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Photocatalytic properties of aminated graphitic carbon dots based on citric acid

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To design robust composite photocatalytic systems for hydrogen generation, efficient binding of the photoabsorber and the catalyst is critical. When using carbon dots as photoabsorbers, the efficiency of such binding can be easily controlled by varying their surface groups. In the present work, the structural and optical properties of graphitic as well as aminated graphitic carbon dots were prepared and investigated. The aminated carbon dots were obtained from the original citric acid-based by attaching dimethyl ethylenediamine and dimethylaminopropylamine molecules. The use of the obtained carbon dots as photoabsorbers in photocatalytic systems allowed us to establish the dependence of hydrogen generation on the charge and size of their surface groups. The analysis of the obtained experimental data showed that the use of dimethyl ethylenediamine molecules for amination of the carbon dots surface allows to enhance hydrogen generation by 2.7 times.

Keywords: photocatalysis, hydrogen generation, carbon dots, photoluminescence, luminescence decay time, atomic force microscopy, infrared absorption spectroscopy.

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Introduction

Carbon dots (CD) are referred to a class of carbon nanomaterials with a quite complex internal structure that may vary significantly depending on the used precursors and synthesis conditions [1–5]. It is commonly believed that the CD structure has a lot of molecular-type optical centers [4,6–11]. These molecular centers and the competition between them define the main optical properties of CD. Bright and stable visible range luminescence of CDs makes them suitable for sensoric and optoelectronic applications [12–15].

The capability to absorb solar radiation in a wide visible spectral range allows them to be used as light absorbers in photocatalytic hydrogen generation systems [16,17]. It is extremely important to modify the surface of CDs to ensure effective binding to the catalyst. Light absorbers in the form of CDs that have been used to date in photocatalytic hydrogen generation systems have negatively charged carboxylate groups [16,17], whereas the most effective Du Bois type molecular catalysts generally have negatively charged phosphonic groups in a neutral aqueous medium. Thus, the CD surface modification with the achievement of positively charged equivalent CDs seems to be very promising for effective binding of the CD-based photoabsorber to the Du Bois catalysts with phosphonic end groups and, accordingly, for enhancing hydrogen generation. This CD surface modification will not only improve the binding of components in a photocatalytic hydrogen generation system, but will also make it possible to study the contribution of various CD surface groups to the overall functionality of the photocatalytic hydrogen generation system.

In this paper, the structural and optical properties of aminated graphitic CDs were identified and studied. At the first stage, graphitic CDs with carboxyl groups on the surface were obtained by pyrolysis of citric acid. Then, CD surface amination was performed with addition of dimethylethylenediamine (*DMEN*) and dimethylaminopropylamine (*DMAPA*) molecules. The obtained CD used as light absorbers in the photocatalytic hydrogen generation systems made it possible to detect the influence of the CD surface groups and their sizes on hydrogen generation. The experiment data analysis has shown that molecules with minimum sizes (*DMEN*) used for CD amination enhanced the hydrogen generation to the fullest extent by up to 2.7 times compared with original CDs.

Materials and research techniques

Graphitic CDs (*g-CDots-D*) were produced using the standard pyrolysis technique consisting of two stages [16]. At the first stage, 2 g of citric acid (CA) underwent pyrolysis at 180 °C in an open crucible during 40 h. Then, the obtained product was additionally heated at 320 °C during

