Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 157–159

Synthesis of graphitic carbon nitride-based photocatalysts for hydrogen evolution under visible light

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Photocatalyst synthesis

Melamine and dicyandiamide were chosen as precursors. Usually, 2 g of the precursor was annealed in a ceramic crucible with a lid. The annealing temperature was varied from 450 to 600 °C for 4 h in air. The annealing time was also varied for a temperature of 600 °C and was 2 and 4 h. The obtained g-C_3N_4 was ground in a mortar to a yellow powder. 1 or 3 wt% platinum was deposited on the prepared photocatalysts by impregnation with hexachloroplatinic acid followed by reduction with a 2.5-fold excess of sodium borohydride. The samples were dried at 50 °C for 4 h after decantation several times.

Photocatalyst characterization

The photocatalysts were characterized using UV-VIS spectroscopy, X-ray diffraction measurements. The specific surface areas of the photocatalysts were obtained from the low-temperature N_2 adsorption-desorption (N_2 adsorption at 77 K) using an ASAP 2400 apparatus. UV-VIS diffuse reflectance spectra were obtained on a Shimadzu UV-2501 PC spectrophotometer with an ISR-240A diffuse reflectance unit. X-ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer in the 2θ angle range from 20 to 80° using the Cu Kα radiation. The mean sizes of crystallites were estimated from the full width at half maximum of the corresponding peaks using the Scherrer formula.

The UV-VIS spectra were recalculated in Kubelka–Munk coordinates as follows:

$$F(R) = (1 - R/100)^2/(2R/100),$$

where R is the reflectance (%). The optical band gap (E_g) for the synthesized photocatalysts was estimated using the Tauc model for direct allowed transitions by plotting $[F(R)\times h\nu]^2$ *versus* $h\nu$.

The structure of the photocatalysts were studied by HRTEM using a ThemisZ electron microscope (Thermo Fisher Scientific, USA) operated at an accelerating voltage of 200 kV.

Photocatalytic tests

The activity of the synthesized materials was estimated by the photocatalytic hydrogen evolution from aqueous solutions of 10 vol% triethanolamine (TEOA) under irradiation with a monochromatic LED with maximum emission at a wavelength of 450 nm. 0.1 M NaOH solution was used to prepare the TEOA solution. 50 mg of catalyst was added to 100 ml of the solution, and the mixture was sonicated for 10 min and purged with argon for 20 min to remove oxygen. Thereafter, the suspension was placed in a reactor and illuminated with an LED (30 W, China, 40 mV/cm^2, Figure S1). The hydrogen concentration was measured on an LKhM-8 gas chromatograph (Khromos, Russia) equipped with a thermal conductivity detector and a zeolite column with argon as a carrier gas.

The following calculation was used to determine the apparent quantum efficiency (AQE):

$$\text{AQE}\ (\%) = (W / 34) \times 100\%,$$

where W is the rate of the hydrogen formation in μmol min^{-1}. The estimated photon flux was 34 μEinstein·min^{-1}.

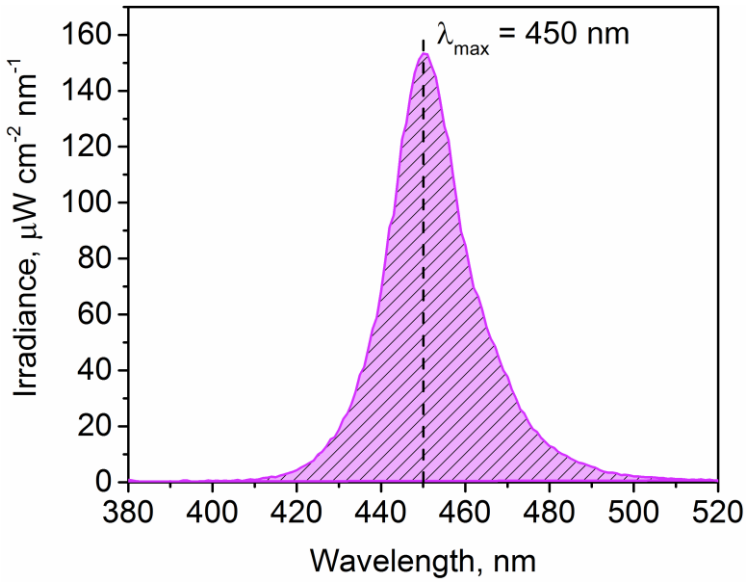

Figure S1 Emission spectrum of a 450 nm LED used as a light source in all photocatalytic tests.

