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Supporting Information

Nitrodopamine Modified MnO_2 NS-MoS_2 QDs Hybrid Nanocomposite for Extra- and Intracellular Detection of Glutathione

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Table S1. The crystallite size of the designed pure MnO_2 NS and surface-modified ND@MnO_2 NS and DA@MnO_2 NS.

S. No	(hkl)	MnO_2 NS			ND@MnO_2 NS			DA@MnO_2 NS		
		2θ (°)	FWHM (β)	Crystallite Size (nm)	2θ (°)	FWHM (β)	Crystallite Size (nm)	2θ (°)	FWHM (β)	Crystallite Size (nm)
1	(001)	12.29°	4.5933	1.82	14.22°	9.5439	0.88	14.8°	4.3958	1.90
2	(002)	18.54°	7.0156	1.2	18.74°	12.8279	0.66	18.97°	9.111	0.92
3	(110)	36.39°	21.2331	0.41	37.25°	15.2853	0.57	37.01°	28.1328	0.31
4	(020)	65.66°	431.352l	0.02	65.87°	258.092	0.04	65.55°	233.04	0.04
			Average	**0.86**		**Average**	**0.54**		**Average**	**0.79**

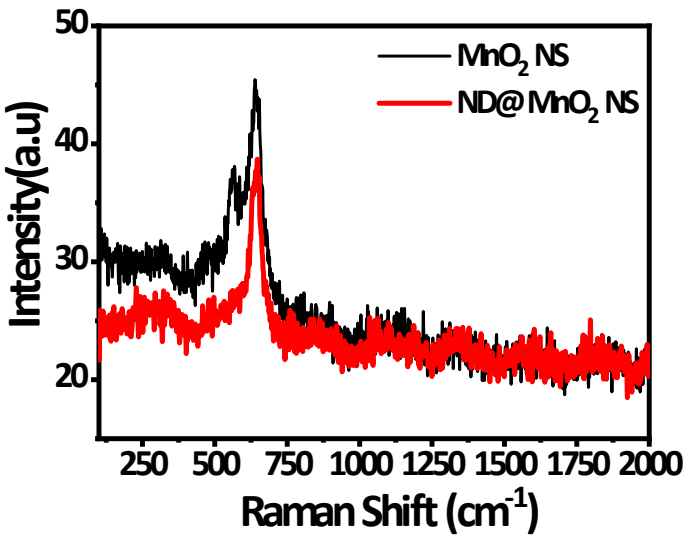
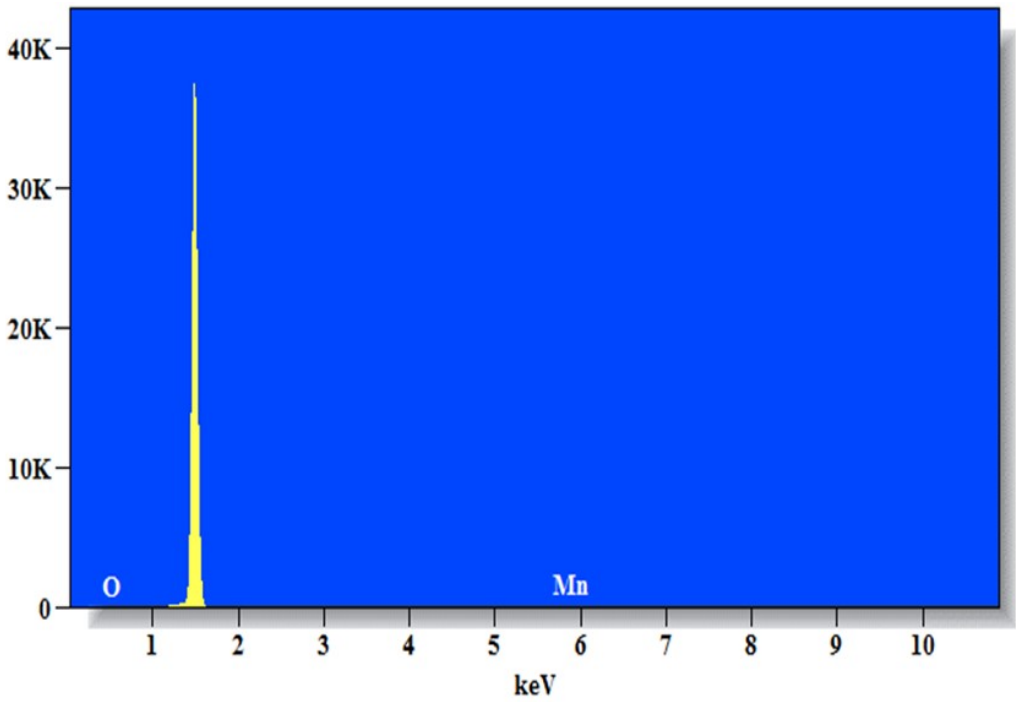


Figure S1. Raman spectrum of a) MnO_2 NS, and b) ND@MnO_2 NS.

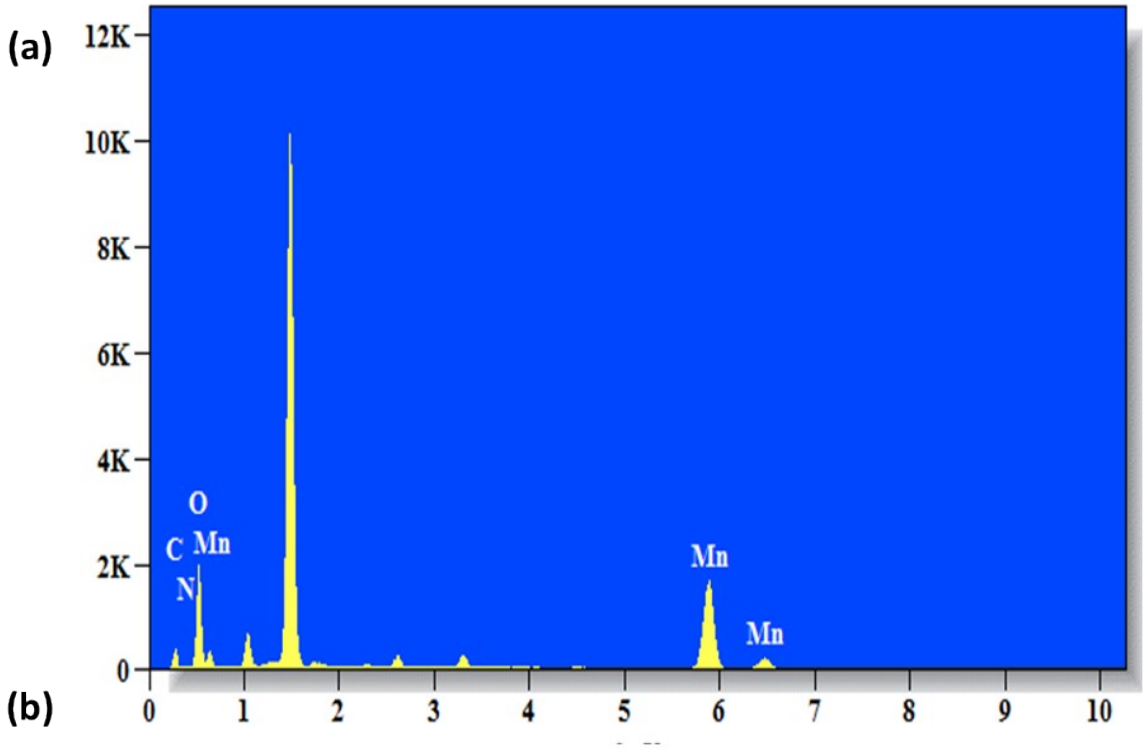
(a)



