Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Water-soluble MoS_2 quantum dots for facile and sensitive fluorescent sensing of alkaline phosphatase activity in serum and live cells based on inner filter effect

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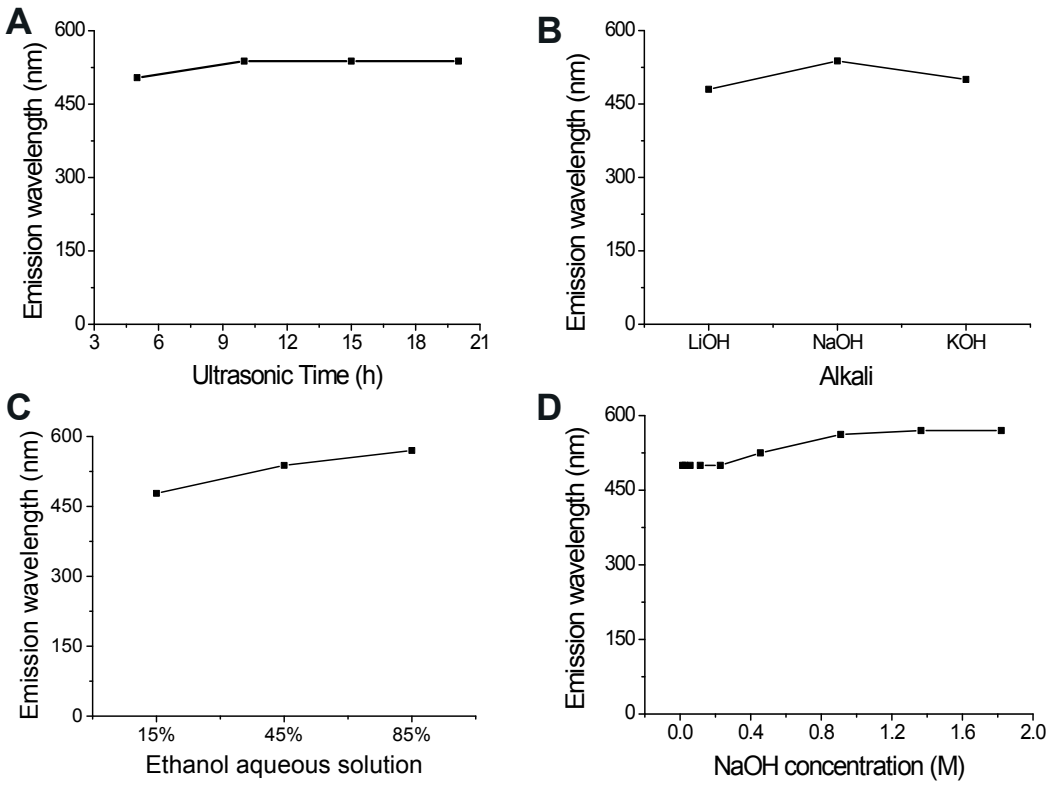

Figure S1. The emission wavelength of MoS_2 QDs prepared under (A) different ultrasonic time (5 to 20 h), (B) 0.4 g different alkalis (LiOH, NaOH, KOH), (C) 11 mL different ethanol aqueous solution (15%, 45% and 85%) and (D) different NaOH concentrations (0.140 mol/L to 1.820 mol/L).

