Electronic Supplementary Material (ESI) for Analytical Methods

Polyvinyl pyrrolidone modified ZnS nanoparticles as a highly selective and sensitive nanosensor for iodide ion

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Materials and methods:

All chemicals used were of analytical grade or of the highest purity available. All solutions were prepared with double-distilled, deionised Milli-Q water (18 MΩ cm). Zinc acetate dihydrate Zn $(CH_3COO)_2 \cdot 2H_2O$, sodium sulfide (Na_2S) and polyvinylpyrrolidone (PVP) were purchased from Sigma-Aldrich. A 1×10^{-2} M iodide stock solution was prepared by dissolving 0.166 g of potassium iodide (Merck) in water and diluting to 100 mL in a volumetric flask and standardized according to reported procedure[1]. Working standard solutions were prepared daily in deionised water.

Synthesis of PVP capped ZnS nanoparticles (PVP-ZnSNps)

The PVP-ZnSNps were prepared by a soft chemical method as reported by Mandel and coworkers with some modification [2]. 5 mg of PVP was dissolved in 50 ml of water and stirred for 20 min. Then 5 ml of 0.1 M Zn $(CH_3COO)_2 \cdot 2H_2O$ solution was added with constant stirring. The pH of the solution was adjusted to 8.0 by 0.1 N NaOH. Further, 10 ml of freshly prepared 0.05 M aqueous solution of Na_2S was added drop wise to get a transparent colorless aqueous dispersion of PVP-ZnSNps. This dispersion was stirred for 20 min and then refluxed for 8 h. Here we maintain 1:1 molar ratio of Zn: S. The dispersed nano particles were collected from aqueous solution with the addition of a known amount of acetone (5 ml) and by centrifugation at 8000 rpm. Immediate flocculation of nanoparticles occurred. To remove unreacted sulfide and excess PVP, the particles were washed thrice with acetone and water. The purified PVP-ZnSNps were dried under vacuum.

Physicochemical Characterization of PVP-ZnSNps

Nanoparticle characterization is essential to establish a control on the size of the nanoparticles during synthesis and for understanding the morphology as well as their applicability. Herein, the optical properties of the nanoparticles were measured by UV–Vis absorption and fluorescence spectroscopy through Jasco V-570 UV–Vis. Spectrometer and Fluorolog Horiba Jobin Yvon spectro fluorimeter respectively at room temperature (25± 2ºC). Interactions between the ligand and the nanoparticles were evaluated by FT-IR spectra; which was recorded on Bruker Tensor-27 FT-IR spectrometer. Transmission electron micrograph (TEM) was recorded by JEOL, JEM-2100(200 kV) to observe the morphology of nanoparticles.

3.2.4 Detection of Iodide (I^-)

The procedure followed to investigate the anion recognition ability of PVP-ZnSNps is as follows. Stock solutions (1×10^{-2} M) of various anions (F^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, S^{-2}, ClO_4^-, CN^-, IO_3^-) were prepared and diluted as and when required. A series of solutions were prepared in 5 ml volumetric flasks each containing 0.5 ml of various anions (1×10^{-5} M), PVP-ZnSNps (1ml, 1×10^{-5} M) and phosphate buffer solution (2 ml, pH 7.4). The final volume of the resulting mixture was made up to 5 ml by the addition of deionized water. The fluorescence spectra were obtained using a fluorescence spectrophotometer operated at an excitation wavelength of 485 nm.

3.2.5 Analysis of real samples

Seawater (collected from the Gulf of Khambhat, Gujarat) and river water samples (collected from Sabarmati River Ahmedabad) and local tap water was filtered through a 0.22 µm membrane filter paper and used for analysis without any further purification process.

Samples of edible salt (0.3g) were dissolved in 5 ml deionized water. Prior to analysis these sample solutions were treated for 10 minutes with 5.0 mM ascorbic acid to reduce IO_3^- to I^-. The resulting solution was filtered through 0.22 µm membrane filter paper and used for analysis.

