

Supporting Information

One-pot synthesis of poly(vinylpyrrolidone)-encapsulated color-emitting silicon quantum dots for sensitive and selective detection of 2,4,6-trinitrophenol

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Chemicals

N-[3-(trimethoxysilyl)propyl]-ethylenediamine (DAMO), poly(vinylpyrrolidone) (PVP) (K 30), 2,4,6-trinitrophenol (TNP) was purchased from Taishan Chemical Factory. Phenol, benzene, 2-nitrobenzaldehyde (2-NBAD), 4-nitrobenzaldehyde (4-NBAD), 4-nitrobenzoic acid (4-NBA), aniline, di-nitroaniline (DN-Aniline), glutathione (GSH), catechol (CC), hydroquinone (HQ), 2-aminophenol (2-A-phenol), 3-aminophenol (3-A-phenol), 3-benzenediol (resorcinol), 2-nitrophenol (2-N-phenol) and 4-nitrophenol (4-N-phenol), were purchased from Sigma-Aldrich. NaH₂PO₄ and Na₂HPO₄ were purchased from Tianjin Guangfu Technology Development Co., Ltd. Phosphate buffered saline solutions (PBS) were obtained with 10 mM NaH₂PO₄ and Na₂HPO₄. All reagents are of

analytical grade and used without any further purification. All solutions were prepared using deionized water in experimental procedures.

Apparatus and characterization

Transmission electron microscopy (TEM) image was obtained with Spectra 300 (ThermoFisher Scientific). Fourier transform infrared spectrum (FT-IR) was conducted on a Nicolet Nexus 670 spectrometer using KBr pellets. X-ray photoelectron spectra (XPS) performance was conducted using PHI-5702 machine. Absorption spectra were recorded on TU-1901 UV-Vis spectrometer. Lifetime and quantum yield were performed by a time-correlated-single-photo-counting (TCSPC) system from FL 920 spectrometer with $\lambda_{\text{ex}} = 350$ nm. By setting the emission and excitation slits at 5 nm, the fluorescence analysis was conducted by RF-5301 spectrofluorophotometer.

Synthesis conditions

In this study, PVP and DAMO were used as reducing agent and silicon source respectively. The synthetic design of PVP-Si QDs was demonstrated in Scheme 1. PVP-Si QDs were prepared in one easy step by mixing PVP and DAMO. When the volume of DAMO was 1 mL and the amount of PVP was 0.35 g, the reaction time was 4 h, and the reaction temperature was 110 °C, the highest fluorescence intensity was obtained. In the control experiment, under the same reaction conditions, as demonstrated in Fig. S1 under the excitation wavelength at 350 nm, the FL intensity for only PVP (black line) was negligible; that of only DAMO was also very weak with the emitted wavelength at 437 nm (red line). Therefore, the emission peak was observed with the high FL intensity of PVP-Si QDs synthesized by DAMO and PVP (blue line). Briefly, PVP-Si QDs were responsible for further fluorescent analysis.

Analysis of TNP in water samples

The Yellow River water sample was obtained from Lanzhou (Gansu, China). Tap water sample was collected from local laboratory in Lanzhou University (Gansu, China). Drinking water sample was received from one supermarket in Lanzhou (Gansu, China). The samples were centrifuged at 1200 rpm for 15 min and the supernatant was filtered through a 0.22 μm pore membrane. Dilution of all samples was performed using 10.0 mM PBS buffer solution (pH 7.4) before detection [1]. The fluorescence emission spectra were tested under excitation wavelength at 350 nm after 1 min at room temperature. The concentration of TNP in water samples was determined by the working curve.