(b)

Element	Net Counts	Weight %	Atom %	Formula
O	103	16.216	39.925	O
Mn	462	83.784	60.075	Mn
Total		100.000	100.000	

Figure S2. a) EDX data of MnO_2 NS, and b) quantitative weight percentage data of elements present in the MnO_2 NS.

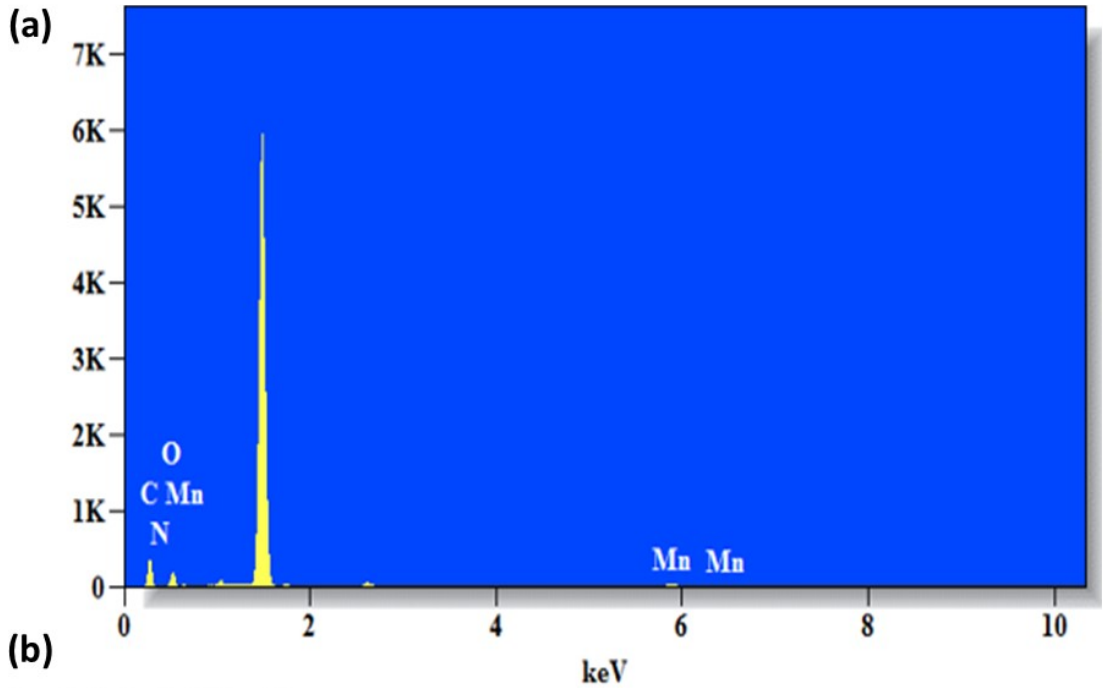


(b)

Quantitative Results for: Base(1)

Element	Net Counts	Weight %	Atom %	Formula
C	2513	8.747	19.305	C
N	532	3.153	5.968	N
O	9722	27.436	45.457	O
Mn	25298	60.663	29.271	Mn

Figure S3. a) EDX data of ND@MnO_2 NS, and b) quantitative weight percentage data of elements present in the ND@MnO_2 NS.



(b)

Quantitative Results for: Base(11)

Element	Net Counts	Weight %	Atom %	Formula
C	2303	28.37	36.15	C
N	267	15.95	17.43	N
O	1246	45.58	43.60	O
Mn	669	10.10	2.81	Mn
Total		100.00	100.00	

Figure S4. a) EDX data of DA@MnO_2 NS, and b) quantitative weight percentage data of elements present in the DA@MnO_2 NS.