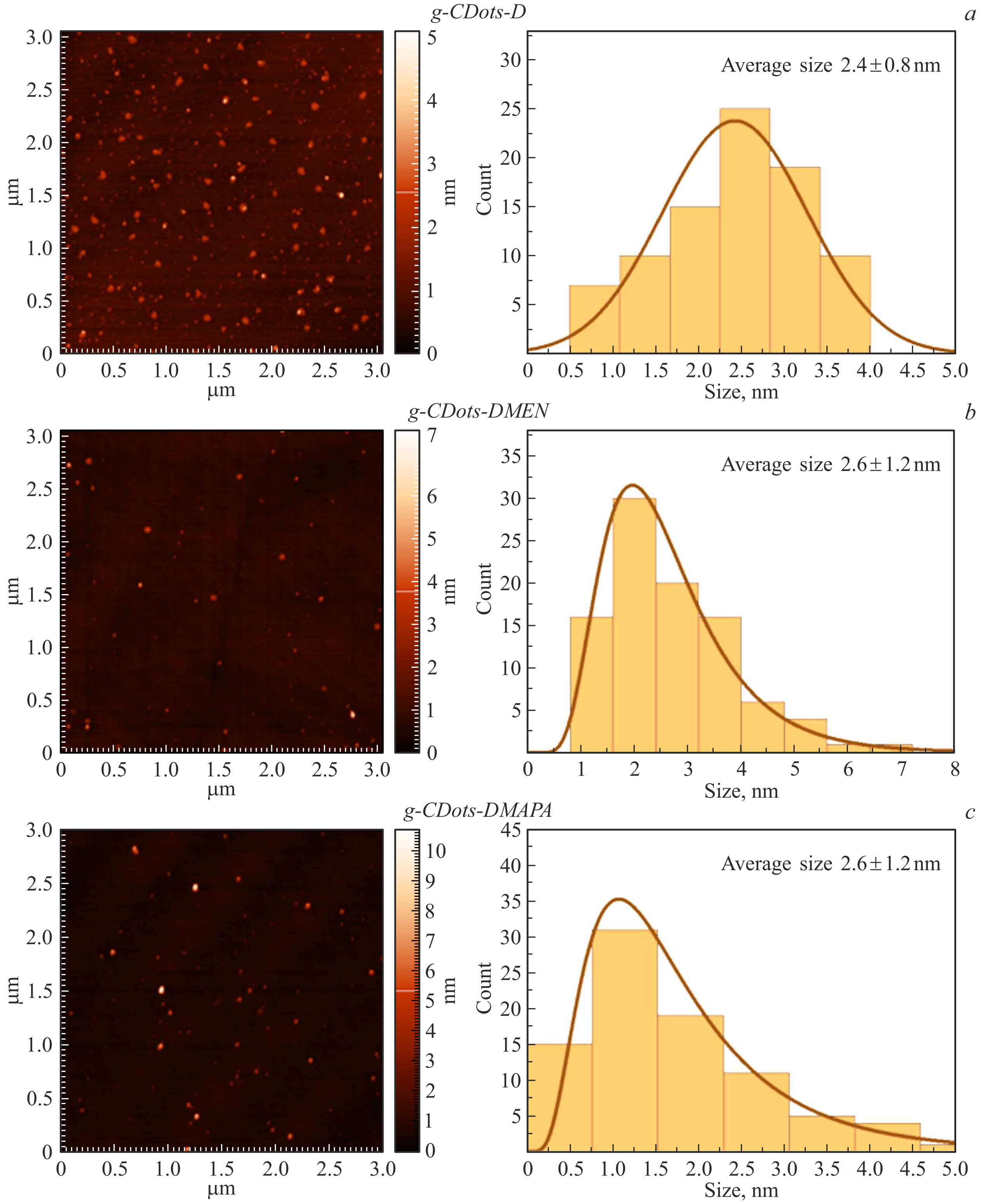

Figure 1. AFM images for *g-CDots-D*, *g-CDots-DMAPA* and *g-CDots-DMEN* and the corresponding size distribution histograms.

100 h. The obtained viscous product was dissolved in water with adding aqueous NaOH solution to obtain CDs coated with sodium carboxylates. The prepared CDs were purified to remove low-molecular organic matter through dialysis during 7 days (membrane size was 3.5 kDa). The dialyzed *g-CDot-D* water suspension was dried in a freeze drier to get brown powder. To modify the CD surface, 200 mg of *g-CDots-D* was dissolved in 15 mL of thionyl chloride

and heated with boiling during 3 h. The thionyl chloride was stripped in a rotary evaporator, then 10 mL of the corresponding amine *DMEN* or *DMAPA* was added to the reaction mixture and heated with agitation at 50 °C during 5 h. Excess amine was stripped in the rotary evaporator and then the modified CDs were purified by dialysis during 3 days (membrane size - 3.5 kDa). The dialyzed water suspension was dried in the freeze drier to get *g-CDots-DMEN* and *g-CDots-DMAPA* in the form of powder weighing 150 mg each.

Synthesis of the Du Bois (NiP) catalyst containing the electroactive $[\mathrm{Ni(P{-}2N_2)^2}]^{2+}$ core with an external coordination sphere in the form of phosphonic acid fragments was conducted using a technique described in [18].

CD absorption spectra were recorded using the UV-3600 spectrophotometer (Shimadzu, Japan). CD luminescence and luminescence excitation spectra were obtained using the Cary Eclipse spectrofluorimeter (Varian, Australia). FTIR absorption spectra of CDs were recorded using the Tensor II FTIR spectrophotometer (Bruker, USA) in the attenuated total internal reflection mode.

The size of CDs was obtained using the Solver Pro-M (NT-MDT) atomic force microscope (AFM). For this, 70 μL of the CD solution was deposited to the mica surface by centrifugation with the following parameters: 5 s at 500 r/min and 25 s at 2000 r/min. Then, the CDs deposited to the mica substrate were annealed for 15 min at 130 °C and subsequently used to measure the CD sizes.

