Electronic Supplementary Material (ESI) for RSC Advances.

A hybrid nanocomposite of CeO_2-ZnO-chitosan as an enhanced sensing platform for highly sensitive voltammetric determination of paracetamol and its degradation product *p*-aminophenol

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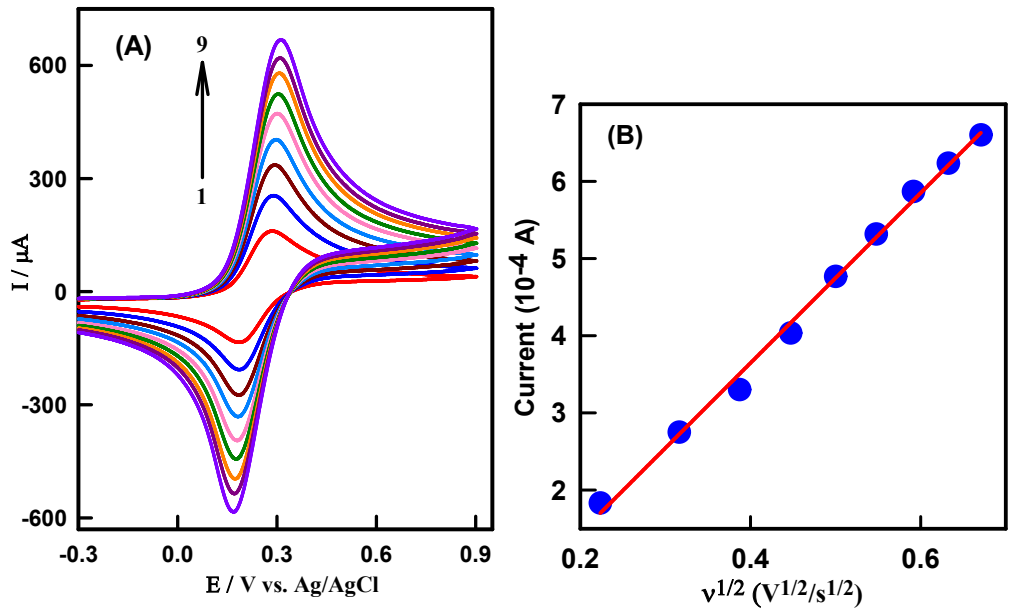

Fig.S1: (A) CV profiles of the CeO_2-ZnO–CS/GCMPE in 5 mM $[Fe(CN)_6]^{-3/-4}$ with different scan rates (50,100,150, 200, 250, 300, 350, 400 and 450 mVs^{-1}). (B) Plot of I_P vs. $\nu^{½}$

