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Mn^{2+}-doped ZnS–CdS alloy nanocrystals for the photocatalytic hydrogen evolution reaction

Yurii A. Kabachii, Sergey Yu. Kochev, Olga Yu. Antonova, Sergey S. Abramchuk, Alexandre S. Golub, Artyom A. Astafiev, Andrei N. Kostrov and Victor A. Nadtochenko

Chemicals

Zinc acetate dihydrate ($Zn(OAc)_2$•$2H_2O$, 98%), cyclohexane (99+%, for spectroscopy), 1-octadecene (**ODE**, 90%, tech.,), tetramethylammonium hydroxide (25 wt% in methanol), manganese(II) chloride ($MnCl_2$, anhydrous, 99%),–oleic acid (90%, tech.), oleylamine (**OlAm**, C18 content 80-90%) cadmium acetate dihydrate ($Cd(OAc)_2$•$2H_2O$, ≥98%), stearic acid (95%) were purchased from Merck and used as received. Zinc stearate (ZnO 12.5-14%, Alfa Easar), Sulfur (reagent grade, 100 mesh, Sigma-Aldrich) and magnesium turnings (Mg, 99%, Sigma-Aldrich) were used without further purification. Anhydrous methyl alcohol (**MeOH**) was prepared from chemically pure grade MeOH by boiling with Mg methylate. Manganese stearate (**$MnSt_2$**) was synthesized from $MnCl_2$, tetramethylammonium hydroxide and stearic acid in anhydrous MeOH according to the method reported previously[S1]. OlAm was degassed at 60 °C for 30 min under vacuum in Schlenk tube and stored under argon. Copolymer of 2-(methacryloxy)ethyltrimethylammonium methyl sulfate and stearyl methacrylate was synthesized as described[S2]. Nanocrystals (**NCs**) were obtained according to a modified by us method published earlier[S3].

Installation for the synthesis of nanocrystals

Nanocrystal synthesis was carried out under argon atmosphere in a three-neck 100 or 50 mL round-bottom flask equipped with a magnetic stirrer, a reflux condenser and a rubber stopper with a thermocouple and a heating mantle connected to the thermostat. The open end of the reflux condenser may be operatively connected either to a vacuum line or to an argon gas pipe, equipped with an outlet of argon into the atmosphere through a bubble counter, to prevent accidental entry of air into the flask during the experiment.

Zn and Cd precursor mixture was prepared by the following typical procedure. A mixture of $Cd(OAc)_2 \cdot 2H_2O$ 102.9 mg (0.386 mmol), $Zn(OAc)_2 \cdot 2H_2O$ 72.4 mg (0.330 mmol), 1 mL of oleic acid (3.15 mmol) and 1 mL of ODE in the 50 mL Schlenk tube was stirred at 130 C for 30 min under argon flow, evacuated for 20 min, then cooled and mixed with 7.5 mL of ODE.

NCs from an alloy of Zn and Cd sulfides, ***Sample*** *1*

Sulfur 21.3 mg (0.665 mmol) was dissolved in 1.7 mL of degassed ODE in the 25 mL Schlenk tube at 135°C for a 15-20 min. After that the solution was cooled to room temperature and stored under argon. The Zn and Cd precursor mixture was loaded into the 100 mL three-neck round-bottom flask mentioned above. The mixture was withstanded under vacuum for 20 min while heating to 100°C. Then the flask was filled with argon. After that the flask was heated to 305°C, and OlAm 1 mL and the sulfur solution were injected successively by the syringe. Next, the mixture was stirred at 310°C for 20 min and quickly cooled. Acetone was added to the mixture in a ratio of 1: 1.5. The resulting precipitate was separated from liquid by centrifugation at 5000 rpm. The liquid was discarded. The precipitate was redispersed in heptane and precipitated with acetone. The precipitate was separated from liquid by centrifugation, and the liquid was discarded. The procedure of re-dispersion-precipitation-separation was repeated three times. Final precipitate was dispersed in cyclohexane. Non dispersible residue was separated by centrifugation at 8000 rpm (~20.000g) for 5 min and discarded. As a result, 66 mg of the Sample 1 nanocrystals were obtaned as dispersion in cyclohexane. Analysis of the elemental composition of the nanocrystals, performed by flame atomization atomic absorption spectrometry, showed x=0.37. To obtain nanocrystals with the same molar content of zinc and cadmium, the method was changed.