CD PL decay curves recorded using the MicroTime 100 scanning laser microscope (PicoQuant, Germany) were approximated by the biexponential function

$$I = A_1 e^{\frac{-t}{\tau_1}} + A_2 e^{\frac{-t}{\tau_2}}. \tag{1}$$

The mean CD PL decay time was calculated using the following equation

$$\tau_{av} = \frac{\Sigma_i A_i \tau_i^2}{\Sigma_i A_i \tau_i}, \tag{2}$$

where A_i and τ_i are the amplitude and decay time of the i-th component, respectively.

For the purpose of photocatalytic experiments, 4.175 mg (10 nmol) of CDs and 0.27 mg (10 nmol) of NiP catalyst were mixed in 50 mL of 0.1 M EDTA aqueous solution (electron donor) with pH ~ 6 and shaken in a vortex mixer during 1 min. Then, the mixture was placed into a reaction cell and thermostatting was started (20 °C). For photoexcitation, the Osram XBO-150 lamp and light filtering NaBr and KCl mixture solution were used to obtain exciting light from 220 nm. Then, the system was purged with argon during 30 min, gas chromatographic analysis was started for the total time of 4 h with sampling every 15 min.

Results and discussion

Figure 1 shows the images for graphitic *g-CDots-D* (*a*) and aminated graphitic *g-CDots-DMEN* (*b*), *g-CDots-DMAPA* (*c*) and the corresponding size distribution histograms recorded using the atomic-force microscope (AFM). Original CDs before treatment have a mean size of 1.8 ± 0.8 nm. Amination of the CD surface with *DMEN* and *DMAPA* molecules provides the increase in their size up to 2.6 ± 1.2 nm, which is an indirect evidence of amine binding to the carbon dot surface. Aminated graphitic *g-CDots-DMEN* and *g-CDots-DMAPA* have the same size because the *DMAPA* molecule is longer than the *DMEN* molecule only by one methylene group. Distribution of *g-CDots-DMEN* and *g-CDots-DMAPA* becomes wider by size compared with original CDs, which may be attributed to a minor modification of a part of CDs during surface amination.

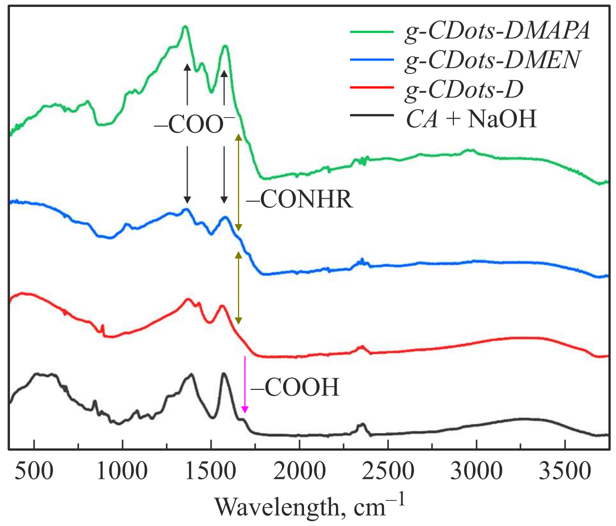

Figure 2. FTIR absorption spectra of *g-CDots-D*, *g-CDots-DMAPA*, *g-CDots-DMEN* and NaOH-neutralized CA molecules. Characteristic frequencies are marked with arrows.

The surface structure of original graphitic *g-CDots-D*, aminated graphitic *g-CDots-DMEN* and *g-CDots-DMAPA* was identified and monitored using the FTIR absorption spectroscopy. Figure 2 shows the TIR absorption spectra of graphitic *g-CDots-D*, aminated graphitic *g-CDots-DMEN* and *g-CDots-DMAPA* and precursor (citric acid, CA) neutralized using NaOH for comparison. The FTIR absorption spectrum of *g-CDots-D* is characterized by two characteristic bands at 1396 and 1566 cm^{-1} corresponding to symmetric and asymmetric stretching of the neutralized carboxyl groups on the CD surface. The shift in the position of the CD bands relative to the CA molecular precursor (1385 and 1566 cm^{-1}) occurs because they are formed by the residues of the carboxyl groups of CA molecules on the CD surface. The FTIR absorption spectrum of graphitic *g-CDots-DMEN* and *g-CDots-DMAPA* is also characterized, besides the bands at 1350 and 1574 cm^{-1} corresponding to symmetric and asymmetric stretching vibrations of carboxyl groups, by the presence of another characteristic band at 1662 cm^{-1} that corresponds to stretching of the secondary amide (-CONHR). The presence of