For the urine samples; 2 ml of acetonitrile and 6 ml of de-ionized water was added alongwith 2 ml urine in centrifuge tubes. The tubes were vortex mixed for 1 min. and centrifuged at 1500

rpm for 15 minutes. The supernatant of these solutions were taken and filtered through a 0.22 µm membrane filter paper prior to use.

Real Samples analysis

In order to confirm the applicability of PVP-ZnSNps nanosensor for analyzing iodide in real samples, they were applied to detect and determine iodide in sea water, river water, tap water, urine sample and edible salt sample. The real samples were analyzed by standard addition method. A known amount of standard iodide solution was spiked in an unknown real sample and the possibility of applying the present optical sensor for analysis of samples was tested by determining the recovery of known amounts of iodide ions added to the samples.

Figure S1

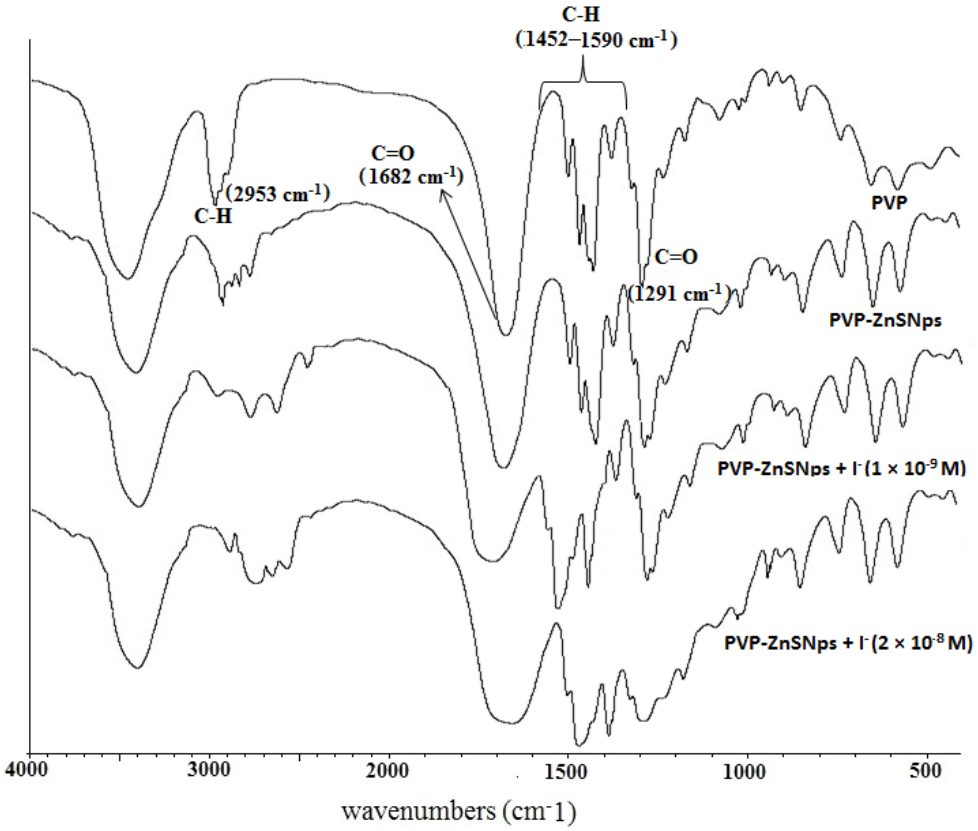

Fig.S1 FT-IR spectra of ZnS Nps and PVP-ZnSNps

Figure S2

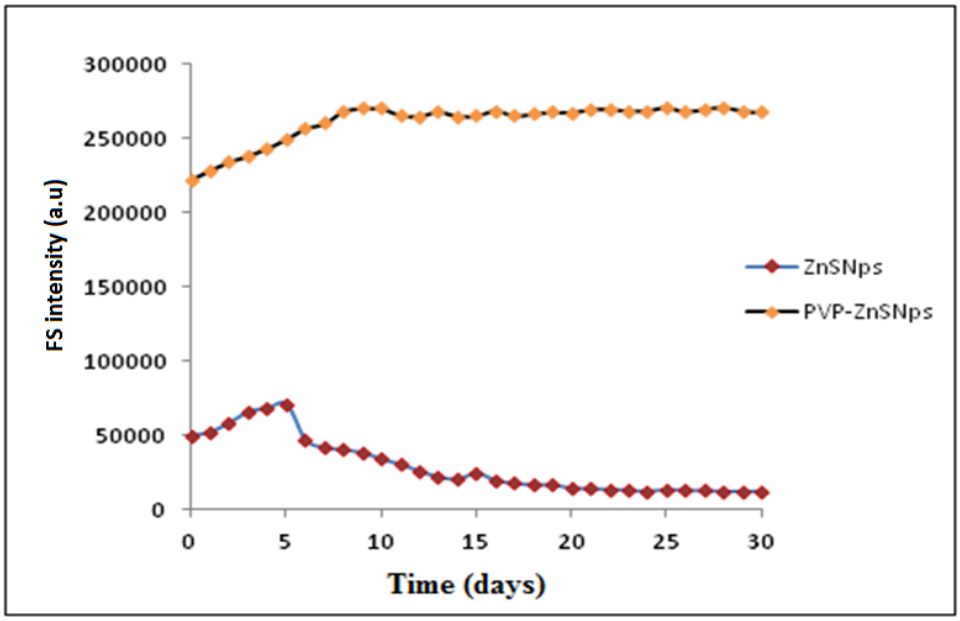

Fig.S2 Stability of ZnSNps and PVP-ZnSNps

Figure S3

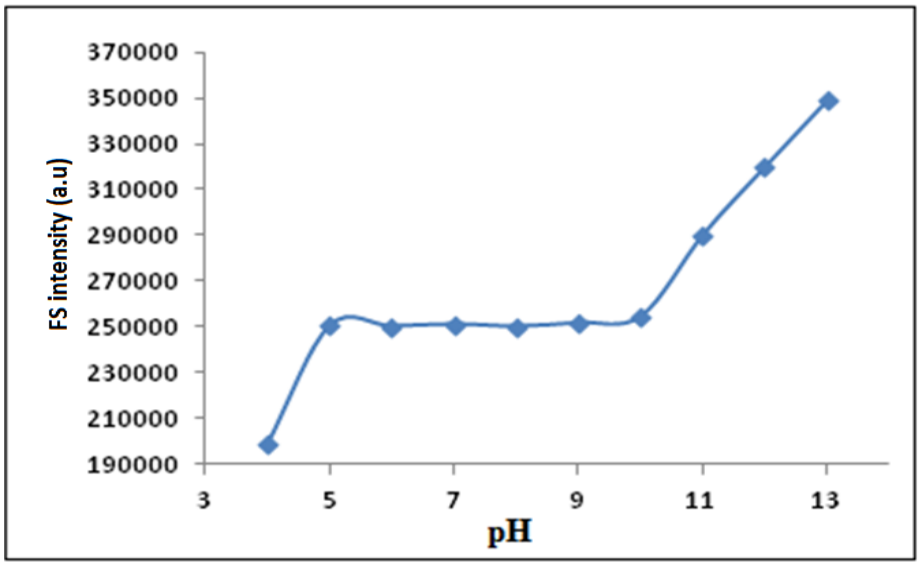

Fig. S3 Effect of pH values on the FS intensity of PVP-ZnSNps

Figure S4

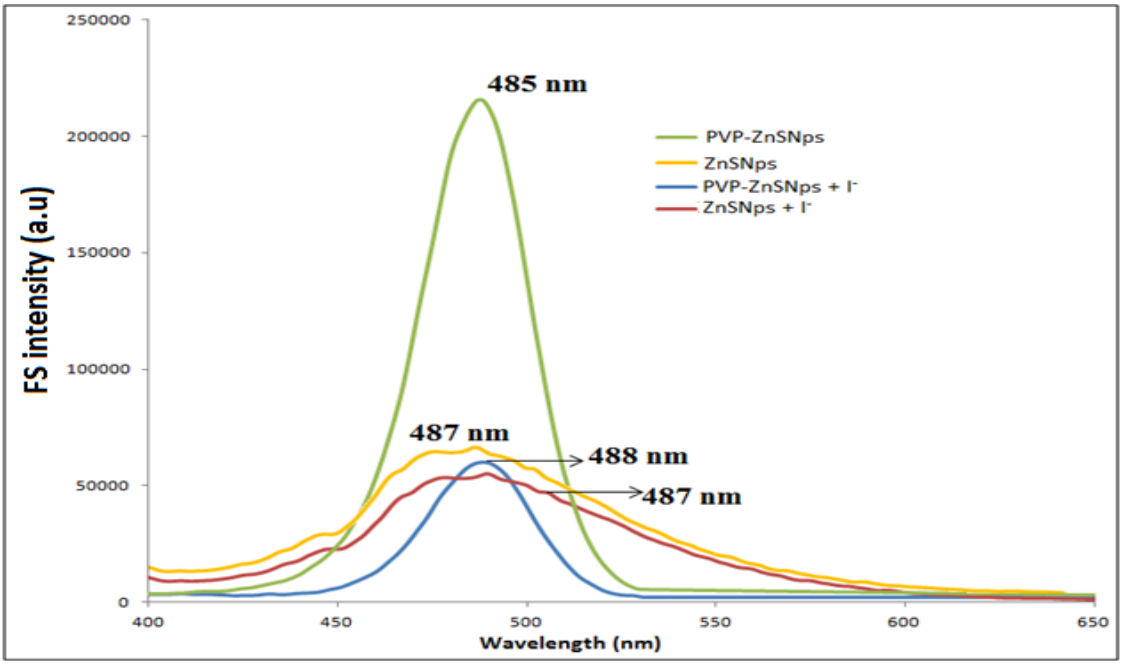