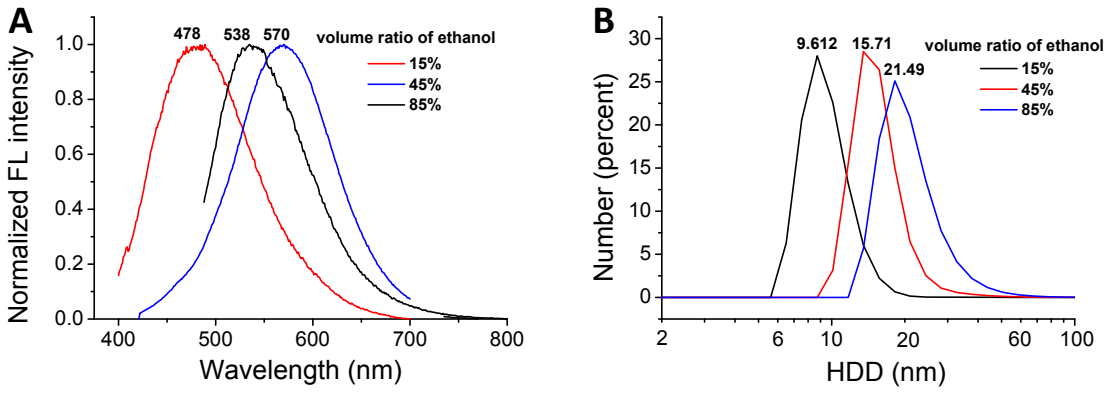

Figure S2. (A) The best fluorescence emission spectra and (B) hydrodynamic diameter (HDD) of MoS_2 QDs synthetized under different volume ratio of ethanol (15%-85%).

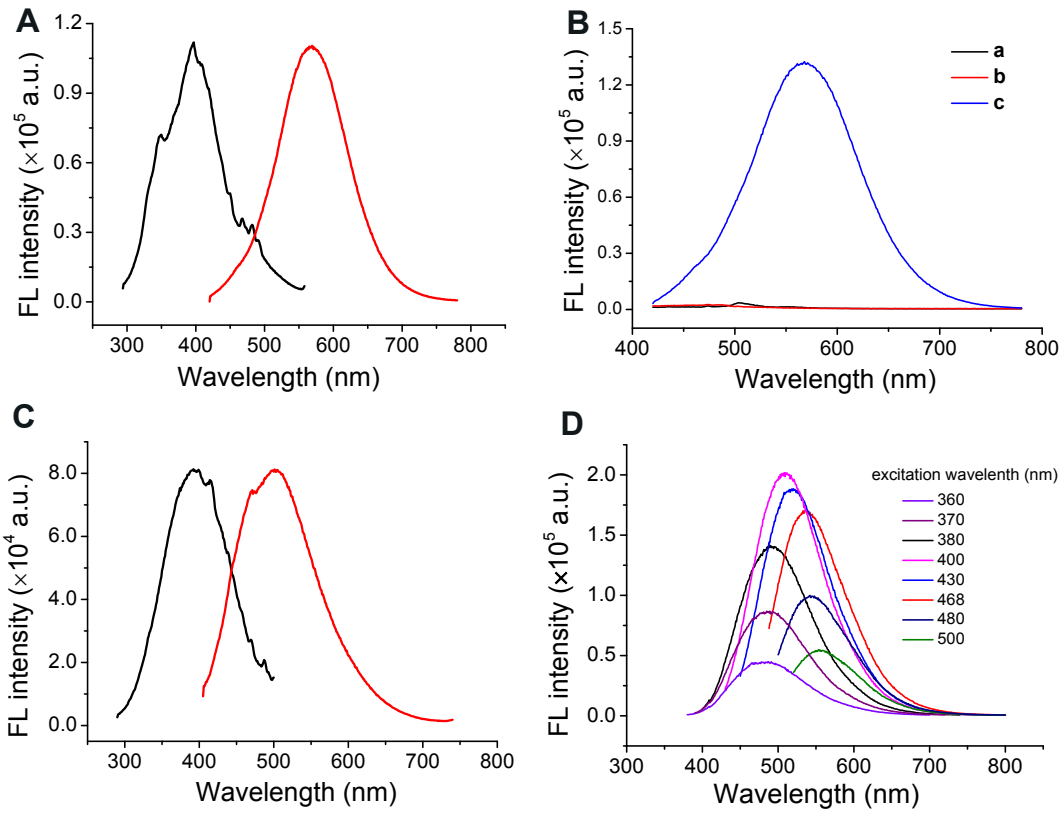

Figure S3. (A) Fluorescence excitation and emission spectra of MoS_2 QDs in the reaction solution (85 vol% ethanol alkaline aqueous solution), (B) fluorescence emission spectra of the reaction solution under different synthesis procedures (in the presence of a) NaOH, b) MoS_2 and c) both MoS_2 and NaOH), (C) fluorescence excitation and emission spectra of MoS_2 QDs after post-treatment (neutral aqueous solution) and (D) excitation depend emission spectra of MoS_2 QDs in neutral aqueous solution (excitation from 360 nm to 500 nm). The black line and red line in A and C refers to the excitation and emission spectrum, respectively.

