Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary

Gold nanoparticles supported on zirconium, tin and ruthenium oxides for reagentless electrochemical sensing of hydrogen peroxide

Fig. S1A. CV behaviors of RuO_2-AuNP (curve a, b), ZrO_2-AuNP (curve c, d) and SnO_2-AuNP (curve e, f) modified GCEs in PBS measured at a scan rate 5 mVs^{-1}

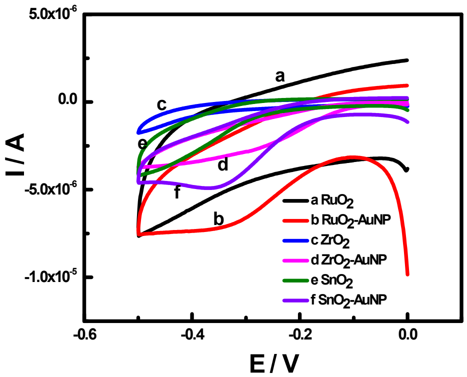
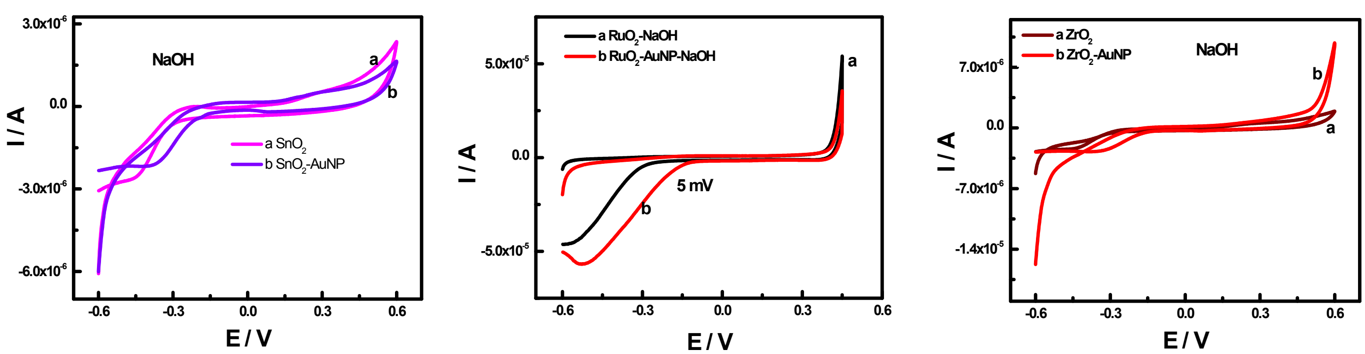


Fig. S1B. CV behaviors of RuO_2-AuNP (curve a, b), ZrO_2-AuNP (curve c, d) and SnO_2-AuNP (curve e, f) modified GCEs in NaOH measured at a scan rate 5 mVs^{-1}



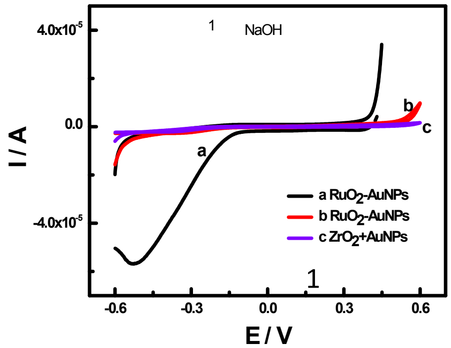


Fig. S1C. current versus pH plots (A) RuO_2-AuNP , (B) ZrO_2-AuNP and (C) SnO_2-AuNP modified GCEs. (D). Effect of AuNP deposition time on the H_2O_2 detection on the RuO_2 surface