Fig.S4 Effect of iodide solution on FS intensity of ZnSNps and PVP-ZnSNps

Figure S5

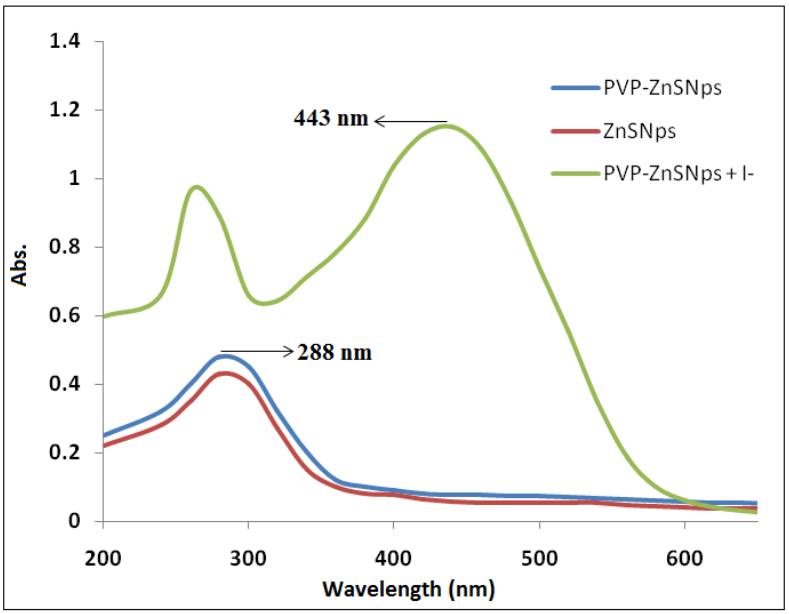

Fig. S5 Absorption spectra of ZnSNps, PVP-ZnSNps and PVP-ZnSNps + I-

Figure S6

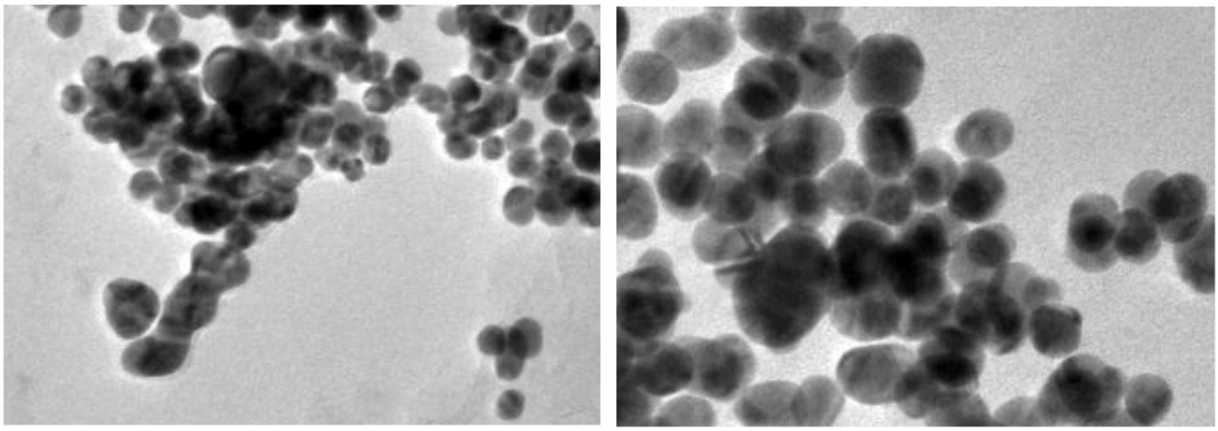

Fig. S6: TEM images after the addition of I^- in PVP-ZnSNps

Figure S7

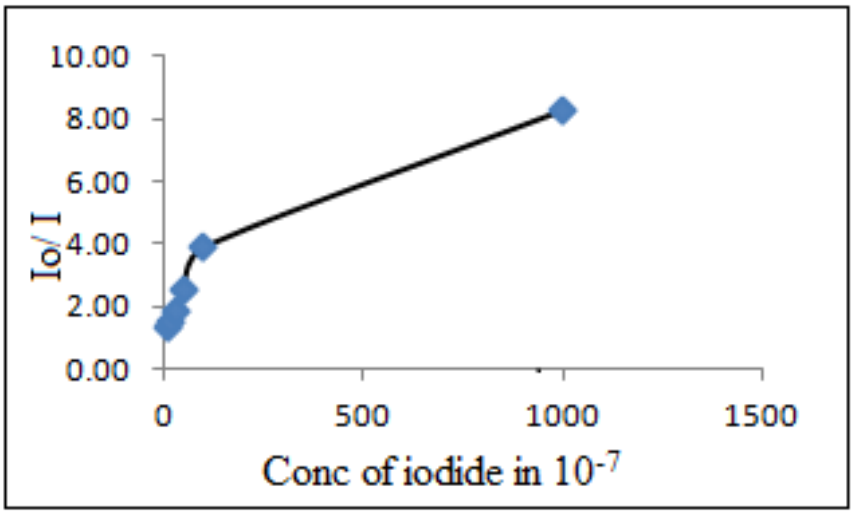

Fig. S7: Stern-Volmer plot for quenching of PVP-ZnSNps fluorescence by iodide.