NCs from an alloy of Zn and Cd sulfides, ***Sample*** *2*

A mixture of $Cd(OAc)_2 \bullet 2H_2O$ 95.4 mg (0.358 mmol), $Zn(OAc)_2 \bullet 2H_2O$ 78.6 mg (0.358 mmol), 0.523 mL of oleic acid and 1 mL of ODE in the 50 mL Schlenk tube was stirred at 130 C for 30 min under argon flow, evacuated for 20 min, then cooled and mixed with 7.5 mL of ODE. Sulfur 23 mg (0.719 mmol) was dissolved in 1.8 mL of degassed ODE in the 25 mL Schlenk tube at 135°C for a 15-20 min. After that the solution was cooled to room temperature and stored under argon. Oleic acid 470 μL was mixed with octadecene 0.52 mL, degassed under vacuum and kept in argon. The Zn and Cd precursor mixture was loaded into the 100 mL three-neck round-bottom flask. The mixture was withstanded under vacuum for 20 min while heating to 100°C. Then the flask was filled with argon. After that the flask was heated to 305°C, and OlAm 1 mL and the sulfur solution were injected successively by the syringe. The mixture was stirred at 310°C for 10 min. Then, the prepared oleic acid solution was added; the mixture was stirred for another 10 min and cooled to room temperature. Nanocrystals were isolated in the same way as Sample 1. As a result, 80 mg of the Sample 2 nanocrystals were obtaned as dispersion in cyclohexane.

Mn^{2+}-doped NCs from an alloy of Zn and Cd sulfides, ***Sample*** *3*

Sulfur 25.4 mg (0.791 mmol) was dissolved in ODE 1.8 mL in a Schlenk tube under argon atmosphere at heating. The Zn and Cd precursor mixture and $MnSt_2$ 46.7 mg (0.075 mmol) were loaded into the 100 mL three-neck round-bottom. The mixture was withstanded under vacuum for 20 min while heating to 100°C. Then the flask was filled with argon. After that the flask was heated to 305°C, and OlAm 1 mL and the solution of sulfur were injected successively by the syringe. Then, the mixture was stirred at 310°C for 20 min and quickly cooled. Nanocrystals were isolated as described for Sample 1. Finally, 110 mg of nanocrystals Sample 3 were yielded as dispersion in cyclohexane.

Cd precursor

A mixture of $Cd(OAc)_2 \cdot 2H_2O$ (102.9 mg, 0.358 mmol), 0.239 mL of HO1 (212 mg, 0.752 mmol) and 1 mL of ODE in the 25 mL Schlenk tube was stirred at 130 C for 30 min under argon flow, evacuated for 20 min, then cooled and mixed with 1.5 mL of ODE under argon.

Zn precursor

A mixture of $Zn(OAc)_2 \cdot 2H_2O$ ((335.4 mg 1.582 mmol), 1.034 mL of oleic acid (920 mg, 3.26 mmol) and 3 mL of ODE in the 50 mL Schlenk tube from ambient temperature up to 130 ^{o}C, withstanding under this temperature first for 15 minutes in argon, then for 20 minutes in vacuum, and cooling. Next, the mixture was mixed with 3 mL of ODE, degassed under vacuum at 100 ^{o}C, cooled down to ambient temperature and stored under argon.

Sulfur stock solution

The sulfur stock solution was prepared by dissolution of 48.7 mg (1.518 mmol) of sulfur in 8 mL of degassed ODE in the 25 mL Schlenk tube at 135°C for a 15-20 min. After cooling to room temperature solution was stored under argon.

*Mn^{2+}-doped NCs from an alloy of Zn and Cd sulfides coated with a ZnS shell, **Sample** 4*

2.5 ML of the Zn and Cd precursor mixture, $MnSt_2$ 11.7 mg (0.019 mmole) and 7.5 mL of ODE were loaded into the 100 mL the three-neck round-bottom flask. The mixture was withstanded under vacuum for 20 min while heating to 100°C, and then the flask was filled with argon. After that the flask was heated up to 305°C, and 0.136 mL of OlAm and 1 mL of the sulfur stock solution were injected successively by the syringe; the mixture was stirred at 310°C for 20 min and cooled to 240°C. Next, OlAm 1.023 mL (828 mg, 3.097 mmol) was added to the mixture. Then the remaining sulfur stock solution and the Zn precursor heated to 100°C were injected alternately in five steps (0.55, 0.89, 1.32, 1.83 mL, and the rest). The period between each injection was 10 min. After the last one the reaction mixture was withstanded at this temperature for 10 min and finally was cooled down to the ambient temperature. NCs were isolated using the method mentioned above for Sample 1. Finally, 153 mg of nanocrystals Sample 4 were yielded as dispersion in cyclohexane.