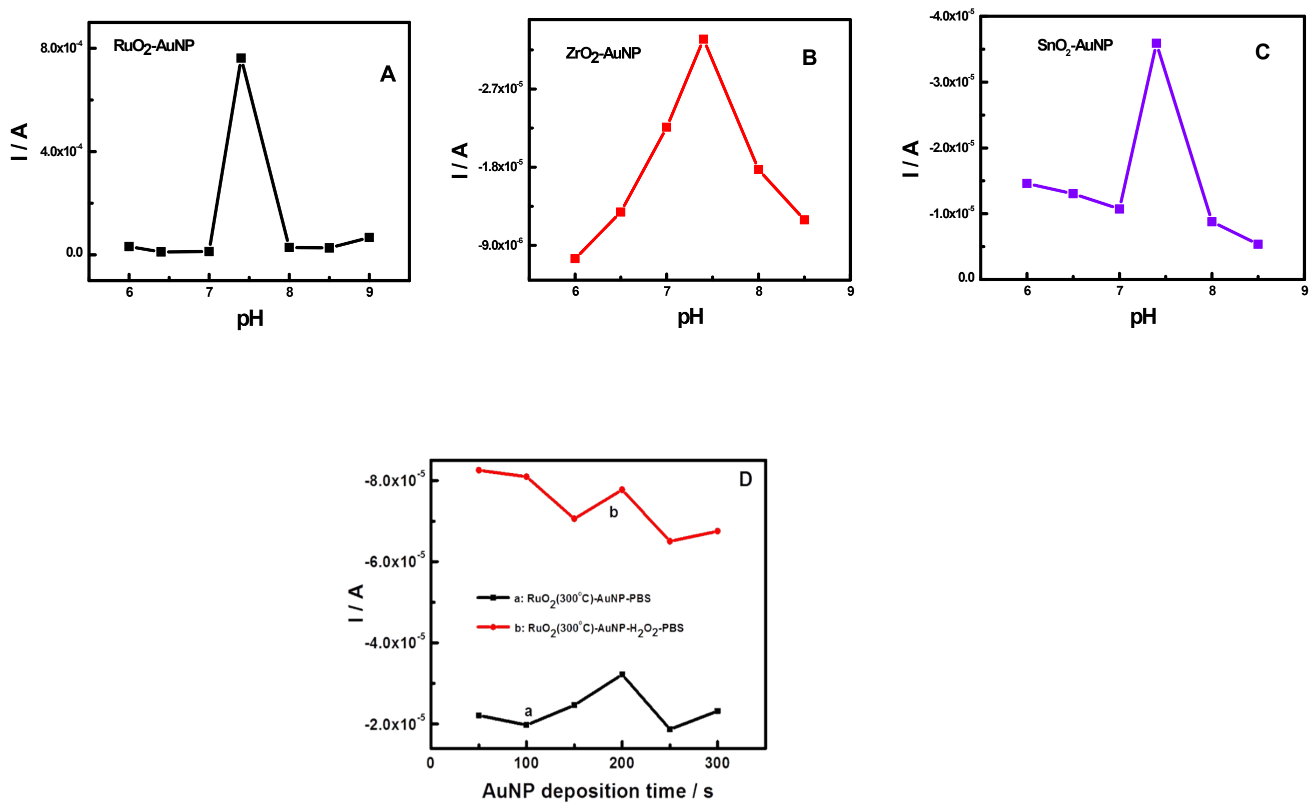
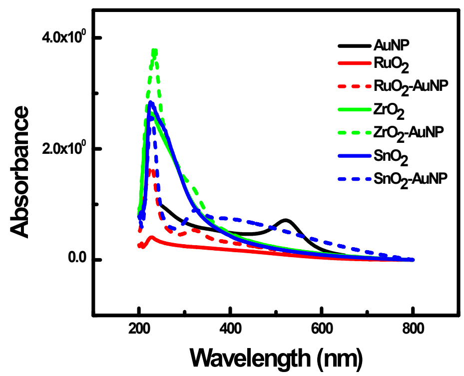


Fig. S2. UV – visible spectra of RuO_2 (curve a) , RuO_2-AuNP (curve b), ZrO_2 (curve a), ZrO_2-AuNP (curve b) SnO_2 (curve a) and SnO_2-AuNP (Curve b)