Figure S8

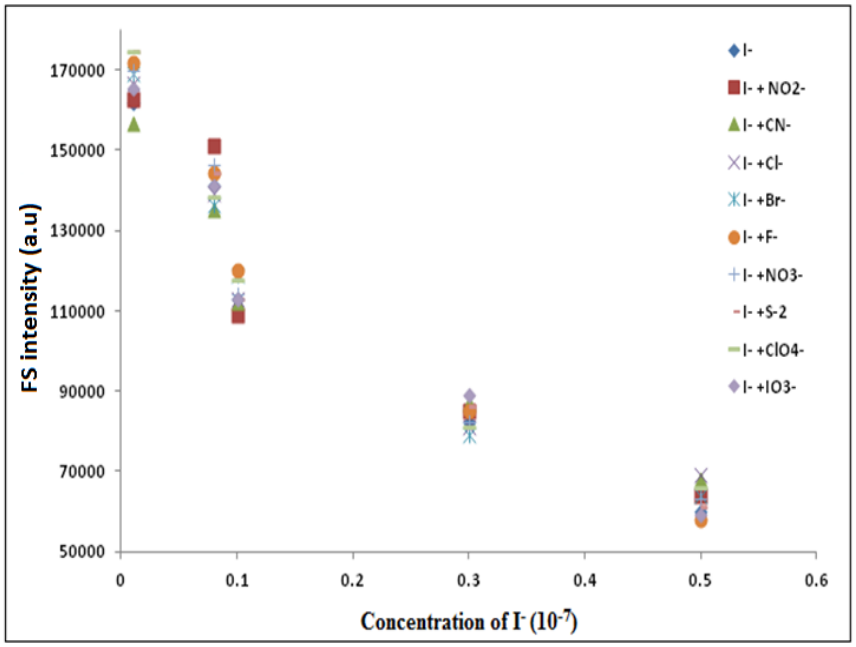

Fig.S8. The fluorescence quenching of PVP-ZnSNps in the presence of I^- and the mixtures with equal amount of other anions

Table S1 : Comparision table of proposed nanosensor with previously reported I^- sensor

Reagents	**Detection**	**Linear ranges**	**Limit of detection**	**Reference**
Cu@Au NPs	Colorimetric	0-10 $\times 10^{-6}$ M	6×10^{-6} M	3
Glutathionate- Au_{25}	fluorescence	1×10^{-3} M- 100×10^{-3}M	3.2×10^{-3} M	4
FITC−BSA−Au NPs	Fluorescence	1 -1000 $\times10^{-9}$ M	50 $\times10^{-9}$ M	5
	Redox	3.94×10^{-6} - 5.51×10^{-5} M	7.44×10^{-7} M	6
Carbazole dimer	fluorescence	1.0×10^{-6} - 1.0×10^{-4} M	8.0 $\times10^{-7}$ M	7
Mercuric(II)-(p-(di methyl amino) benzylidene) thio semicarbazide Complax	fluorescence	0 - 4.00$\times10^{-6}$ M	4.5×10^{-7} M	8
Fluorescein-5-iso thio cyanate-modified Au NPs	fluorescence	10.0–600.0 $\times10^{-9}$ M	10 $\times10^{-9}$ M	9
Triethanolamine-capped CdSe quantum dots	fluorescence	0 - 3.5×10^{-5} M	2.8×10^{-7} M	10
Anthracene - 5,10,15,20-tetraphenylporphyrin (TPP) Complex	fluorescence	1.0 × 10^{-6} - 2.5 × 10^{-4} M		11
PVP-ZnSNps	**Fluorescence + Absorbance**	**2× 10^{-9} - 1×10^{-7} M**	**3.4 ×10^{-9} M**	**Proposed nanosensor**

Table S2 : Real sample analysis

Samples	Amount of added iodide	Amount of founded iodide	Recovery (%) (n=3)
Sea water	----	1.617×10^{-9}	---
	0.01×10^{-7}	2.598×10^{-9}	99.27 ±1.6
	0.08×10^{-7}	10.482×10^{-9}	98.98 ±1.2
	0.5×10^{-7}	59.923×10^{-9}	99.08 ±1.4
River water	----	1.420×10^{-9}	---
	0.01×10^{-7}	2.417×10^{-9}	99.87 ±1.1
	0.08×10^{-7}	10.497×10^{-9}	100.77 ±0.9
	0.5×10^{-7}	59.94×10^{-9}	99.08 ±1.5
Tap water	----	1.182×10^{-9}	---
	0.01×10^{-7}	2.195×10^{-9}	100.06 ±1.4
	0.08×10^{-7}	10.159×10^{-9}	99.65 ±1.6
	0.5×10^{-7}	59.674×10^{-9}	99.19 ±1.3
Urine Sample	----	0.982×10^{-9}	---
	0.01×10^{-7}	1.977×10^{-9}	99.75 ± 1.2
	0.08×10^{-7}	9.852×10^{-9}	98.71 ± 1.7
	0.5×10^{-7}	59.464×10^{-9}	99.35 ± 1.1
Edible salt	----	15.121×10^{-9}	---
	0.01×10^{-7}	16.312×10^{-9}	101.18 ± 0.9
	0.08×10^{-7}	24.118×10^{-9}	99.20 ± 1.2
	0.5×10^{-7}	73.496×10^{-9}	99.17 ± 1.3

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