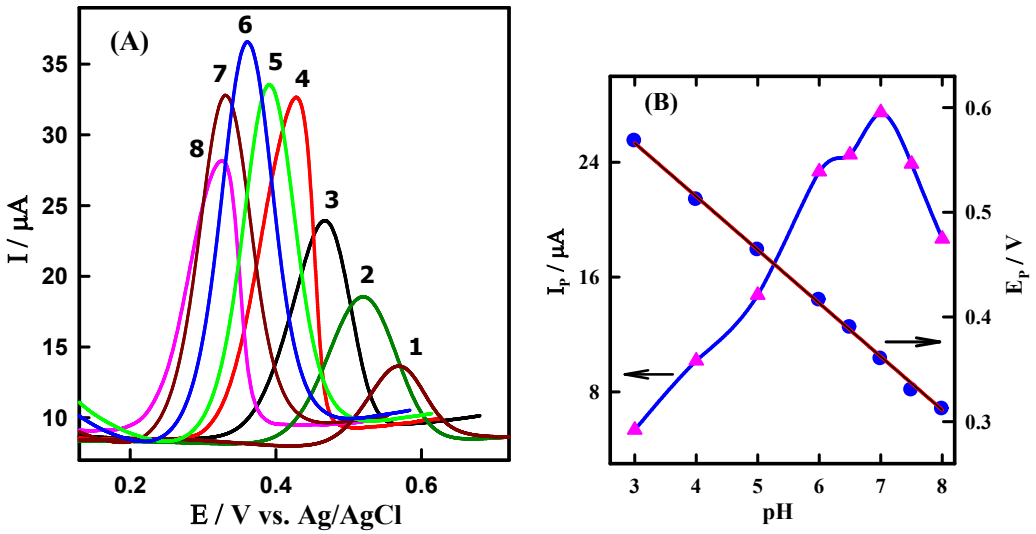

Fig.S2: (A) SW voltammograms of 6.20×10^{-7} M PAR on the surface of CeO_2-ZnO–CS/GCMPE at different pH values (PBS): (1) pH 3.0, (2) pH 4.0, (3) pH 5.0, (4) 6.0, (5) 6.5, (6)7.0, (7) 7.5 and (8) 8.0. Accumulation potential, -0.2 V; accumulation time, 60s; scan increment, 8 mV; frequency, 120 Hz and pulse height, 35 mVpp. (B) Effect of pH on E_P (●) and I_P (▲).

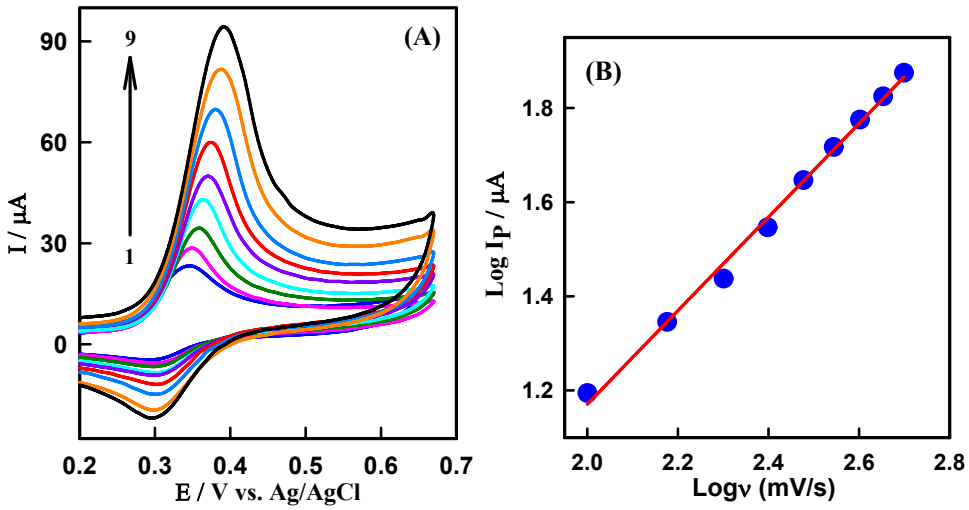

Fig.S3: (A) CVs of 3.85 µM PAR on surface of CeO_2-ZnO–CS/GCMPE at various scan rates; (1) 100, (2) 150, (3) 200, (4) 250, (5) 300, (6) 350, (7) 400, (8) 450 and (9) 500 mVs^{-1} in PBS of pH 7.0. (B) Plot of Log I_P vs. Log ν.