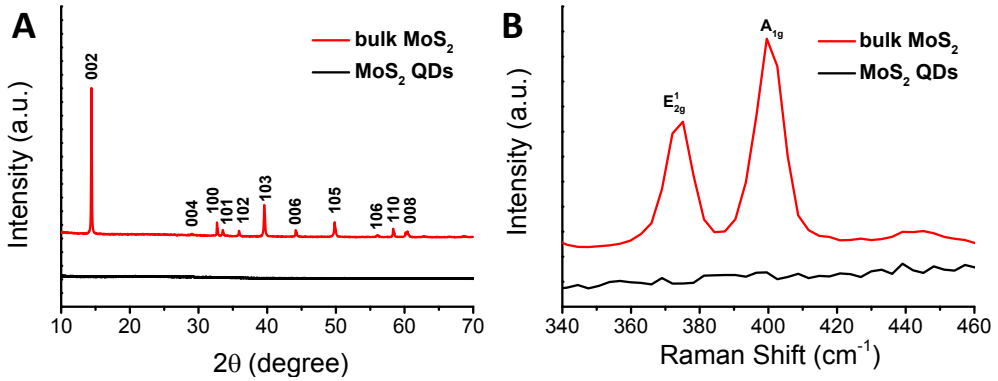

Figure S4. (A) XRD patterns and (B) Raman spectra of bulk MoS_2 powder (red line) and MoS_2 QDs (black line).

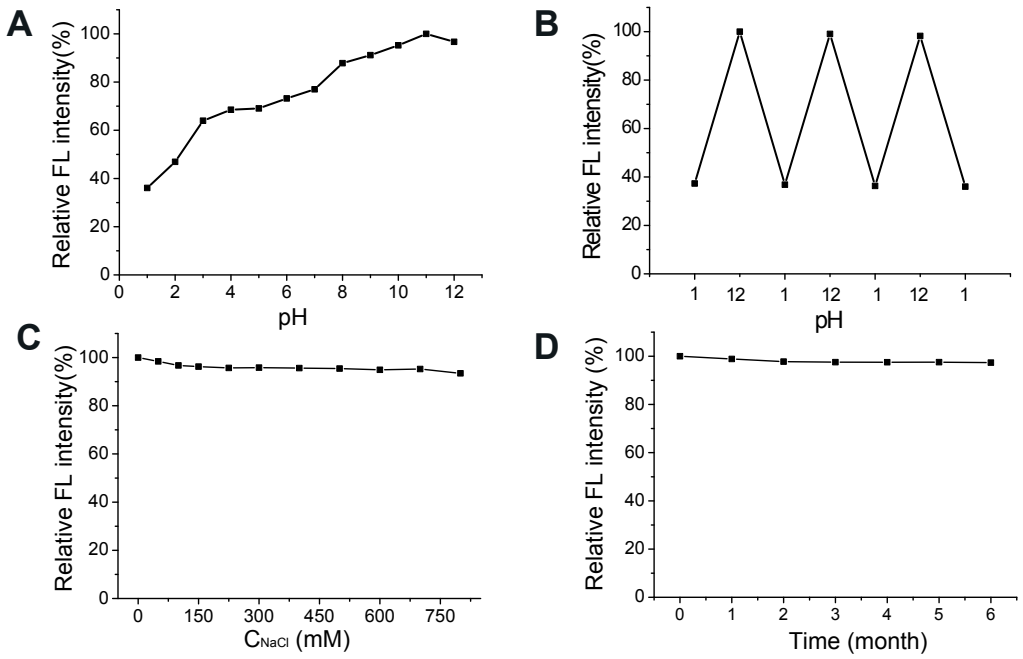

Figure S5. The FL intensity change of MoS_2 QDs (A) under different pH range (1-12), (B) from pH 1 to pH 12 for different circles, (C) under different NaCl concentration (0-800 mM) and (D) under different storage time (0-6 month).