Preparation of the fish tissues samples

Carp and Weever fishes were bought from a local supermarket (Lanzhou, Gansu). The pretreatment steps of the fish samples are as follows: after being ground, 20.0 g of the fish tissue was mixed with 20 mL of acetonitrile and extracted with an ultrasonic instrument at room temperature for 60 min. After centrifugation, the supernatant was collected and filtered. Then, anhydrous sodium sulfate was added to the above mixture. Subsequently, the acetonitrile was evaporated and dried at 50 $^{\circ}\text{C}$. Finally, the prepared samples were mixed with 10 mM PBS solution (pH 7.4) for further use [2].

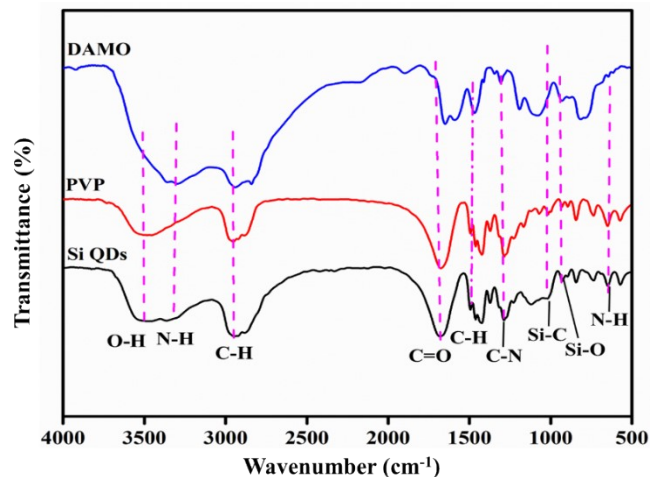


Fig. S1. FT-IR spectra of DAMO (blue line), PVP (red line) and the synthesized PVP-Si QDs (black line).

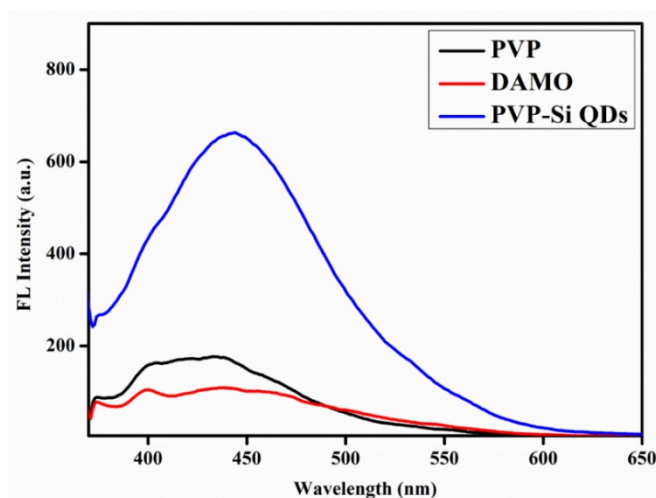


Fig. S2. Fluorescence spectra of only PVP (black line), only DAMO (red line) and the mixed solution of DAMO and PVP (blue line) under the same reaction conditions.

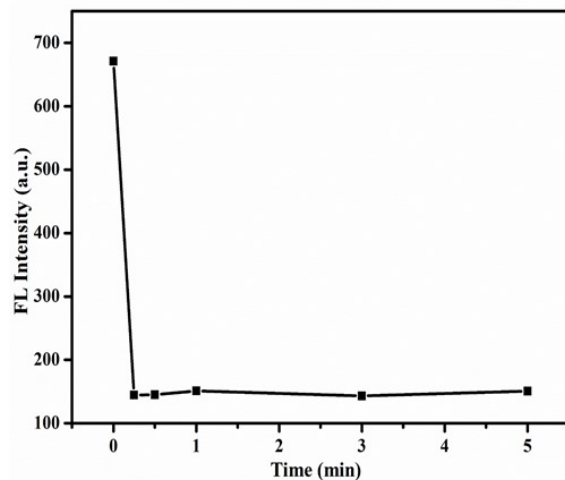


Fig. S3. Time-dependent interaction between PVP-Si QDs and TNP (80 μM) at room temperature.