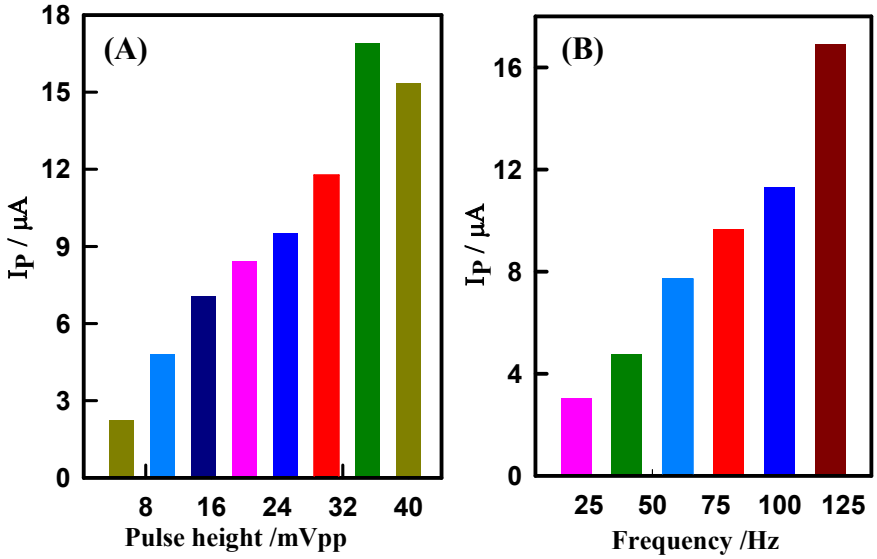

Fig.S4: (A) Plot of I_P versus pulse height and (B) Plot of I_P versus frequency

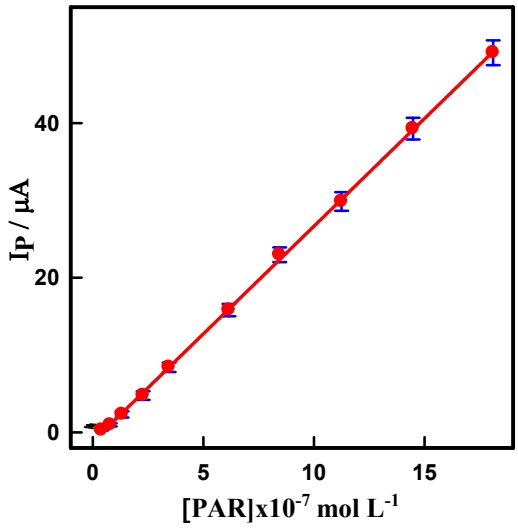

Fig.S5: Calibration plot of I_p(µA) versus [PAR] in presence of 7.05 µM PAP at PBS of pH7.0. Error bar represents the standard deviation of triple measurements.

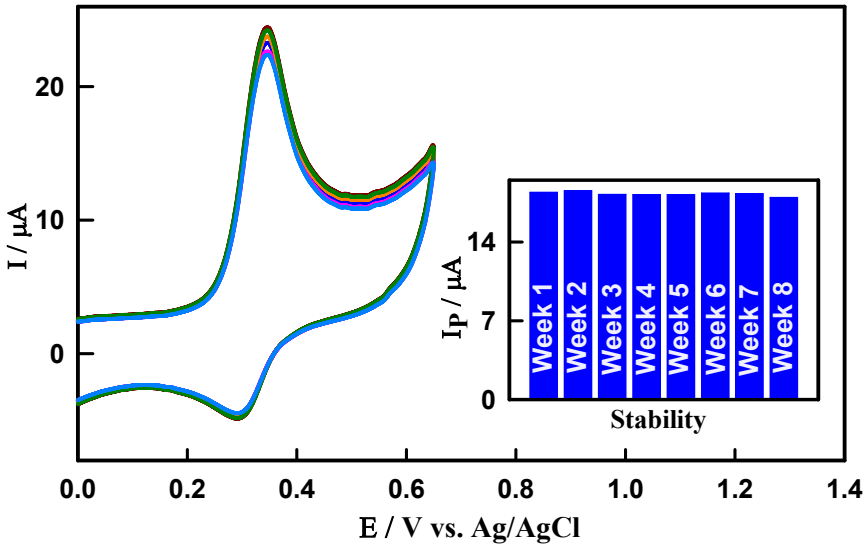

Fig.S6: The CV response of CeO_2-ZnO–CS/GCMPE for the detection of 3.85 µM PAR in PBS solution (pH 7.0) for eight weeks. Inset shows the calibrated histogram of stability test.