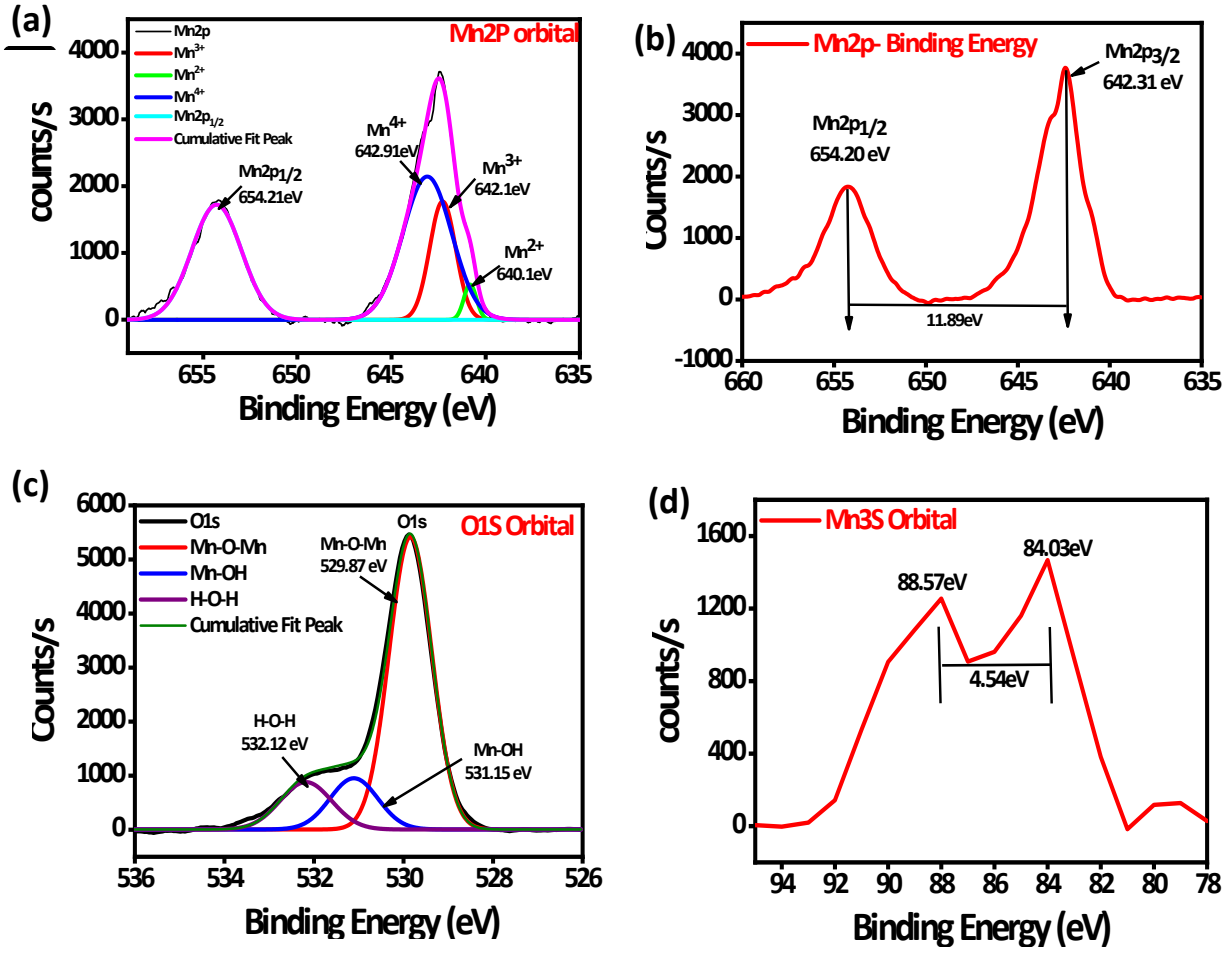


Figure S5. XPS spectra recorded from the MnO_2 NS; XPS spectra of a) Mn2p, b) Mn2P binding energy, and c) O1s orbital d) Mn3s orbital.

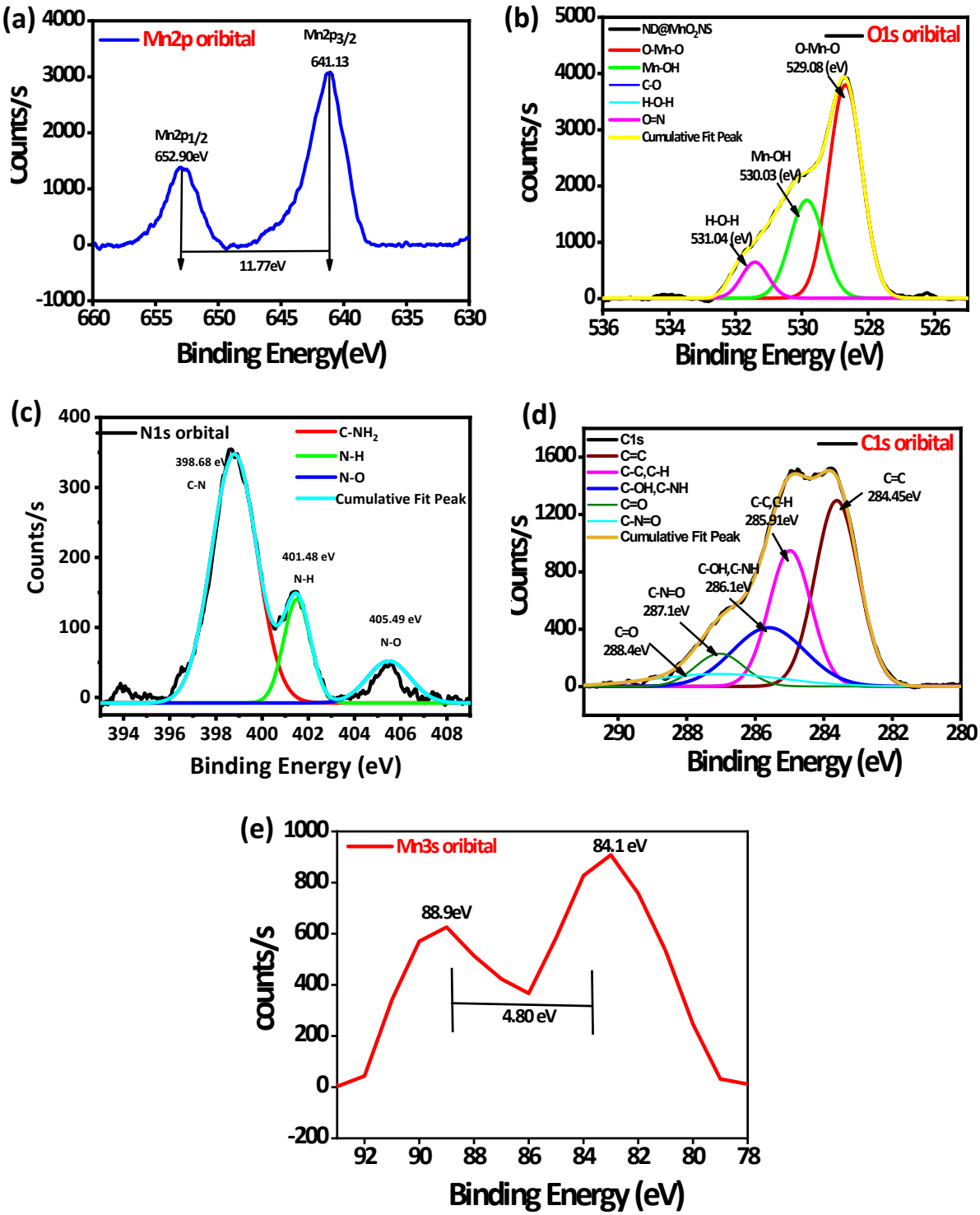


Figure S6. XPS spectra recorded from the ND@MnO_2 NS; XPS spectra of a) Mn2p, b) O1s, c) N1s, d) C1s, and e) Mn3s deconvolution spectra.