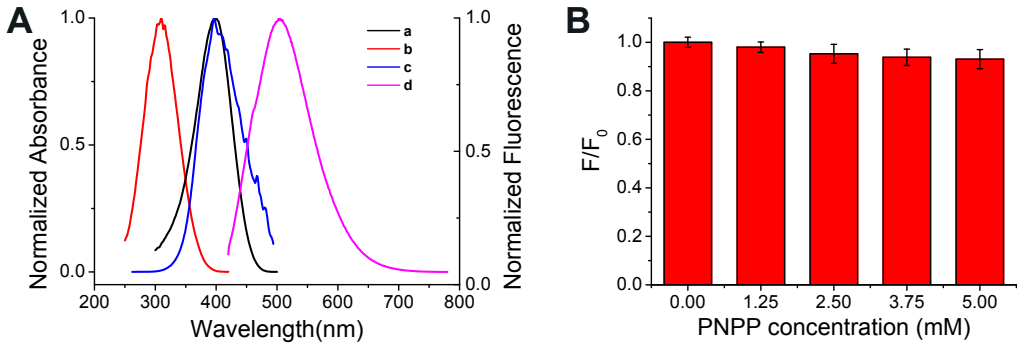

Figure S6. (A) Absorption spectrum of (a) p-nitrophenol, (b) p-nitrophenylphosphat and fluorescece (c) excitation spectrum, (d) emission spectrum of MoS_2 QDs. (B) The fluorescence change of MoS_2 QDs upon addition of various concentrations of PNPP from 0 to 5 mM.

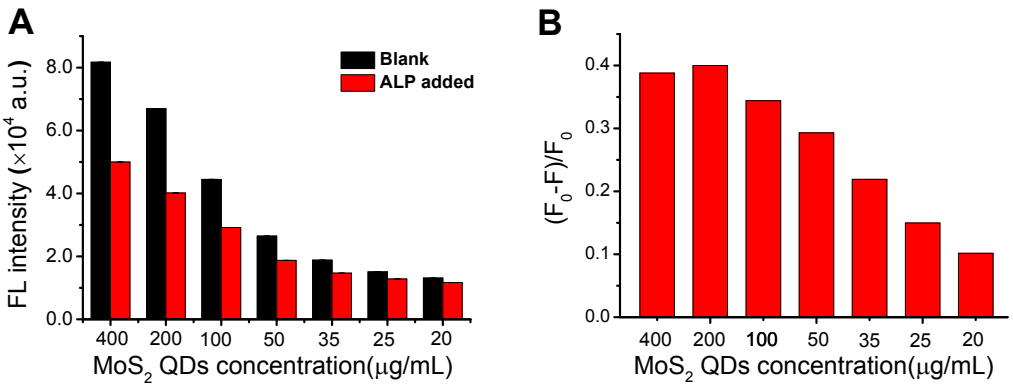

Figure S7. The influence of MoS_2 QDs concentration on the (A) fluorescence intensity and (B) fluorescence quenching efficiency of the reaction system when 10 U/L ALP was added.

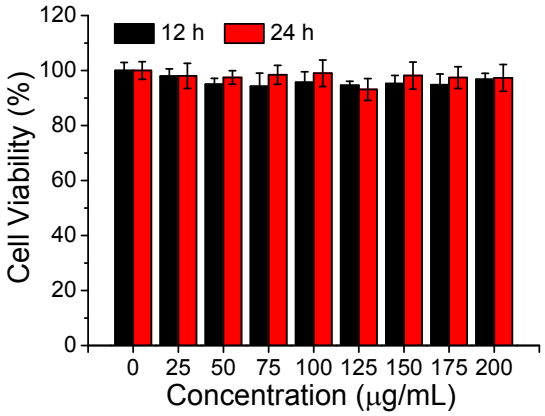

Figure S8. Cell viabilities of MoS_2 QDs using MCF-7 cells as tested model. Cells were treated by 0-200 μg/mL of MoS_2 QDs for 12 h and 24 h. Data were expressed as the means ± SD of data obtained from triplicate experiments.

