>N<sub>4</sub> surface to the cocatalyst particle [56,57]. However, charge transfer mechanisms are varied for different states of platinum [58].



**Figure 5.** (a) H<sub>2</sub> evolution rate; (b) kinetic curves of H<sub>2</sub> evolution. Conditions: C(cat.) = 0.5 g L<sup>-1</sup>; C<sub>0</sub>(EtOH) = 20%, V = 50 mL, t(reaction) = 90 min, λ<sub>max</sub> = 409 nm.

While using metallic platinum as a cocatalyst, an electron from the conduction band of g-C<sub>3</sub>N<sub>4</sub> falls down to the Fermi level of the metal, overcoming the Schottky barrier at the Pt—g-C<sub>3</sub>N<sub>4</sub> contact region [59,60]. Meanwhile, the photogenerated holes remain in the valence band of g-C<sub>3</sub>N<sub>4</sub>; thus, charge carriers—electrons and holes—are spatially separated. As it has one of the highest electron work functions (5.1–5.9 eV), platinum acts as a highly efficient trap for photogenerated electrons, which allows them to significantly increase their lifetime, and, consequently, greatly contributes to increasing the rate of hydrogen evolution [61].

Platinum oxide is a semiconductor with a narrow band gap and a conduction band (CB) position of +1.3 eV, which also allows for heterojunctions of electrons from the CB of g-C<sub>3</sub>N<sub>4</sub> to the CB of PtO [62] (Figure 6). However, in semiconductors with a narrow band gap, electrons and holes can readily recombine, leading to a decrease in photocatalytic activity [58]. Therefore, charge separation in PtO/g-C<sub>3</sub>N<sub>4</sub> photocatalysts is not as efficient as in Pt/g-C<sub>3</sub>N<sub>4</sub>; thus, the lifetime of electrons and H<sub>2</sub> evolution rate are decreased.



**Figure 6.** Scheme of charge transfer mechanisms in PtO/g-C<sub>3</sub>N<sub>4</sub> and Pt/g-C<sub>3</sub>N<sub>4</sub> photocatalysts.

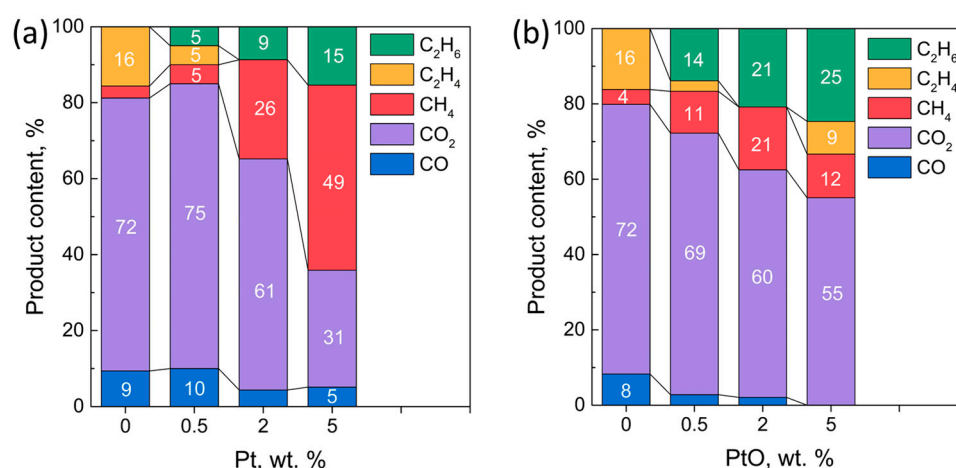
In addition to H<sub>2</sub>, C1-C2 products were detected in the gas phase: carbon oxides, methane, ethene, and ethane. It is worth noting that the deposition of a cocatalyst—both platinum and its oxide—significantly accelerates the rate of H<sub>2</sub> formation, but not its byproducts, hence allowing a great increase in the selectivity of the target process (Table 2).



**Table 2.** Reaction products in the gas phase after 90 minutes of the light irradiation.

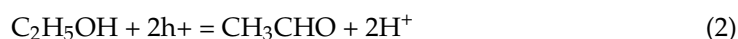
| Photocatalyst                      | Product Amount, $\mu\text{mol}$ |      |               |               |                        |                        | S ( $\text{H}_2$ ), % |
|------------------------------------|---------------------------------|------|---------------|---------------|------------------------|------------------------|-----------------------|
|                                    | $\text{H}_2$                    | CO   | $\text{CO}_2$ | $\text{CH}_4$ | $\text{C}_2\text{H}_4$ | $\text{C}_2\text{H}_6$ |                       |
| g- $\text{C}_3\text{N}_4$          | 0.19                            | 0.03 | 0.23          | 0.01          | 0.05                   | 0                      | 36.3                  |
| 0.5% Pt/g- $\text{C}_3\text{N}_4$  | 18.6                            | 0.02 | 0.15          | 0.01          | 0.01                   | 0.01                   | 98.9                  |
| 2% Pt/g- $\text{C}_3\text{N}_4$    | 17.1                            | 0.01 | 0.14          | 0.06          | 0                      | 0.02                   | 98.7                  |
| 5% Pt/g- $\text{C}_3\text{N}_4$    | 18.8                            | 0.02 | 0.12          | 0.19          | 0                      | 0.06                   | 98.0                  |
| 0.5% PtO/g- $\text{C}_3\text{N}_4$ | 12.6                            | 0.01 | 0.25          | 0.04          | 0.01                   | 0.05                   | 97.2                  |
| 2% PtO/g- $\text{C}_3\text{N}_4$   | 10.3                            | 0.01 | 0.29          | 0.08          | 0                      | 0.10                   | 95.5                  |
| 5% PtO/g- $\text{C}_3\text{N}_4$   | 6.6                             | 0    | 0.38          | 0.08          | 0.06                   | 0.17                   | 90.5                  |

Moreover, an increase in the load of the cocatalyst reduces the proportion of carbon oxides and increases the relative content of hydrocarbons (Figure 7a,b). However, in the case of photocatalysts of the PtO/g- $\text{C}_3\text{N}_4$  series, the concentration of hydrocarbons increases with the concentration of  $\text{CO}_2$ , which leads to a significant decrease in the selectivity of the photocatalytic  $\text{H}_2$  production process. For both series of photocatalysts, the amount of ethane released after 90 min increases with cocatalyst loading. At the same time, the amount of ethylene is generally reduced compared to unmodified g- $\text{C}_3\text{N}_4$ .