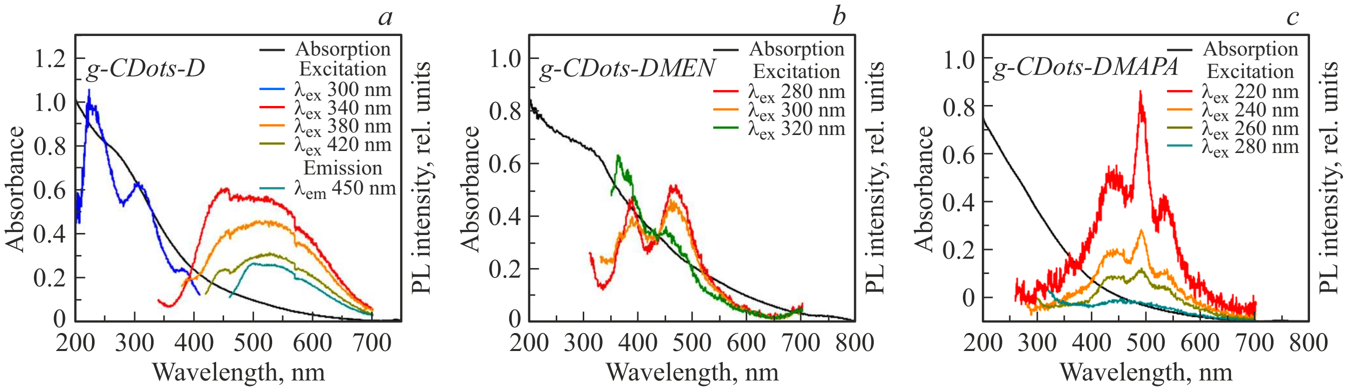

Figure 3. Absorption, PL and PL excitation spectra of *g-CDots-D* (*a*), *g-CDots-DMEN* (*b*) and *g-CDots-DMAPA* (*c*) at various excitation and recording wavelengths as shown in the figure legend.

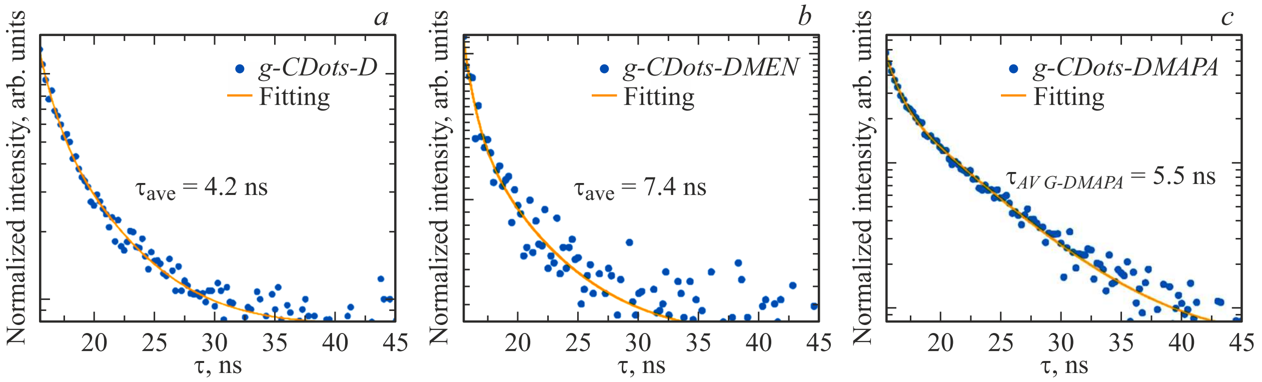

Figure 4. PL decay curves of *g-CDots-D* (*a*), *g-CDots-DMEN* (*b*) and *g-CDots-DMAPA* (*c*) with excitation at 410 nm.

this secondary amide band is due to covalent binding of the carboxyl groups of CDs to the amino groups of *DMEN* (for *g-CDots-DMEN*) or *DMAPA* (for *g-CDots-DMAPA*) molecules.

Figure 3 shows absorption and luminescence spectra of graphitic *g-CDots-D* (*a*), *g-CDots-DMEN* (*b*), *g-CDots-DMAPA* (*c*). Original graphitic *g-CDots-D* are characterized by absorption from UV to the nearest visible spectrum region with a typical arm at 290 nm. The absorption spectra of aminated graphitic *g-CDots-DMEN* and *g-CDots-DMAPA* have the same form with a more pronounced arm for *CDots-DMEN* and a less pronounced arm for *g-CDots-DMAPA*.