To determine size of the Sample 4 cores, a separate experiment was carried out. We conducted the experiment in similar manner to the synthesis of Sample 4, but after step of stirring for 20 min at 310C, the reaction was stopped by cooling the reaction mixture to room temperature. The resulting nanocrystals were isolated and their size was determined by TEM.

NCs from an alloy of Zn and Cd sulfides coated with a ZnS shell (**Sample 5**) were synthesized by a method similar to that described for Sample 4, but without the addition of manganese stearate.

*ZnS NCs, **Sample** 6*

Zinc stearatate 125 mg (0.198 mmol) and 10 mL of ODE were loaded into the 100 mL the three-neck round-bottom flask. The mixture was withstanded under vacuum for 20 min while heating to 110°C, and then the flask was filled with argon. After that the flask was heated up to 305°C, and 0.131 mL (105.9 mg, 0.396 mmol) of OlAm and 1.0 mL of the sulfur stock solution were injected successively by the syringe; the mixture was stirred at 290°C for 20 min and cooled to 240°C. Next, OlAm 1.023 mL (828 mg, 3.097 mmol) was added to the mixture at that temperature. Then the remaining sulfur stock solution (7 mL) and the Zn precursor heated to 100°C were injected alternately in five steps (0.55, 0.89, 1.32, 1.83 mL, and the rest). The period between each injection was 10 min. After the last one the reaction mixture was withstanded at this temperature for 20 min and finally was cooled down to the ambient temperature. NCs were isolated using the method mentioned above for Sample 1. Finally, 148 mg of nanocrystals Sample 6 were yielded as dispersion in cyclohexane.

*ZnS/CdS core/shell NCs, **Sample** 7*

The sulfur 21.8 mg (0.680 mmol) was dissolved in 2.4 mL of degassed ODE in the 25 mL Schlenk tube at 135°C for a 15-20 min. After that the solution was cooled to room temperature and stored under argon. Zinc stearate 226.4 mg and 5 mL of ODE were loaded into the 50 mL the three-neck round-bottom flask. The mixture was withstanded under vacuum for 20 min while heating to 110°C, and then the flask was filled with argon. After that the flask was heated up to

305°C, and 0.236 mL (191 mg, 0.716 mmol) of OlAm and 1.2 mL of the sulfur solution were injected successively by the syringe; the mixture was stirred at 305°C for 10 min and cooled to 240°C. Still 0.2 mL of the sulfur solution was added and the mixture was stirred for 10 min. Then, OlAm 0.248 mL (201 mg, 0.752 mmol) and Cd precursor 0.45 mL were injected to the flask. Subsequently, the sulfur solution (0.4, 0.6 mL) and Cd precursor (0.9, 1.35 mL) were injected alternately. The period between each injection was 10 min. After the last one the reaction mixture was withstanded at this temperature for 20 min and finally was cooled down to the ambient temperature. The mixture was diluted with acetone in a ratio of 1:2.5. The precipitate was redispersed in hexane precipitated by acetone in a ratio of 1:3 and separated by centrifugation at 5000 rpm. The upper liquid layer was discarded. The procedure of re-dispersion-precipitation-separation was repeated three times using hexane and acetone in a ratio of 1:2. At last time entire liquid was isolated from solid precipitate and discarded. Solid precipitate was redispersed in hot hexane, precipitated by acetone in a ratio of 1:3 and separated by centrifugation. Final precipitate was dispersed in cyclohexane. Non dispersible residue was separated by centrifugation at 8000 rpm (~20.000g) for 5 min and discarded. Finally, 102 mg of nanocrystals ZnS/CdS were yielded as dispersion in cyclohexane.