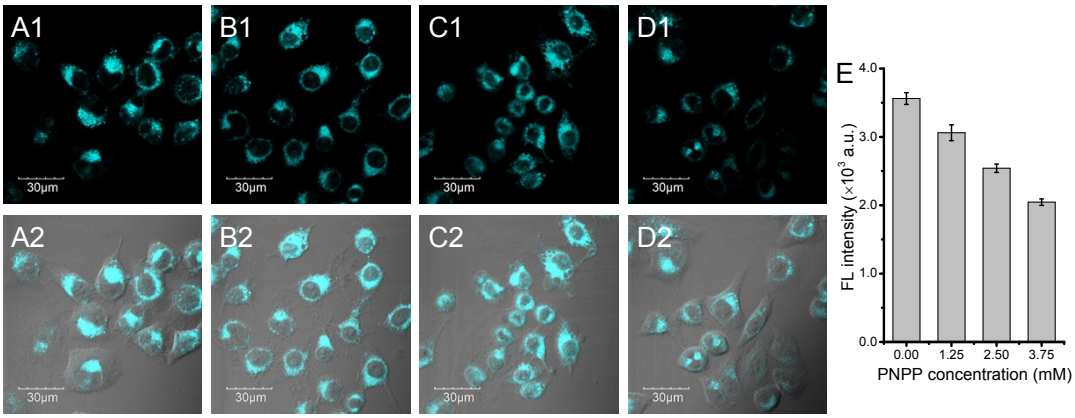

Figure S9. Confocal fluorescence microscopy of MoS_2 QDs (100 μg/mL) applied to ALP sensing in MCF-7 cells. Fluorescent images and merged fluorescent images of MoS_2 QDs located MCF-7 cells in the presence of (A1-A2) 0 mM PNPP, (B1-B2) 1.25 mM PNPP, (C1-C2) 2.5 mM PNPP and (D1-D2) 3.75 mM PNPP with an incubation time of 2 h. (E) Mean FL intensity of MCF-7 cells with different concentrations of PNPP in A-D (0-3.75 mM). The emission intensities collected in optical windows were collected at 475-525 nm upon the excitation at 405 nm for MoS_2 QDs.

Table S1 Comparison of performance of the new method with other reported ones.

Method	Materials used	Linear range (U/L)	Detection limit (U/L)	Application		Ref.
				Human serum samples	Cell imaging	
FL	PPi-Cu^{2+}/CQDs	16.7–782.6	1.1	NO	NO	[1]
FL	Au NCs	0.1–10	0.1	NO	NO	[2]
FL	coumarin@ Tb-GMP	25–200	10	NO	NO	[3]
FL	β-CD/QDs	0–800	10	NO	NO	[4]
FL	$PPESO_3$	0–30	0.5	standard addition method	NO	[5]
FL	SAHH-based probe	8–100	1	NO	NO	[6]
FL	AAP/CQDs	4.6–383.3	1.4	NO	NO	[7]
FL	Pdots@RB-hy	0.005–15	0.0018	standard addition method	NO	[8]
FL	AAP/GQDs	1.0–90	0.14	standard addition method	NO	[9]
EC	FAPP	–	0.4	NO	NO	[10]
ECL	PP/CdSe NPs	2.0–25	2.0	standard addition method	NO	[11]
EC	PMB/HP	0.1–10	0.1	NO	NO	[12]
Abs	ATP/Cit-AuNPs	–	8.0	NO	NO	[13]
Abs	AAP-Au/AgNRs	5.0–100	3.3	Clinical diagnosis	NO	[14]
FL	β-CD/CQDs	3.4–100	0.9	NO	NO	[15]
Abs	ATP/CTAB-AuNPs	100–600	10	Clinical diagnosis	NO	[16]
FL	PLP/AuNCs	1.0–200	0.05	standard addition method	NO	[17]
FL	MoS_2 QDs	0.1–5	0.1 (Lowest detect activity)	Clinical diagnosis	Yes	this work

CQDs: carbon quantum dots; Au NCs: gold nanoclusters; GMP: guanine monophosphate; β-CD/QDs: β-cyclodextrin-modified quantum dots; SAHH: S-adenosylhomocysteine hydrolase; GQDs: Graphene quantum dots; FAPP: ferrocenylaminophenyl phosphate; PMB/HP: 3'-Phosphorylated methylene blue labeled hairpin probe; PP: Phenyl phosphate;
FL: Fluorescence; EC: Electrochemistry; Abs: Colorimetry; ECL: Electrochemiluminescence.

Reference

[1] Z.S. Qian, L.J. Chai, Y.Y. Huang, C. Tang, J.J. Shen, J.R. Chen, H. Feng, A real-time fluorescent assay for the detection of alkaline phosphatase activity based on carbon quantum dots, Biosensors and Bioelectronics 68 (2015) 675-680.