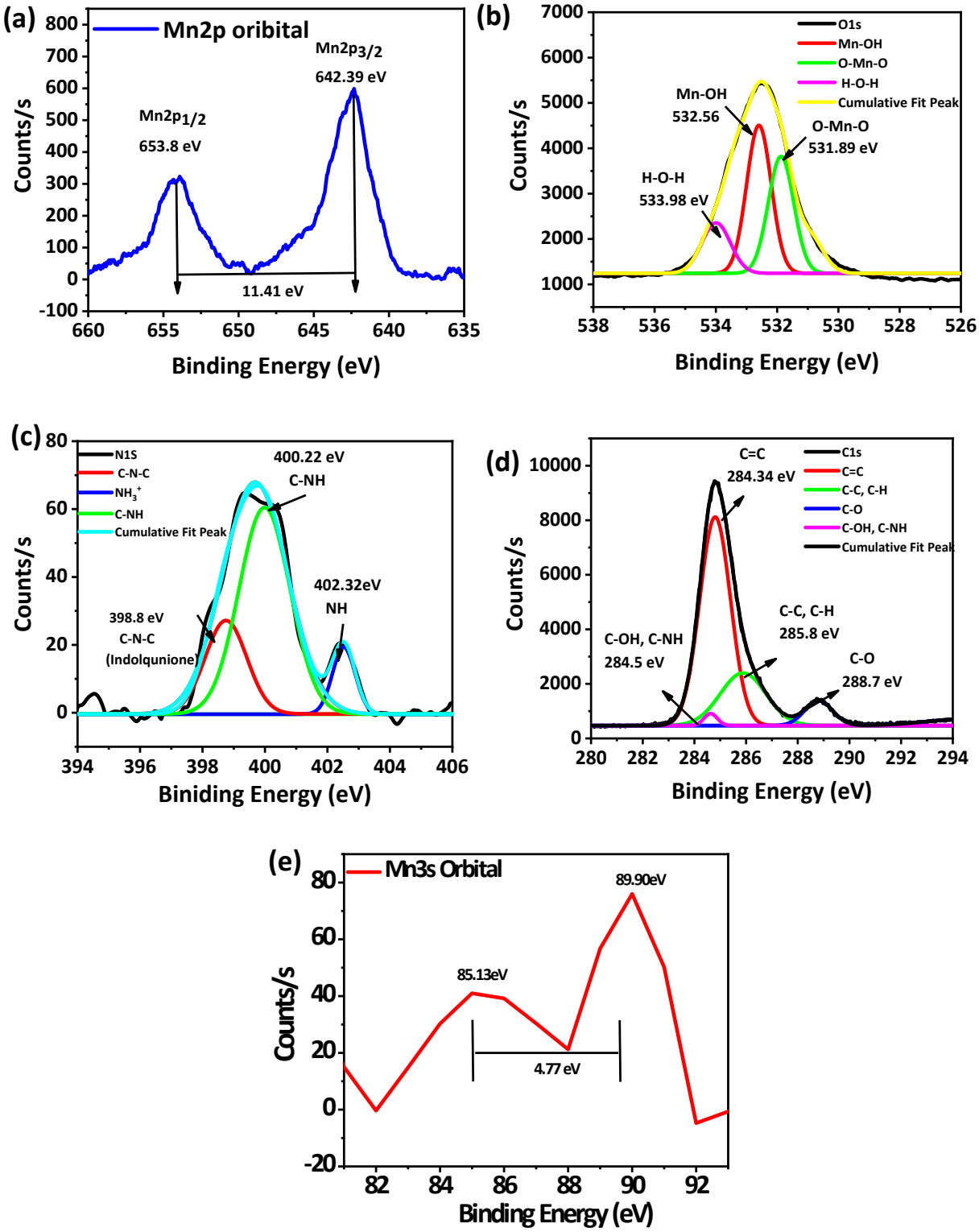
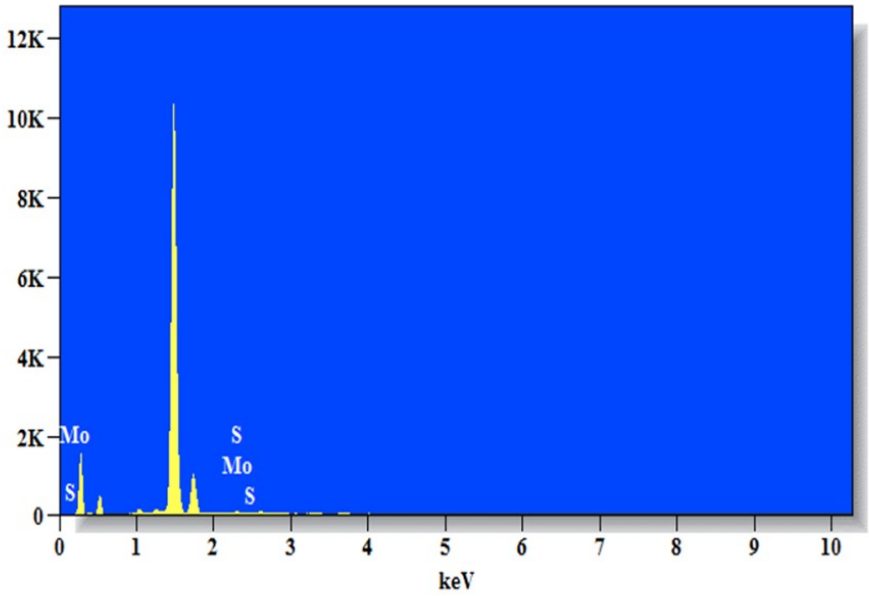


Figure S7. XPS spectra recorded from the DA@MnO_2 NS; XPS spectra of a) Mn2p, b) O1s, c) N1s, d) C1s, and e) Mn3s deconvolution spectra.

(a)



(b)

Quantitative Results for: Base(2)

Element	Net Counts	Weight %	Atom %	Formula
S	685	37.695	64.419	S
Mo	675	62.305	35.581	Mo
Total		100.000	100.000	

Figure S8. a) EDX data of MoS_2 QDs, and b) quantitative weight percentage data of elements present in the MoS_2 QDs.