Preparation of aqueous dispersions of NCs

A hydrophilization procedure, which allows nanocrystals to be dispersed in water, was carried out by treating initially hydrophobic nanocrystals with an amphiphilic polyelectrolyte, copolymer of 2-(methacryloxy)ethyltrimethylammonium methyl sulfate and stearyl methacrylate, according to the described method[S4,S5]. Typically, nanocrystals (1 mg) were precipitated with ethanol from dispersion in cyclohexane, the precipitate was separated by centrifugation and redispersed in 0.5 ml of chloroform. Then dispersion was mixed with solution containing 3 mg of the copolymer of 2-(methacryloxy)ethyltrimethylammonium methyl sulfate and stearyl methacrylate in 0.5 mL of chloroform and 0.1 mL of ethanol, followed by the addition of 0.1 mL of DMSO. The volatile components were removed from mixture *in vacuo*, and the residue was dispersed in required volume of water.

Photocatalytic experiments

The hydrogen evolution reaction was carried out at 25° C in a three -necked glass reactor with a flat bottom and top with a volume of 100 ml, equipped with a thermostatically controlled jacket, a magnetic stirrer, a rubber stopper with a diaphragm, an inlet and outlet for argon. The photocatalytic hydrogen evolution reaction was carried out under illumination of 10 ml of a 0.01% aqueous dispersion of NCs with light. A 1.9 W laser with a wavelength of 445 nm or an arc metal-halogen lamp with a power of 570 W with a continuous spectral power distribution close to sunlight was used as light sources. The thickness of the illuminated dispersion layer was 20 mm, the diameter of the laser beam was 6 mm with a luminous flux density of 3.40 $W\cdot cm^{-2}$. The lamp illuminated the entire volume and provided a luminous flux density from 0 to 1.24 $W\cdot cm^{-2}$. To absorb the holes, 1 g of ascorbic acid was added. Periodically, gas samples were taken from the reactor using a 250 μL micro syringe equipped with a valve. The H_2 content in the samples was determined using a TSVET-800 gas chromatograph (OOO Tsvet) with a thermal conductivity detector and installed packed columns 2 m long filled with 80-100 mesh NaX zeolite. The chromatograph was preliminarily calibrated against hydrogen by the absolute calibration method. The measurements were carried out at a columns temperature of 50° C, argon was used as a carrier gas, a flow rate of 30 ml min^{-1}.

Characterization

TEM images were obtained using a LEO 912 AB OMEGA (Karl Zeiss) microscope with accelerating voltage of 100 kV. The particle size was determined using ImageJ software. At least 300 particles were used for particle size.

Powder X-ray diffraction patterns were recorded on a D8 Advance Vario diffractometer (Bruker AXS) equipped with a Ge(111) monochromator and a LynxEye position-sensitive detector in the θ–2θ transmission geometry using the CuKα1 radiation and an angular range of 10–90° with a step of 0.01°. The samples were deposited on the Kapton film (DuPont). Diffraction pattern profiles were fit using the TOPAS 5 program package (Bruker AXS). For this purpose, the hkl phases of hexagonal and cubic modifications of reference compounds (ZnS, CdS, ZnCdS) with constrained unit cell dimensions and refinable intensities of the peaks were applied in Pawley refinement. The phase contents were evaluated by the intensity contribution to the diffraction pattern of corresponding phases. The crystallite sizes were determined from the broadening of the Lorentzian component of the peaks.

Elemental microanalysis for determining cadmium, zinc and manganese concentration was performed by micro-Kjeldahl digestion (acid mineralization) with subsequent analysis by atomic absorption spectrometry on the atomic absorption spectrometer with flame atomization KVANT-2AT (CORTEC, Russia).

UV–vis absorption spectra (UV) were recorded with a Shimadzu 3600 UV–vis near-infrared spectrophotometer. Cyclohexane was used as the solvent. Photoluminescence (PL) and photoluminescence excitation (PLE) experiments were performed on a fluorometer Shimadzu RF-5301PC spectrofluorimeter. The excitation wavelength was 360 nm. All optical measurements were performed at room temperature under ambient conditions. The quantum yield of NCs was estimated with coumarin and rhodamine as a PL reference[S6].