**Figure 7.** Distribution of products in the gas phase without  $\text{H}_2$  over Pt/g- $\text{C}_3\text{N}_4$  (a) and PtO/g- $\text{C}_3\text{N}_4$  (b). Conditions:  $C(\text{cat.}) = 0.5 \text{ g L}^{-1}$ ;  $C_0(\text{EtOH}) = 20\%$ ,  $V = 50 \text{ mL}$ ,  $t(\text{reaction}) = 90 \text{ min}$ ,  $\lambda_{\text{max}} = 409 \text{ nm}$ .

During the photocatalytic process, at the first stage, ethanol is oxidized on the photocatalyst surface to acetaldehyde (Equation (2)), which then, under the action of light, decomposes into methane and CO (Equation (3)) [63,64].



Simultaneously, on the surface of the photocatalyst, the  $\text{H}^+$  reduction process occurs with the formation of  $\text{H}_2$ .

Dehydration of ethanol leads to the formation of a small amount of ethylene (Equation (4)), which is then hydrogenated to form ethane (Equation (5)):



It should be noted that the rate of hydrogen formation on composite photocatalysts significantly exceeds the rate of formation of hydrocarbons. Thus, it can be concluded that the decomposition of acetaldehyde and the dehydration of water occur to a small extent.

The rate of H<sub>2</sub> evolution as well as of selectivity in the presence of the photocatalysts considered in this work, compared to some platinized ones reported in the literature, are shown in Table 3.

**Table 3.** Comparison of the activity and selectivity of the synthesized photocatalysts with literature data.

| Photocatalyst                                          | Light Source | C <sub>0</sub> (ethanol) | W(H <sub>2</sub> ), mmol h <sup>−1</sup> g <sub>cat</sub> <sup>−1</sup> | S(H <sub>2</sub> ), % | Reference     |
|--------------------------------------------------------|--------------|--------------------------|-------------------------------------------------------------------------|-----------------------|---------------|
| Pt/TiO <sub>2</sub>                                    | Hg lamp      | 25%                      | 84.6 mmol after 4 h                                                     | 93.8                  | [45]          |
| 0.29% Pt/TiO <sub>2</sub>                              | 380-nm LED   | 10%                      | 5.3                                                                     | -                     | [51]          |
| 0.20% Pt/CdS                                           | AM1.5G       | neat ethanol             | 11.5                                                                    | -                     | [65]          |
| 3% Pt/UCN/Nb <sub>2</sub> O <sub>5</sub>               | AM1.5G       | neat ethanol             | 0.56                                                                    | -                     | [66]          |
| Pt-Ag/Ag <sub>3</sub> PO <sub>4</sub> -WO <sub>3</sub> | Xe lamp      | 20%                      | 4.0 mmol after 12 h                                                     | -                     | [67]          |
| 0.5% Pt/g-C <sub>3</sub> N <sub>4</sub>                | 409-nm LED   | 20%                      | 0.6                                                                     | 98.9                  | Present study |

The activity of the photocatalysts synthesized in this work does not exceed the values reported in the literature for CdS and TiO<sub>2</sub>-based photocatalysts; however, it is at the level of Nb<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub>-based photocatalysts. It is also worth noting that the selectivity of the hydrogen evolution process exceeds the value presented in the literature for platinized TiO<sub>2</sub>.

#### 4. Conclusions

In this work, photocatalysts based on g-C<sub>3</sub>N<sub>4</sub> modified with Pt and PtO were synthesized and studied in H<sub>2</sub> evolution from ethanol solution under visible light irradiation. Characterization of the photocatalysts using a set of research methods showed that photodeposition from H<sub>2</sub>PtCl<sub>6</sub> solution leads to a uniform distribution of platinum oxide particles over the surface of g-C<sub>3</sub>N<sub>4</sub>. The use of NaBH<sub>4</sub> solutions for reduction makes it possible to deposit particles of metal platinum on the surface of g-C<sub>3</sub>N<sub>4</sub>, which, despite their uneven distribution, lead to a higher rate of H<sub>2</sub> formation than platinum oxide. An increase in the metallic platinum content leads to a gradual decrease in carbon dioxide and a significant increase in methane in the gas phase. As the PtO loading increases, the amount of carbon dioxide grows, and a large amount of ethane is produced, which on the whole results in a decrease in the relative carbon dioxide content as the platinum oxide content increases. Thus, both the state of platinum and its content affect not only the rate of hydrogen formation, but also the rate of the formation of the reaction by-products, which confirms the need to control the selectivity of the hydrogen formation process from organic electron donors.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app132111739/s1>, Figure S1: XRD patterns of (a) 5% Pt/g-C<sub>3</sub>N<sub>4</sub> and (b) 5% PtO/g-C<sub>3</sub>N<sub>4</sub>; Figure S2: Tauc plot of unmodified g-C<sub>3</sub>N<sub>4</sub>.

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