[2] Y. Chen, W. Li, Y. Wang, X. Yang, J. Chen, Y. Jiang, C. Yu, Q. Lin, Cysteine-directed fluorescent gold nanoclusters for the sensing of pyrophosphate and alkaline phosphatase, Journal of Materials Chemistry C 2 (2014) 4080-4085.

[3] J. Deng, P. Yu, Y. Wang, L. Mao, Real-time ratiometric fluorescent assay for alkaline phosphatase activity with stimulus responsive infinite coordination polymer nanoparticles, Analytical chemistry 87 (2015) 3080-3086.

[4] L. Jia, J.-P. Xu, D. Li, S.-P. Pang, Y. Fang, Z.-G. Song, J. Ji, Fluorescence detection of alkaline phosphatase activity with β-cyclodextrin-modified quantum dots, Chemical Communications 46 (2010) 7166-7168.

[5] Y. Li, Y. Li, Z. Liu, X. Su, Sensitive fluorometric detection of alkaline phosphatase using a water-soluble conjugated polymer, RSC Advances 4 (2014) 42825-42830.

[6] J.-H. Lin, W.-L. Tseng, A method for fluorescence sensing of adenosine and alkaline phosphatase based on the inhibition of S-adenosylhomocysteine hydrolase activity, Biosensors and Bioelectronics 41 (2013) 379-385.

[7] Z. Qian, L. Chai, C. Tang, Y. Huang, J. Chen, H. Feng, Carbon quantum dots-based recyclable real-time fluorescence assay for alkaline phosphatase with adenosine triphosphate as substrate, Analytical chemistry 87 (2015) 2966-2973.

[8] J. Sun, H. Mei, F. Gao, Ratiometric detection of copper ions and alkaline phosphatase activity based on semiconducting polymer dots assembled with rhodamine B hydrazide, Biosensors and Bioelectronics 91 (2017) 70-75.

[9] H. Huang, B. Wang, M. Chen, M. Liu, Y. Leng, X. Liu, Y. Li, Z. Liu, Fluorescence turn-on sensing of ascorbic acid and alkaline phosphatase activity based on graphene quantum dots, Sensors and Actuators B: Chemical 235 (2016) 356-361.

[10] S. Goggins, C. Naz, B.J. Marsh, C.G. Frost, Ratiometric electrochemical detection of alkaline phosphatase, Chemical Communications 51 (2015) 561-564.

[11] H. Jiang, X. Wang, Alkaline phosphatase-responsive anodic electrochemiluminescence of CdSe nanoparticles, Analytical chemistry 84 (2012) 6986-6993.

[12] L. Zhang, T. Hou, H. Li, F. Li, A highly sensitive homogeneous electrochemical assay for alkaline phosphatase activity based on single molecular beacon-initiated T7 exonuclease-mediated signal amplification, Analyst 140 (2015) 4030-4036.

[13] W. Zhao, W. Chiuman, J.C. Lam, M.A. Brook, Y. Li, Simple and rapid colorimetric enzyme sensing assays using non-crosslinking gold nanoparticle aggregation, Chemical Communications (2007) 3729-3731.

[14] Z. Gao, K. Deng, X.-D. Wang, M. Miró, D. Tang, High-resolution colorimetric assay for rapid visual readout of phosphatase activity based on gold/silver core/shell nanorod, ACS applied materials & interfaces 6 (2014) 18243-18250.

[15] C. Tang, Z. Qian, Y. Huang, J. Xu, H. Ao, M. Zhao, J. Zhou, J. Chen, H. Feng, A fluorometric assay for alkaline phosphatase activity based on β-cyclodextrin-modified carbon quantum dots through host-guest recognition, Biosensors and Bioelectronics 83 (2016) 274-280.

[16] C.M. Li, S.J. Zhen, J. Wang, Y.F. Li, C.Z. Huang, A gold nanoparticles-based colorimetric assay

for alkaline phosphatase detection with tunable dynamic range, Biosensors and Bioelectronics 43 (2013) 366-371.

[17] M.I. Halawa, W. Gao, M. Saqib, S.A. Kitte, F. Wu, G. Xu, Sensitive detection of alkaline phosphatase by switching on gold nanoclusters fluorescence quenched by pyridoxal phosphate, Biosensors and Bioelectronics 95 (2017) 8-14.