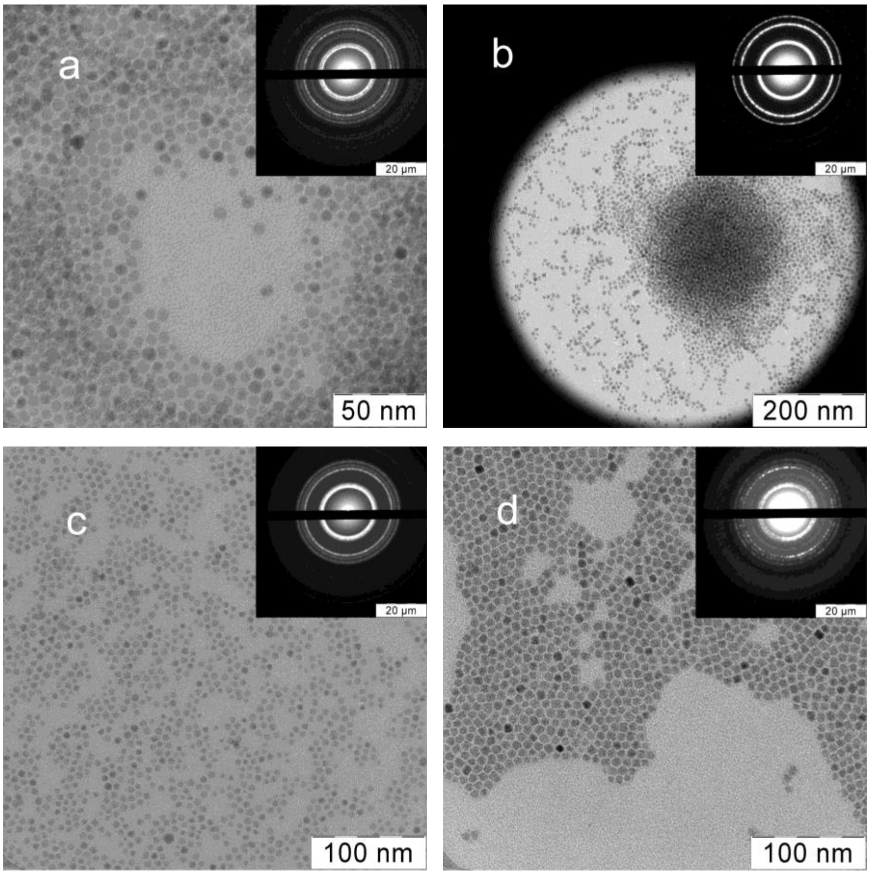

Figure S1. TEM images and electron diffraction patterns of NCs: (a) ZnCdS alloy NCs, Sample 2, (b) ZnS NCs, Sample 6, (c) Mn^{2+}-doped ZnCdS alloy NCs, Sample 3 and (d) Mn^{2+}-doped ZnCdS/ZnS core/shell NCs, Sample 4.