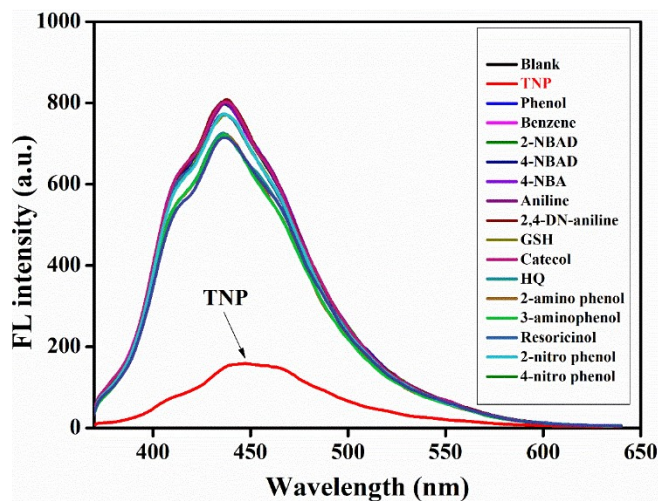


Fig. S4. Fluorescent spectra of PVP-Si QDs in the presence of TNP (80 μM) and other kinds of molecules, $\lambda_{\text{ex}} = 350 \text{ nm}$.

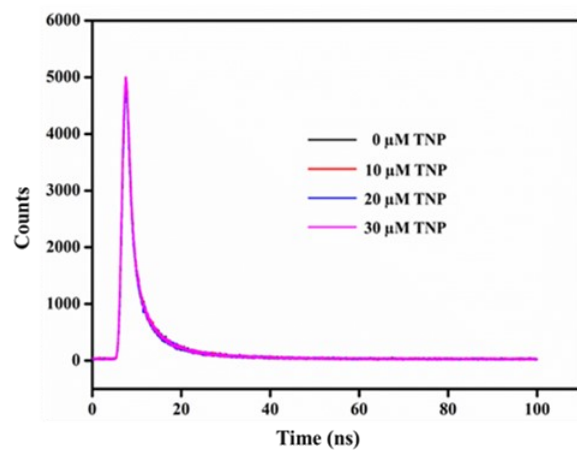


Fig. S5. Lifetimes of steady state FL of PVP-Si QDs with different concentrations of TNP.

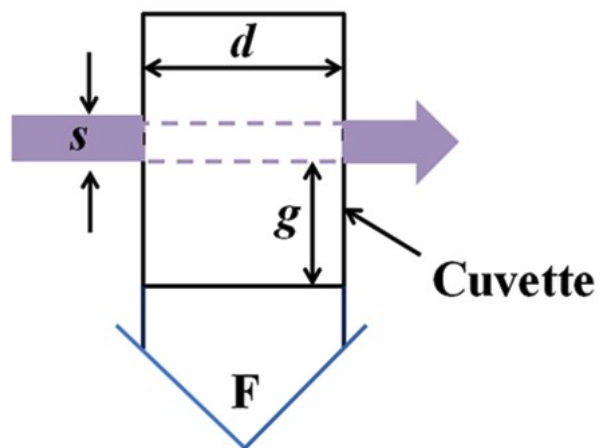


Fig. S6. The parameters used in equation (1).