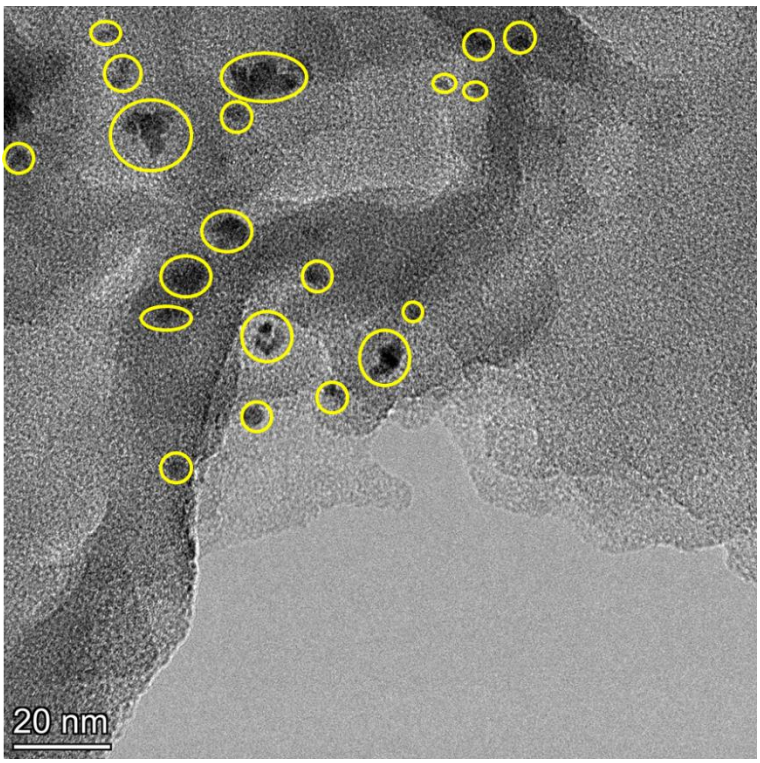

Figure S2.High-resolution transmission electron microscopy image of the 1% Pt/g-C_3N_4 photocatalyst.

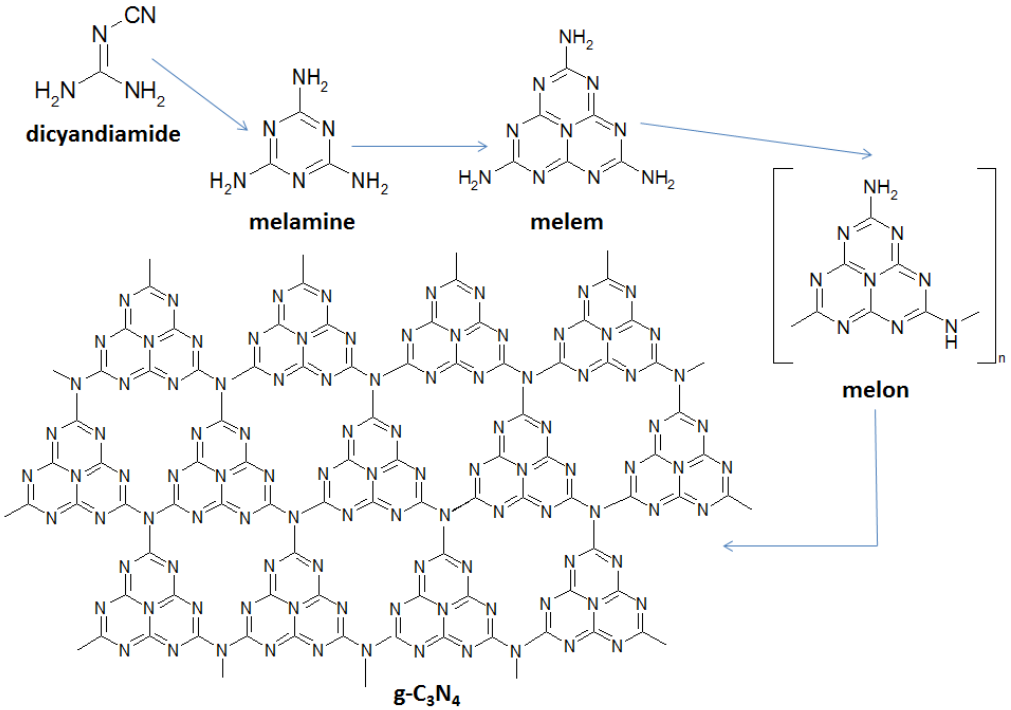

Figure S3 A route for g-C_3N_4 preparation from melamine and dicyandiamide.