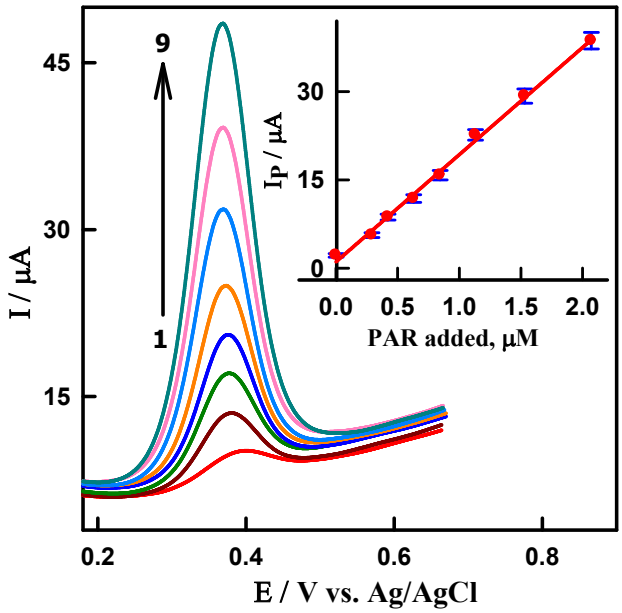

Fig.S7: SW voltammograms for determination of PAR in Panadol tablet solution using CeO_2-ZnO–CS/GCMPE. (1) Background, (2) tablet sample, (3) 2 + 0.29, (4) 2 + 0.42 , (5) 2 + 0.63, (6) 2 + 0.85, (7) 2 + 1.13, (8) 2 +1.53 and (9) 2 + 2.07 µM PAR. Inset: Plot of I_P (µA) versus [PAR] added. Error bar represents the standard deviation of triple measurements.

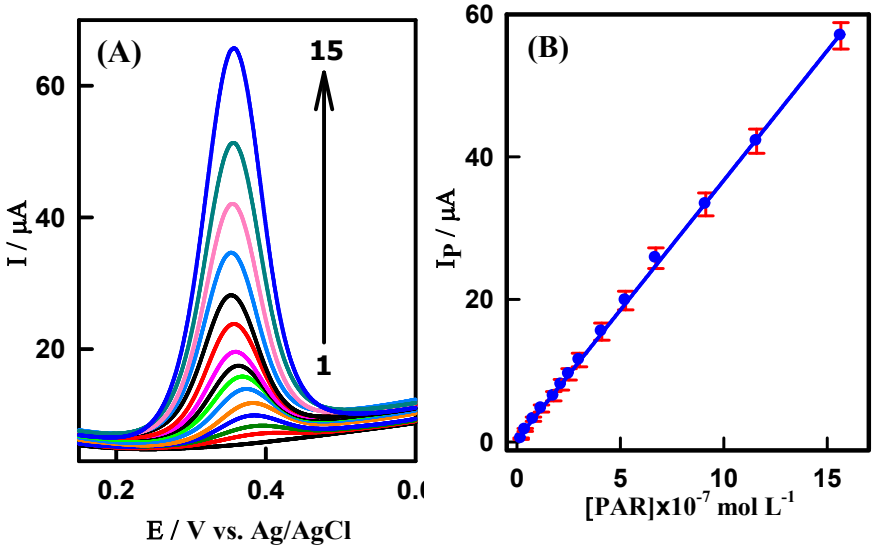

Fig.S8: (A) SW voltammograms for determination of PAR spiked in human serum samples using CeO_2-ZnO–CS/GCMPE, [PAR]: 1) 0.0, 2) 1.99×10^{-8}, 3) 3.96×10^{-8}, 4) 7.94×10^{-8}, 5) 1.18×10^{-7}, 6) 1.77×10^{-7}, 7) 2.14×10^{-7}, 8) 2.51×10^{-7}, 9) 3.02×10^{-7}, 10) 4.10×10^{-7}, 11) 5.25×10^{-7}, 12) 6.71×10^{-7}, 13) 9.12×10^{-7}, 14) 1.16×10^{-6} and 15) 1.57×10^{-6} M PAR. (B) Calibration plot of I_p(µA) versus [PAR]. Error bar represents the standard deviation of triple measurements.

Table S1:

Electrochemical data of 5 mM $[Fe(CN)_6]^{-3/-4}$ in 0.1M KCl at different working electrodes.

Electrodes	ΔE_P (mV)	I_{Pa} (μA)	*A (cm^2)
GCPE	345	79.99	0.070
CeO_2-ZnO–CS/GCPE	107	233.3	0.826

*A, active surface area (cm^2)

Table S2:

Comparison of the proposed electrochemical sensor with other electrodes used in the determination of PAR in absence and presence of PAP.