The features observed in the absorption spectra are in complete agreement with the data obtained previously for similar graphitic CDs [16,17]. Figure 3, *a* shows that graphitic *g-CDots-D* are characterized by wide PL in the range of 400–700 nm, whose form remains almost unchanged as the excitation wavelength varies from 300 nm to 420 nm in increments of 40 nm. Whereas for aminated graphitic *g-CDots-DMEN*, two peaks at 388 nm and 468 nm are observed in the PL spectrum. For aminated graphitic *g-CDots-DMAPA*, the PL spectrum has three peaks at 440, 489 and 531 nm with the highest intensity of the central peak. The features observed in the PL spectra of aminated graphitic CDs may suggest a molecular nature of the luminescence centers, which agrees with the data obtained previously for the same CDs [19].

Figure 4 shows the PL decay kinetics PL decay of *g-CDots-D* (*a*), *g-CDots-DMEN* (*b*), *g-CDots-DMAPA* (*c*) with excitation at 410 nm. The approximation by biexponential function (1) of the PL decay curves provided the mean decay times equal to 4.2 (*g-CDots-D*), 7.4 (*g-CDots-DMEN*) and 5.5 ns (*g-CDots-DMAPA*). The data obtained agree with the typical PL decay times for CDs [16,17,19].

For the photocatalytic hydrogen generation experiments, CDs were mixed with the NiP catalyst with 1:1 molar ratio in the aqueous solution with pH 6 in the presence of an electron donor in the form of EDTA. Figure 5 shows the outlines of hydrogen generation when using photoabsorbers is the form of graphitic (*g-CDots-D*) and aminated graphitic (*g-CDots-DMEN* and *g-CDots-DMAPA*) CDs. Original graphitic *g-CDots-D* yield 16.8 μL of generated hydrogen during 4 h. Amination of the CD surface increases the hydrogen yield during the same time up to 36.7 μL and 45.4 μL for *g-CDots-DMAPA* and *g-CDots-DMEN*. Large amount of generated hydrogen for *g-CDots-DMEN*

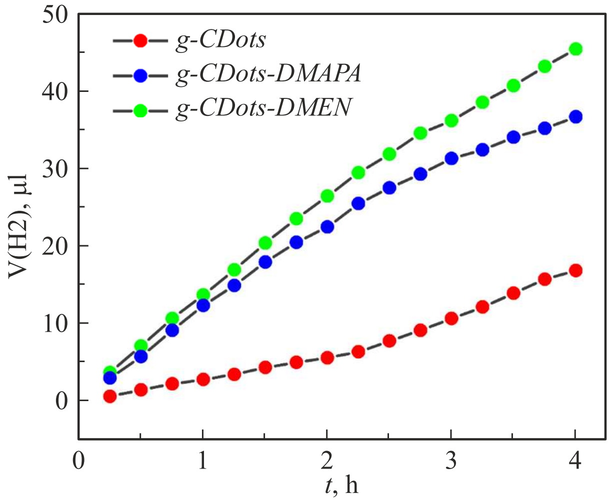

Figure 5. Outlines of hydrogen generation by the photocatalytic CD/NiP systems (CD: *g-CDots*, *g-CDots-DMAPA*, *g-CDots-DMEN*) in water with pH 7 using EDTA as an electron donor.

compared with *g-CDots-DMAPA* may be attributed to more effective charge transfer from CDs to the catalyst due to a shorter length of the *DMEN* molecule compared with the *DMAPA* molecule. Thus, the CD surface amination enhances hydrogen generation in these photocatalytic systems by 2.7 times.

Conclusion

In this paper, the structural and optical properties of graphitic and aminated graphitic CDs based on citric acid have been identified and studied. The FTIR absorption spectroscopy method has been used to identify the presence of carboxyl groups on the CD surface. These surface groups were used for CD amination by the *DMEN* and *DMAPA* molecules. The optical properties of obtained CDs have been investigated using the UV-VIS absorption spectroscopy and luminescence spectroscopy. The graphitic and aminated graphitic CDs are supposed to have molecular centers. The obtained CDs used as light absorbers together with the Du Bois $[Ni(P_2N_2)^2]^{2+}$ molecular catalyst containing an external coordination sphere with phosphonic groups have made it possible to identify the influence of the CD surface amination and the amine length on the hydrogen generation. It has been shown that the CD amination by the DMEN molecules enhances the hydrogen generation by 2.7 times. It has been also found that the hydrogen generation efficiency depends on the aliphatic chain length of the amine — a shorter chain turns to be more effective for the photocatalytic purposes

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Conflict of interest

The authors declare that they have no conflict of interest.

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