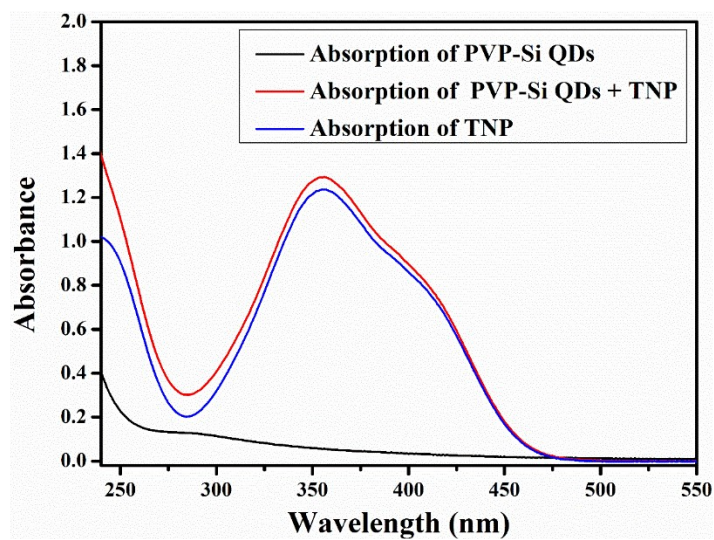


Fig. S7. UV-vis absorption spectra of TNP (blue line), PVP-Si QDs before mixing TNP (black line) and after mixing TNP (red line).

Table S1.

Comparison of the present PVP-Si QDs with other reported probes for the detection of TNP.

Material	Method	Synthesized time	Linear range (μM)	LOD (μM)	Ref.
CuNCs	Fluorescence	8 h	2-40	0.98	3
GSH-CuNCs	Fluorescence	1 h	9.9-43	2.74	4
NACs	Fluorescence	10 min	0.-24	2.1	5
N-GQDs	Fluorescence	40 min	0-16	0.92	6
NP-CDs	Fluorescence	6 h	25-350	23	7
PI-CONs	Fluorescence	4 days	0.5-10	0.25	8
N@CDs	Fluorescence	10 h	1-75	2.45	9
Cys-CuNCs	Fluorescence	2 h	2.5-25	0.19	10
NFPNs	Fluorescence	8 h	0.5-150	0.7	11
PVP-Si QDs	Fluorescence	4 h	0.5-80	0.34	This work

Table S2.

Influence of different concentrations of TNP on fluorescence lifetime of PVP-Si QDs.

TNP concentration (μM)	Fluorescence lifetime (ns)
0	4.26
10	4.23
20	4.21
30	4.30

Table S3.

Parameters used to calculate IFE of TNP on the fluorescence of the PVP-Si QDs.

TNP (μM)	A_{ex}^{a}	A_{em}^{b}	CF^{c}	$F_{\text{obsd}}^{\text{d}}$	$F_{\text{cor}}^{\text{e}}$	$E_{\text{obsd}}^{\text{f}}$	$E_{\text{cor}}^{\text{g}}$
0	0.033	0.011	1.09	669.0	727.5	0.000	0.000
5	0.122	0.044	1.19	607.0	723.5	0.092	0.005
10	0.191	0.059	1.31	547.0	716.6	0.182	0.015
20	0.329	0.100	1.56	454.0	708.8	0.321	0.026
30	0.520	0.159	1.98	356.0	704.7	0.468	0.031

^a A_{ex} is the absorbance of the PVP-Si QDs by the addition of TNP at 350 nm.

^b A_{em} is the absorbance of the PVP-Si QDs by the addition of TNP at 437 nm.

^cCorrected factor (CF) is calculated as $F_{\text{cor}}/F_{\text{obsd}}$.

^d F_{obsd} is the measured fluorescence intensity of the PVP-Si QDs upon addition of TNP.

^e F_{cor} is the corrected fluorescence intensity in eq. 1 by removing IFE from the measured fluorescence intensity (F_{obsd}).

^f $E_{\text{obsd}} = 1 - F_{\text{obsd}}/F_{\text{obsd},0}$, in which $F_{\text{obsd},0}$ is the observed FL intensities of the PVP-Si QDs in the absence of TNP.

^g $E_{\text{cor}} = 1 - F_{\text{cor}}/F_{\text{cor},0}$, in which $F_{\text{cor},0}$ is the corrected FL intensities of the PVP-Si QDs in the absence of TNP.