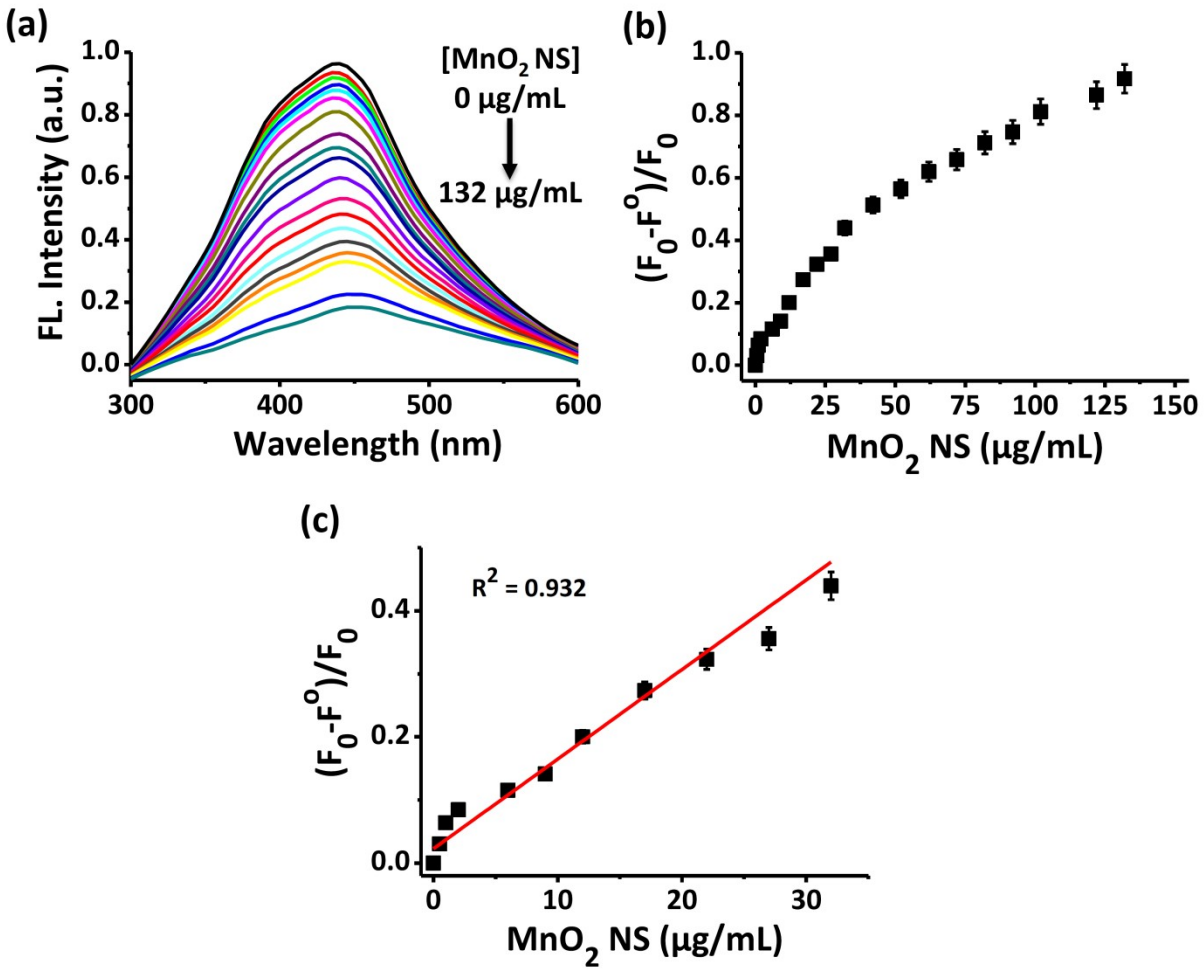


Figure S9. a) Fluorescence spectra of MoS_2 QDs (100 µg/mL) in 1:10 DMF/PBS (1X, pH 7.4) with different concentrations of MnO_2 NS (0-132 µg/mL). The emission spectra of MoS_2 QDs (λ_{ex} = 275 nm and λ_{em} = 435 nm) were recorded just after each addition of MnO_2 NS. b) The kinetic curve at λ_{em} 435 nm for the change in fluorescence intensity ratio with different MnO_2 NS concentrations. c) Relationship between quenching efficiency and the concentrations of MnO_2 NS. F^o and F_0 are fluorescence intensities of MoS_2 QDs in the presence and absence of MnO_2 NS, respectively.