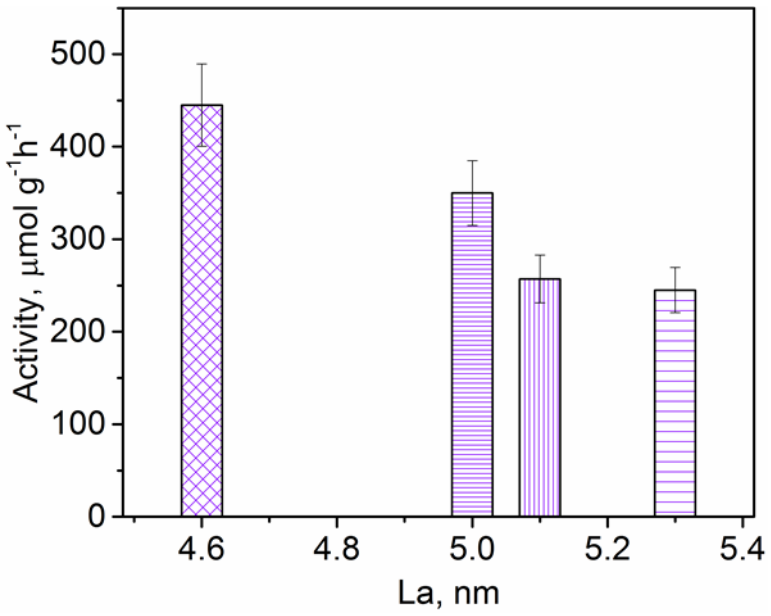

Figure S4 Relationship between the catalytic activity of the samples and the average g-C_3N_4 crystallite size in the plane of the layer.

Table S1 Influence of Pt content in prepared samples on catalytic activity in photocatalytic hydrogen evolution from alkaline (0.1 M NaOH) aqueous TEOA solutions under irradiation with a visible light wavelength of 450 nm.

Sample	Precursor	*T*/°C	Heating time/h	1% Pt		3% Pt	
				Catalytic activity/ μmol g^{-1} h^{-1}	Catalytic activity/ μmol m^{-2} h^{-1}	Catalytic activity/ μmol g^{-1} h^{-1}	Catalytic activity/ μmol m^{-2} h^{-1}
Pt/g-C_3N_4	Melamine	450	4	< 10	< 1	< 10	< 1
	Dicyandiamide						
Pt/g-C_3N_4	Melamine	500					
	Dicyandiamide						
Pt/g-C_3N_4	Melamine	550		229	17.8	63.1	4.89
	Dicyandiamide			297	22.8	78.2	6.02
Pt/g-C_3N_4	Melamine	600		350	12.5	270	9.68
	Dicyandiamide			257	11.4	138	6.11

Table S2 Photocatalytic activity of photocatalysts based on g-C3N4 in the evolution of hydrogen from aqueous solutions of organic compounds under visible light.

Photocatalyst	Sacrificial reagent	Light source	Catalytic activity/ $\mu mol\ g^{-1}\ h^{-1}$	Reference
5% Ag/g-C_3N_4	10 vol% TEOA	300 W Xe lamp	569	[S1]
10% Co_xO_y/g-C_3N_4	20 vol% TEOA	300 W Xe lamp with cutoff ($\lambda \geq 450$ nm)	473	[S2]
1% Pt/g-C_3N_4	10 vol% lactic acid	LED-420	360	[S3]
Co_3O_4@g-C_3N_4/ carbon nanofibers	10 vol% TEOA	300 W Xe lamp	67	[S4]
1% Pt/0.34% P doped g-C_3N_4	10 vol% TEOA	300 W Xe lamp with cutoff ($\lambda \geq 420$ nm)	318	[S5]
0.2% Pt/g-C_3N_4/ 10% $SrTiO_3$	Acid Red 1 + 5 vol% TEOA	300 W Xe lamp	471	[S6]
5% Pt/0.2 mol% Cr_2O_3/ g-C_3N_4	10 vol% TEOA	300 W Xe lamp with cutoff ($\lambda \geq 420$ nm)	210	[S7]
3% 2D Co_2P/g-C_3N_4	10 vol% TEOA	300 W Xe lamp with cutoff ($\lambda \geq 420$ nm)	53	[S8]
0.1% Fe_2P–0.1% Co_2P/ g-C_3N_4	10 vol% TEOA	300 W Xe lamp with cutoff ($\lambda \geq 420$ nm)	347	[S9]
3.5% Ni_2P/g-C_3N_4	10 vol% TEOA	300 W Xe lamp with cutoff ($\lambda \geq 420$ nm)	475	[S10]
1% Pt/g-C_3N_4	10 vol% TEOA	LED-450	450	This work

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