Modified electrodes	Method	pH	Linear range (μM)	LOD (nM)	Ref.
In absence of PAP					
CFE	DPV	4.0	0.02–100	34	[1]
SWCNT/CCE	DPV	1.7	0.08–200	50	[2]
MWCNT-βCD/GCE	DPV	7.4	0.05–300	11.5	[3]
GA@O-CQDs/GCE	DPV	7.0	0.001–10	0.38	[4]
SWCNT-GNS/GCE	DPV	7.0	0.05–64.5	38	[5]
ED-CMWCNT/GCE	DPV	7.0	1–200	92	[6]
AuNP-PGA-SWCNT/PET	DPV	7.2	8.3–145	1180	[7]
SWNT/EPPGE	SWV	7.2	0.005–1	2.90	[8]
PANI–MWCNTs	SWV	5.5	1–100 / 250–1000	250	[9]
MIP	DPV	7.0	1–4000	330	[10]
$ZNFe_2O_4$/CPE	DPV	8.0	6.5–135	400	[11]
CPME with SnS/SnO_2	DPV	4.0	1–36	60	[12]
NCDs/GCE	DPV	7.0	0.5–600	157	[13]
CeO_2-ZnO–CS/GCMPE	SWV	7.0	0.0199– 1.82	0.86	This work
In presence of PAP					
PEDOT/GCE	DPV	7.0	1–100	400	[14]
Cr-SBC/GCE	DPV	7.0	0.008–0.125	6.80	[15]
CS/Au/Pd/rGO	DPV	8.0	1–250	300	[16]
CILE	DPV	7.0	2– 2200	500	[17]
CeO_2-ZnO–CS/GCMPE	SWV	7.0	0.02– 1.94	0.98	This work

DPV: Differential pulse voltammetry, SWV: Square wave voltammetry

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Table S3:

Influence of interferents on the voltammetric responses of 1.20×10^{-7} M PAR at CeO_2-ZnO–CS/GCMPE.

Interferents	Concentration (μM)	Recovery %
Ascorbic acid	200	98.87
Salicylic acid	300	99.43
Tyrosine	200	99.23
Tryptophan	200	97.69
Alanine	300	100.98
Phenylalanine	300	99.18
Glutamic acid	400	98.76
Cysteine	300	99.26
Glucose	500	99.05
Citric acid	400	102.25
Cytosine	100	98.94
Urea	400	99.44
Serine	300	99.18
Aspartic acid	300	99.24

Table S4:
Robustness results of the proposed method (n = 5).

Variables	Recovery %	RSD %	Conditions
pH of the medium (PBS)			E_{acc} = – 0.2 V
6.90	97.86	1.76	E_a = 35 mV
7.10	98.21	1.93	
7.20	98.37	1.83	
Accumulation potential (E_{acc})			pH = 7
– 0.15 V	99.32	1.54	E_a = 35 mV
– 0.25 V	99.21	1.64	
Pulse height (E_a)			pH = 7
33	97.76	1.82	E_{acc} = – 0.2 V
37	98.46	1.42	

Table S5:

Determination of paracetamol in different pharmaceutical formulations at CeO_2-ZnO–CS hybrid nanocomposite modified GCMPE using SWV (n = 3).

Name of drug	Producer company	Stated content (mg/tablet)	Average detected content (mg/tablet)	RSD (%)	Error (%)	Recovery (%)
Calmalgine®	Misr Phar. Co	325	319.71	1.89	–1.62	98.37
Paramol®	Misr Phar. Co	500	491.12	1.95	– 1.77	98.22
Paracetamol®	Adco	500	485.35	2.24	– 2.93	97.07
Panadol®	GlaxoSmithKline	500	493.90	1.38	– 1.22	98.78
Abimol®	GlaxoSmithKline	500	487.85	1.44	– 2.43	97.57
Novaldol®	Sanofi	1000	988.22	1.49	– 1.17	98.82

Table S6:

Regression data of the calibration lines for quantitative determination of PAR in serum samples at CeO_2-ZnO–CS/GCMPE using SWV.

Parameters	Serum sample
Linearity range	1.99×10^{-8} – 1.57×10^{-6}
Slope (μAM^{-1})	3.64×10^{7}
SE of slope	0.025
Intercept (μA)	0.35
SE of intercept	0.16
Coefficient of determination (R^2)	0.9994
LOD (M)	8.24×10^{-10}

Table S7:

Recovery of PAR in serum samples (n = 5).

Added (1×10^{-7} M)	Found (1×10^{-7} M) Mean ± SD	Precision RSD %	Recovery %
1.18	1.15 ± 0.012	1.83	97.46
2.51	2.53 ± 0.051	1.74	100.77
5.25	5.23 ± 0.087	1.94	99.62