Material	Band gap (eV)
RuO_2	2.69
RuO_2-AuNP	2.78
ZrO_2	4.24
ZrO_2-AuNP	3.14
SnO_2	3.01
SnO_2-AuNP	2.88

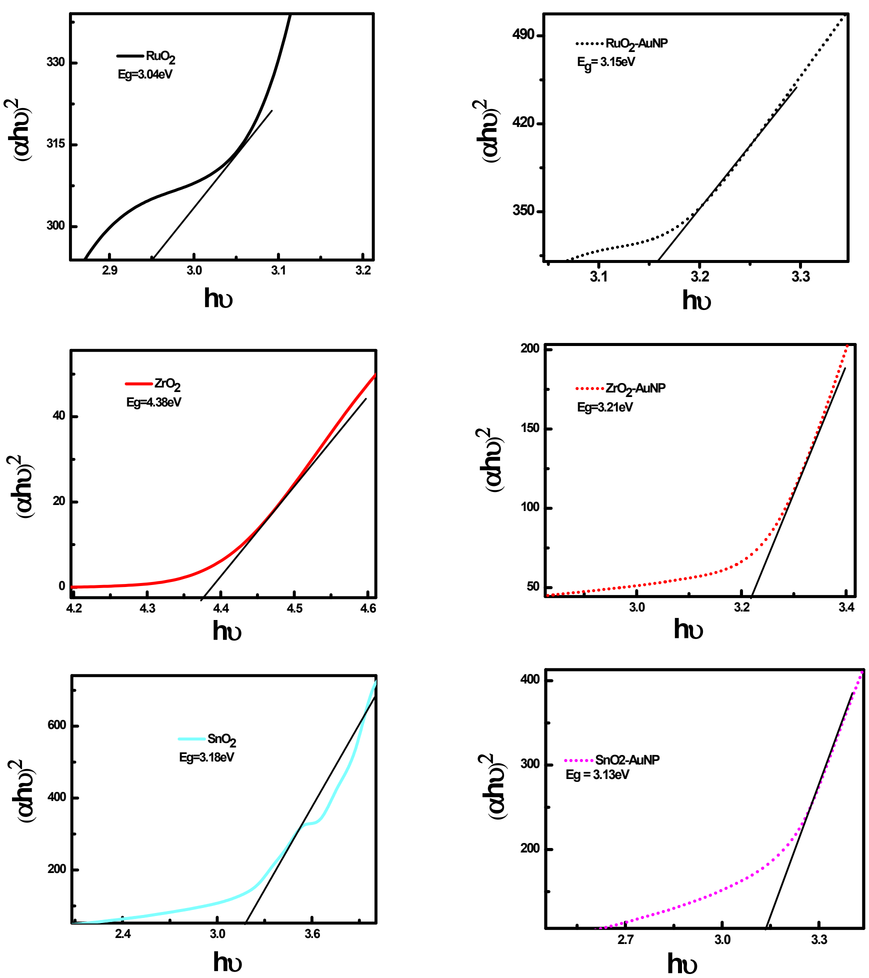


Fig. S3. CV behaviors of RuO_2-AuNP (curve a,b), ZrO_2-AuNP (curve c,d), SnO_2-AuNP (curve e,f), modified GCEs in presence of 0.1 mM $[Ru(NH_3)_6]^{3+}$ in phosphate buffer measured at a scan rate 5 mVs^{-1}. Solid lines indicate the CV behaviors in the absence (curves, a,c,e) and the dotted lines represent the CV behaviors (curves b, d, f) in the presence of 1 mM $[Fe(CN)_6]^{3-/4-}$. Inset : enlarged view of RuO_2 and RuO_2-AuNP.