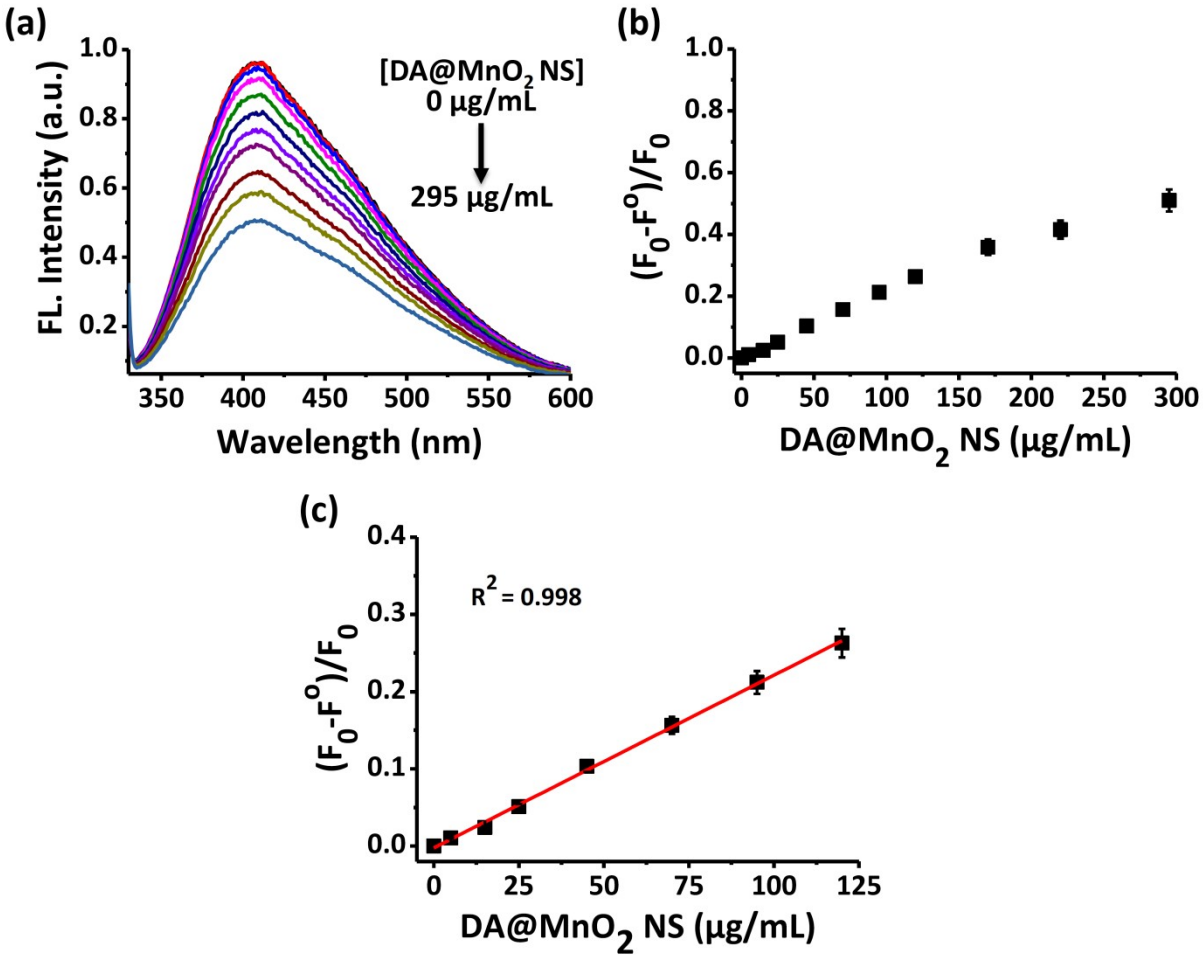


Figure S10. a) Fluorescence spectra of MoS_2 QDs (100 µg/mL) in 1:10 DMF/PBS (1X, pH 7.4) with different concentrations of DA@MnO_2 NS (0-295 µg/mL). The emission spectra of MoS_2 QDs (λ_{ex} = 275 nm and λ_{em} = 435 nm) were recorded just after each addition of DA@MnO_2 NS. b) Kinetic curve at λ_{em} 435 nm for the change in fluorescence intensity ratio with different DA@MnO_2 NS concentrations. c) Relationship between quenching efficiency and the concentrations of DA@MnO_2 NS. F^o and F_0 are fluorescence intensities of MoS_2 QDs in the presence and absence of DA@MnO_2 NS, respectively.

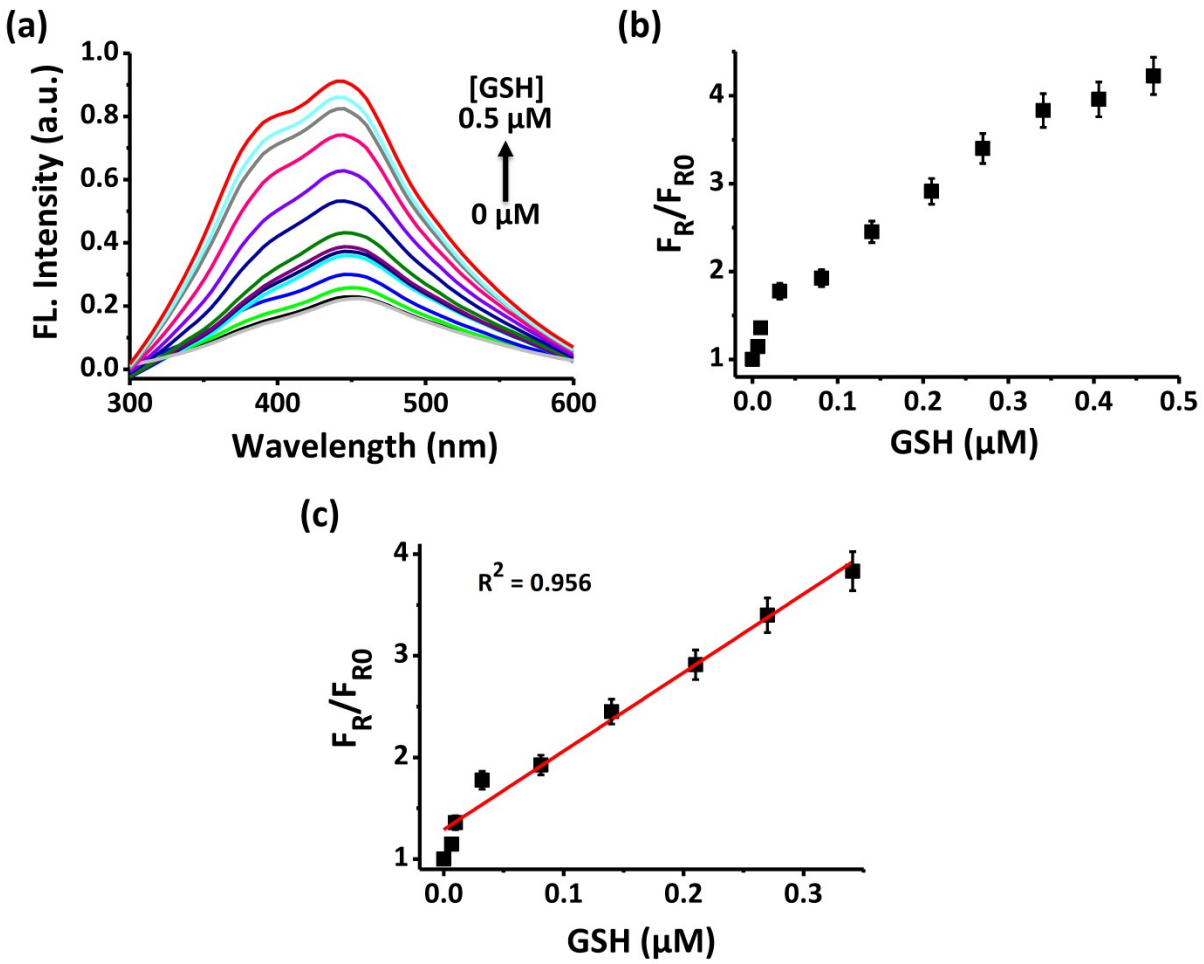


Figure S11. a) Fluorescence spectra of MnO_2 NS@MoS_2 QDs composite in 1:10 DMF/PBS (1X, pH 7.4) with different concentrations of GSH (0-0.5 μM). The emission spectra of MnO_2 NS@MoS_2 QDs (λ_{ex} = 275 nm and λ_{em} = 435 nm) were recorded just after each addition of GSH. b) Kinetic curve at λ_{em} 435 nm for the change in fluorescence intensity ratio with different GSH concentrations. c) Relationship between fluorescence intensity ratio and the concentrations of GSH. F_R and F_{R0} are fluorescence intensities of MnO_2 NS@MoS_2 QDs sensing probe in the presence and absence of GSH, respectively.