References

- [1] Y. Han, Y. Chen, J. Liu, X. Niu, Y. Ma, S. Ma, X. Chen, Room-temperature synthesis of yellow-emitting fluorescent silicon nanoparticles for sensitive and selective

- determination of crystal violet in fish tissues, *Sensor Actuat. B-Chem.* 263 (2018) 508–516, <https://doi.org/10.1016/j.snb.2018.02.163>.
- [2] S. Nsanzamahoro, F.P. Mutuyimana, Y.X. Han, S. Ma, M. Na, J. Liu, Y. Ma, C. Ren, H.L. Chen, X.G. Chen, Highly selective and sensitive detection of catechol by one step synthesized highly fluorescent and water-soluble silicon nanoparticles, *Sensor Actuat. B-Chem.* 281 (2019) 849–856, <https://doi.org/10.1016/j.snb.2018.11.016>.
- [3] D.G. Babar, S.S. Garje, Nitrogen and phosphorus co-doped carbon dots for selective detection of nitro explosives, *ACS Omega* 5 (2020) 2710–2717, <https://doi.org/10.1021/acsomega.9b03234>.
- [4] R. Patel, S. Bothra, R. Kumar, G. Crisponi, S.K. Sahoo, Pyridoxamine driven selective turn-off detection of picric acid using glutathione stabilized fluorescent copper nanoclusters and its applications with chemically modified cellulose strips, *Biosens. Bioelectron.* 102 (2018) 196–203, <https://doi.org/10.1016/j.bios.2017.11.031>.
- [5] W.J. Zhang, S.G. Liu, L. Han, Y. Ling, L.L. Liao, S. Mo, H.Q. Luo, N.B. Li, Copper nanoclusters with strong fluorescence emission as a sensing platform for sensitive and selective detection of picric acid, *Anal. Methods* 10 (2018) 4251–4256, <https://doi.org/10.1039/c8ay01357h>.
- [6] K. Shanmugaraj, S.A. John, Inner filter effect based selective detection of picric acid in aqueous solution using green luminescent copper nanoclusters, *New J. Chem.* 42 (2018) 7223–7229, <https://doi.org/10.1039/C8NJ00789F>.
- [7] M. Kaur, S.K. Mehta, S.K. Kansal, A fluorescent probe based on nitrogen doped graphene quantum dots for turn off sensing of explosive and detrimental water

- pollutant, TNP in aqueous medium, *Spectrochim. Acta A* 180 (2017) 37–43, <https://doi.org/10.1016/j.saa.2017.02.035>.
- [8] C. Zhang, S. Zhang, Y. Yan, F. Xia, A. Huang, Y. Xian, Highly fluorescent polyimide covalent organic nanosheets as sensing probes for the detection of 2,4,6-trinitrophenol, *ACS Appl. Mater. Interfaces* 9 (2017) 13415–13421, <https://doi.org/10.1021/acsami.6b16423>.
- [9] J. Liu, F. Wu, A. Xie, C. Liu, H. Bao, Preparation of nonconjugated fluorescent polymer nanoparticles for use as a fluorescent probe for detection of 2,4,6-trinitrophenol, *Anal. Bioanal. Chem.* 412 (2020) 1235–1242, <https://doi.org/10.1007/s00216-019-02360-6>.
- [10] P. Ghosh, J. Das, A. Basak, S.K. Mukhopadhyay, P. Banerjee, Intracellular fluorometric recognition of explosive and mutagenic nitroaromatics by a luminescent phenanthrene-naphthalene sulfone, *ChemistrySelect* 5 (2020) 8722–8728, <https://doi.org/10.1002/slct.202001295>.
- [11] A. Saravanan, M. Maruthapandi, P. Das, S. Ganguly, S. Margel, J.H.T. Luong, A. Gedanken, Applications of N-doped carbon dots as antimicrobial agents, antibiotic carriers, and selective fluorescent probes for nitro explosives, *ACS Appl. Bio Mater.* 3 (2020) 8023–8031, <https://doi.org/10.1021/acsabm.0c01104>.