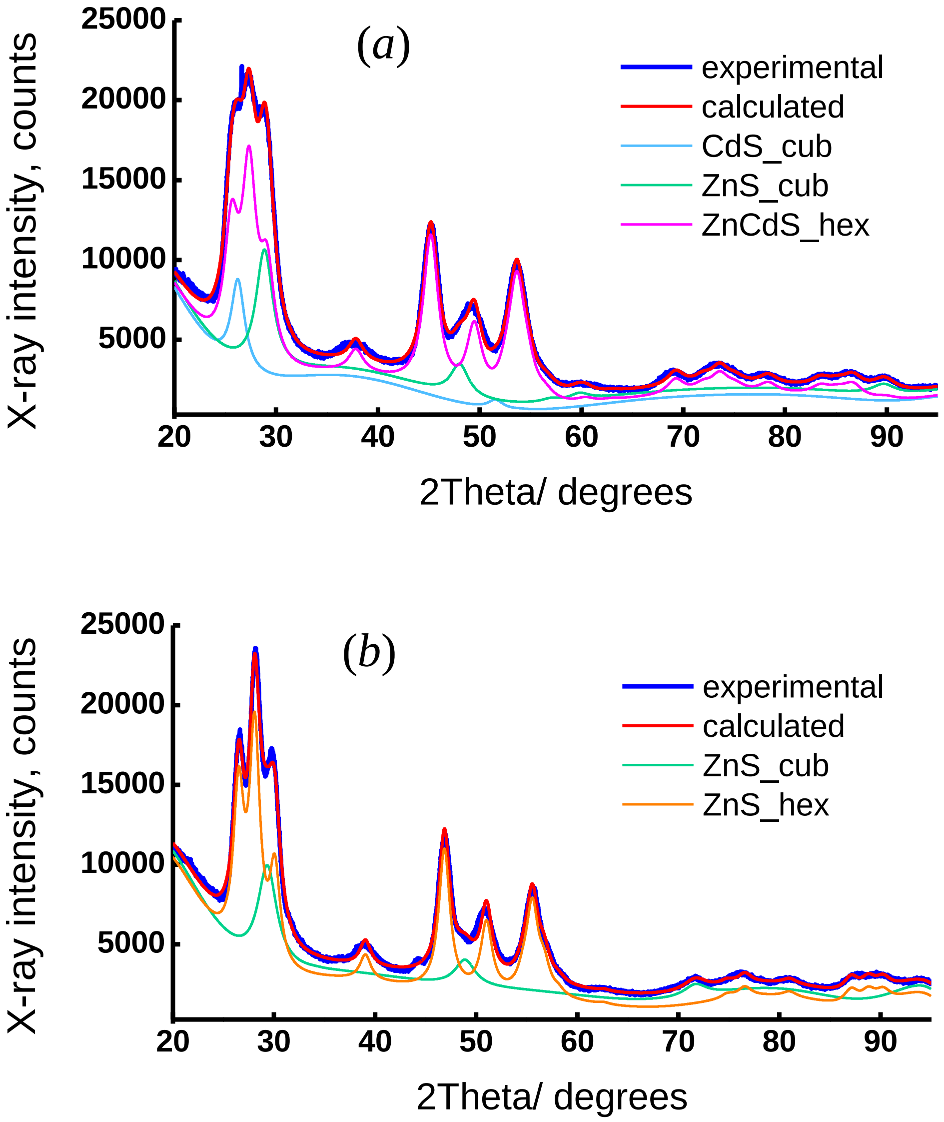

Figure S2. X-ray diffraction patterns of core nanocrystals Sample 2 (*a*) and core/shell nanocrystals Sample 4 (*b*) and their fits. Indices cub and hex denotes cubic or hexagonal phase, respectively.

Table S1. Structural characteristics of Sample 2 nanocrystals

Phase	**Type**	***a*, Å**	***c*, Å**	**D, nm**	**Contribution, %**
ZnS	cubic	5.350		4.6	16
CdS	cubic	5.870		5.8	8
$Zn_xCd_{1-x}S$	hexagonal	4.007	6.511	5.4	76

Table S2. H_2 evolution rate at different luminous flux densities.

Run	Luminous flux density W•cm^{-2}	H_2 evolution rate μmol·h^{-1}	
		sample 4	sample 5
1	0.728	9.57±0.12	34.7±0.2
2	0.523	3.84±0.05	30.5±1.0
3	0.424	3.98±0.17	25.8±1.1
4	0.283	1.21±0.04	18.0±0.4
5	0.124	0.81±0.02	5.42±0.03
6	0.046	0.45±0.01	1.40±0.02

References

S1 A. Gulin, A. Shakhov, A. Vasin, A. Astafiev, O. Antonova, S. Kochev, Y. Kabachii, A. Golub and V. Nadtochenko, *Appl. Surf. Sci*., 2019, **481**, 144.

S2 Yu. A. Kabachii, S. Yu. Kochev, N. D. Lenenko, V. I. Zaikovskii, A. S. Golub, M. Yu. Antipin and P. M. Valetskii, *Polym. Sci., Ser. B*, 2013, **55**, 95 (*Vysokomol. Soedin., Ser. B*, 2013, **55**, 243).

S3 A. Nag, S. Chakraborty and D. D. Sarma, *J. Am. Chem. Soc*., 2008, **130**, 10605.

S4 Yu. A. Kabachii, A. S. Golub’, A. S. Goloveshkin, S. S. Abramchuk, A. V. Shapovalov, M. I. Buzin, P. M. Valetskii and S. Yu. Kochev, *Russ. Chem. Bull., Int. Ed.*, 2014, **63**, 2355 (*Izv. Akad. Nauk, Ser. Khim.*, 2014, 2335).

S5 S. Yu. Kochev, Yu. N. Bubnov, S. S. Abramchuk, O. Yu. Antonova, P. M. Valetsky and Yu. A. Kabachii, *Mendeleev Commun*., 2017, **27**, 310.

S6 S. Fery-Forgues and D. Lavabre, *J. Chem. Educ*., 1999, **76**, 1260.