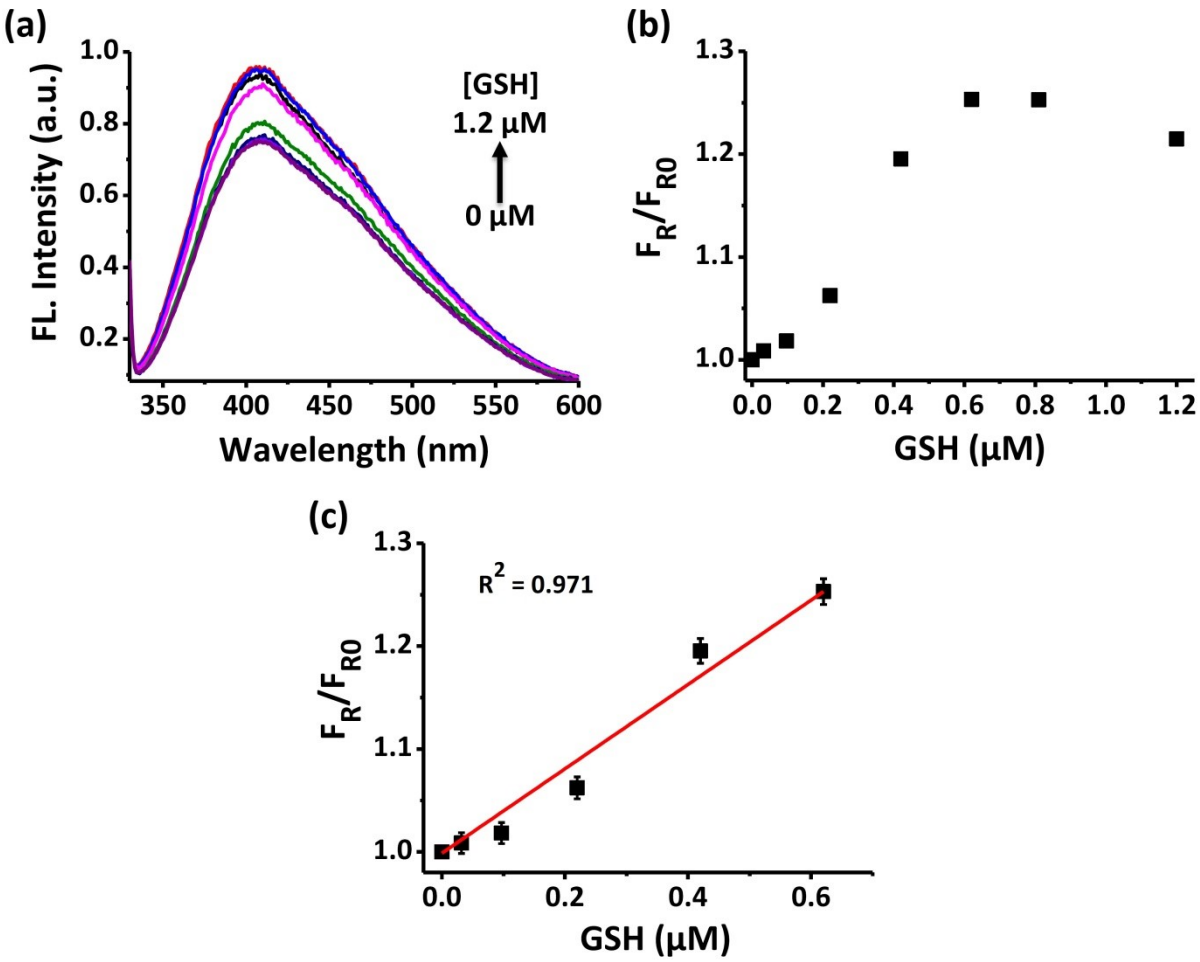


Figure S12. a) Fluorescence spectra of DA@MnO_2 NS@MoS_2 QDs composite in 1:10 DMF/PBS (1X, pH 7.4) with different concentrations of GSH (0-1.2 μM). The emission spectra of DA@MnO_2 NS@MoS_2 QDs (λ_{ex} = 275 nm and λ_{em} = 435 nm) were recorded just after each addition of GSH. b) Kinetic curve at λ_{em} 435 nm for the change in fluorescence intensity ratio with different GSH concentrations. c) Relationship between fluorescence intensity ratio and the concentrations of GSH. F_R and F_{R0} are fluorescence intensities of DA@MnO_2 NS@MoS_2 QDs sensing probe in the presence and absence of GSH, respectively.

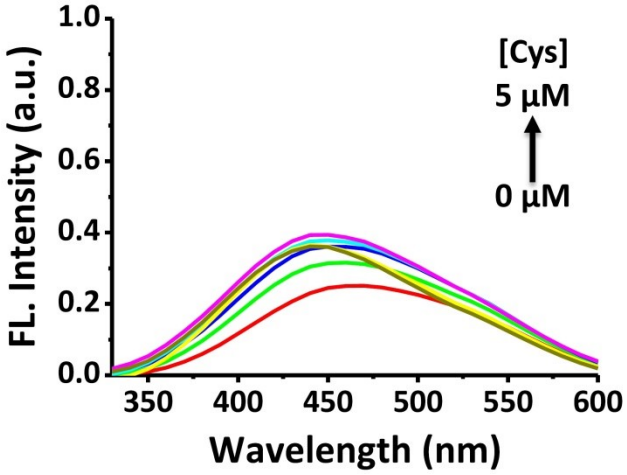


Figure S13. Fluorescence spectra of probe composite (DA@MnO_2 NS@MoS_2 QDs) in 1:10 DMF/PBS (1X, pH 7.4) with different concentrations of Cys (0-5 µM). The emission spectra of probe (λ_{ex} = 275 nm and λ_{em} = 435 nm) were recorded just after each addition of Cys.