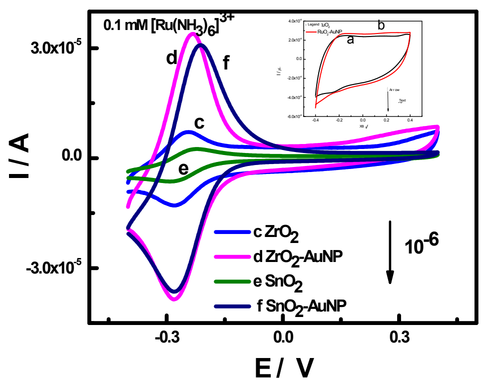


Fig.S4. FTIR spectra of RuO_2 (curve a), RuO_2-AuNP (curve b), ZrO_2 (curve c), ZrO_2-AuNP (curve d) SnO_2 (curve e) and SnO_2-AuNP (Curve f)

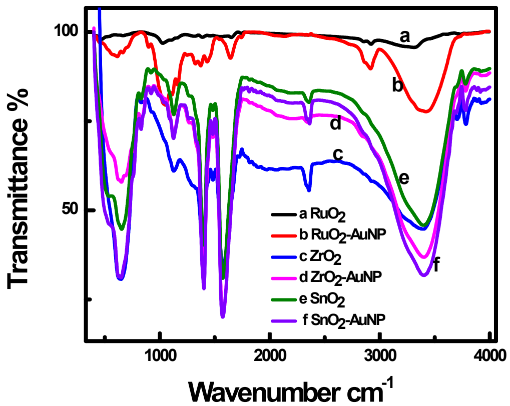


Table S1. XRD parameters for RuO_2, ZrO_2, SnO_2 and RuO_2-AuNP, ZrO_2-AuNP and SnO_2-AuNP

RuO_2	RuO_2-AuNP	ZrO_2	ZrO_2-AuNP	SnO_2	SnO_2-AuNP
-	27.8 **(1 10)**	24.1 (110)	25.2 (320)	26.3 (110)	26.3 (110)
-	35.02 **(101)**	25.2 (320)	28.09 (020)	33.6 (101)	33.7 (101)
-	54.7 **(211)**	27.9 (020)	30.06 (011)	37.8 (200)	37.8 (200)
		30.6 (011)	31.4 (120)	51.5 (211)	51.7 (211)
		31.3 (120)	50.1 (031)	64.6 (112)	57.8 (002)
		35.1 (101)	54.0 (131)		64.6 (112)
		50.4 (031)			
		55.2 (131)			
		62.9 (022)			

Composite	Particle size / nm
RuO2	7.4
RuO2-AuNP	42.8
ZrO2	49
ZrO2-AuNP	60
SnO2	23
SnO2-AuNP	27

Fig. S5. EIS behaviors of RuO_2-AuNP (curve a, b), ZrO_2-AuNP (curve c, d) and SnO_2-AuNP (curve e, f) modified GCEs in absence (curves, a, c, e) and presence of 1 mM H_2O_2 (curves b, d, f)I n phosphate buffer measured in the frequency range 100 kHz to 1 Hz at an applied potential -400 mV and amplitude 5 mV. While solid lines indicate EIS behaviors in the absence (curves, a,c,e) in the presence of 1 mM H_2O_2 (curves b, d, f). Circles are the [R(QR)(QR)W] equivalent circuit fit data.

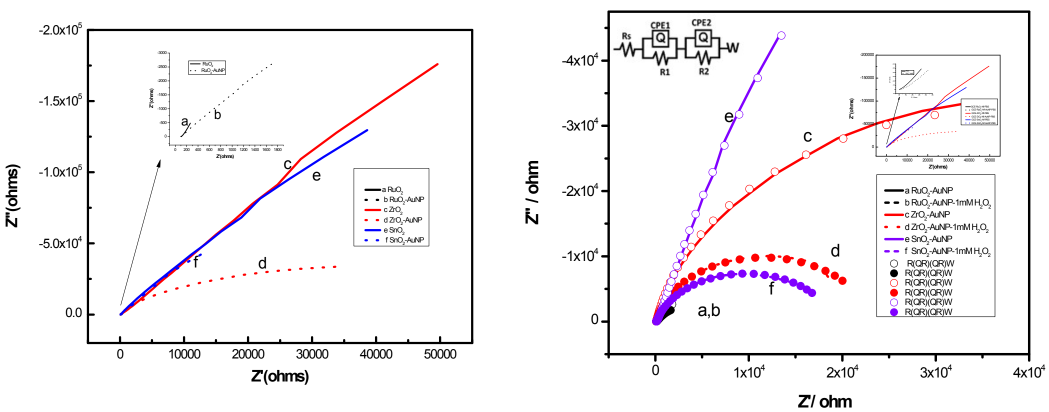


Table S2. Impedance parameters obtained for all three metal oxides in the absence and presence of AuNP fabricated in nafion film in the absence and presence of 1 mM H_2O_2 in phosphate buffer. The circuit used is [R(QR)(QR)W].