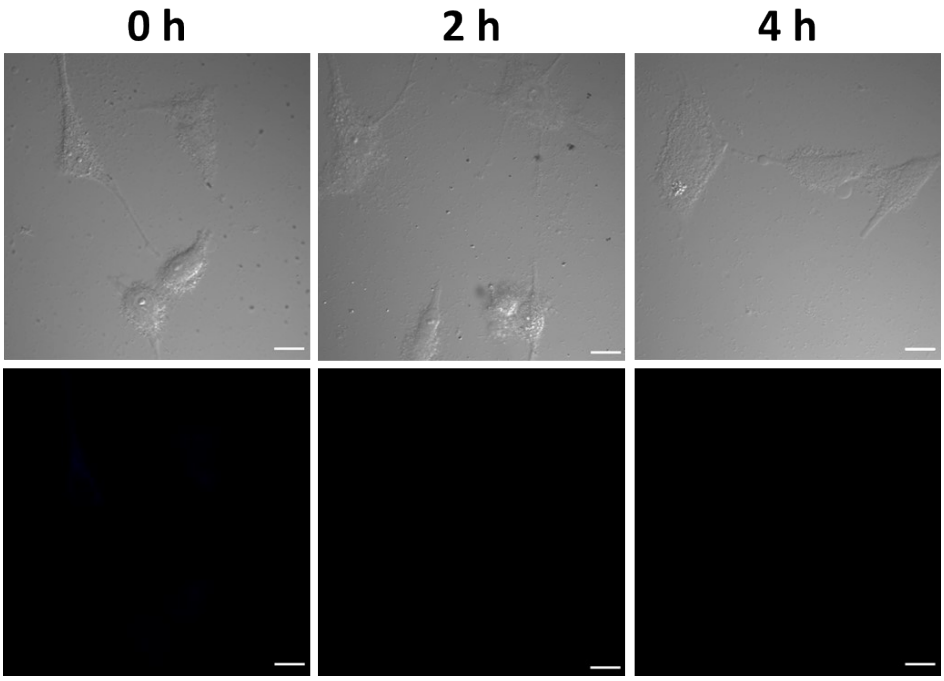


Figure S14. Confocal microscopy images of A549 cells incubated with ND@MnO_2 NS (50 µg/mL) for different time points. Top panels: under bright-field and bottom panels: under fluorescence modes. Scale bar = 10 µm.

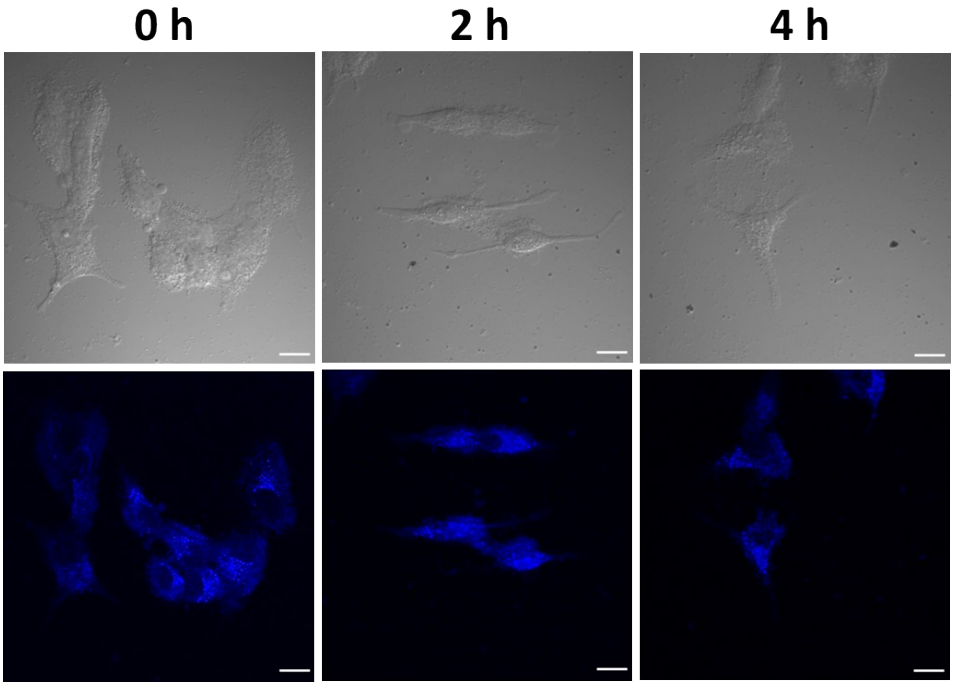


Figure S15. Confocal microscopy images of A549 cells incubated with MoS_2 QDs (50 µg/mL) for different time points. Top panels: under bright-field and bottom panels: under fluorescence modes. Scale bar = 10 µm.

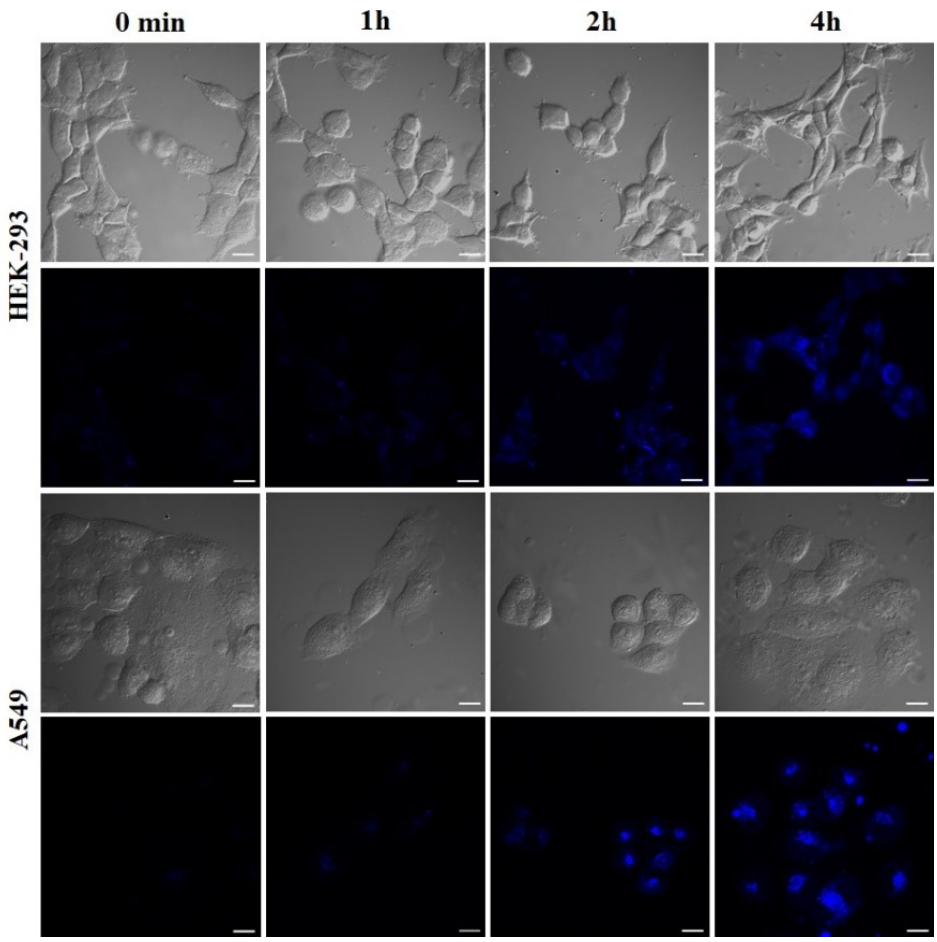


Figure S16. Confocal microscopy images of HEK293 and A549 cells incubated with probe (ND@MnO_2 NS@MoS_2 QDs) (50 μg/mL) for different time points under bright-field and fluorescence modes. Scale bar = 10 μm.