Surfaces	R_s(Ωcm^{-2})	Q_{CPE1} (Fcm^{-2})	n1	R1(Ωcm^{-2})	Q_{CPE2} (Fcm^{-2})	n2	R2 (Ω cm^{-2})	W (Ω s$^{-1/2}$)	χ2
RuO_2	52.500	4.14×10^{-4}	1.00	1.98×10^{3}	9.45×10^{-9}	0.98	1.96×10^{2}	2.50×10^{-4}	3.08×10^{-4}
RuO_2 -1mM H_2O_2	100.0	1.57×10^{-7}	0.68	1.12×10^{3}	4.89×10^{-4}	1.00	1.32×10^{2}	1.86×10^{-4}	4.90×10^{-4}
RuO_2 - AuNP	0.011	2.23×10^{-6}	0.48	1.08×10^{2}	8.25×10^{-5}	0.74	1.72×10^{4}	1.29×10^{-4}	2.48×10^{-4}
RuO_2 – AuNP- 1mM H_2O_2	0.080	1.22×10^{-4}	0.78	4.38×10^{3}	6.14×10^{-6}	0.35	1.20×10^{2}	5.53×10^{-4}	2.44×10^{-4}
ZrO_2	23.78	1.055×10^{-8}	1	1.16×10^{2}	1.226×10^{-6}	0.8314	4.9×10^{15}	0.000975	3.5×10^{-4}
ZrO_2- 1mM H_2O_2	0.01337	1.324×10^{-6}	0.8461	7.181×10^{6}	3.869×10^{-8}	0.8293	132.1	1.085×10^{11}	1.80×10^{-4}
ZrO_2 - AuNP	0.007587	2.735×10^{-6}	0.899	7.64×10^{4}	1.354×10^{-6}	0.5963	117.6	1.43×10^{9}	3.35×10^{-4}
ZrO_2 - AuNP - 1mM H_2O_2	0.005672	6.406×10^{-7}	0.6435	119.8	2.736×10^{-6}	0.9023	2.25×10^{4}	0.00106	3.17×10^{-4}
SnO_2	32.9	1.433×10^{-6}	0.868	1.283×10^{6}	2.144×10^{-8}	0.9561	74.08	2.029×10^{8}	2.03×10^{-4}
SnO_2- 1mM H_2O_2	22.54	3.013×10^{-8}	0.9043	90.58	1.388×10^{-6}	0.8727	3.821×0^{5}	3.284×10^{6}	1.31×10^{-4}
SnO_2 - AuNP	0.03902	3.19×10^{-8}	0.8478	114.6	4.321×10^{-6}	0.9013	3.954×0^{5}	0.0001306	9.5×10^{-5}
SnO_2 - AuNP- 1mM H_2O_2	0.001266	3.3×10^{-6}	0.8335	1.915×10^{4}	1.686×10^{-7}	0.7239	124.2	6.211×10^{19}	2.42×10^{-4}

Fig. S6. (A) Comparative calibration curves of RuO_2-AuNP, ZrO_2-AuNP and SnO_2-AuNP composites obtained for from chrono amperometry measurements made at -0.4 V for the successive addition of H_2O_2. Concentration range studied is 1×10^{-9} to 30×10^{-3} M.

(B) Comparative calibration curves of RuO_2 and RuO_2-AuNP

(c) Comparative calibration curves of $SnO_2$and SnO_2-AuNP. Depicted for showing the superiority of metal oxide-AuNP over the lone metal oxide behavior

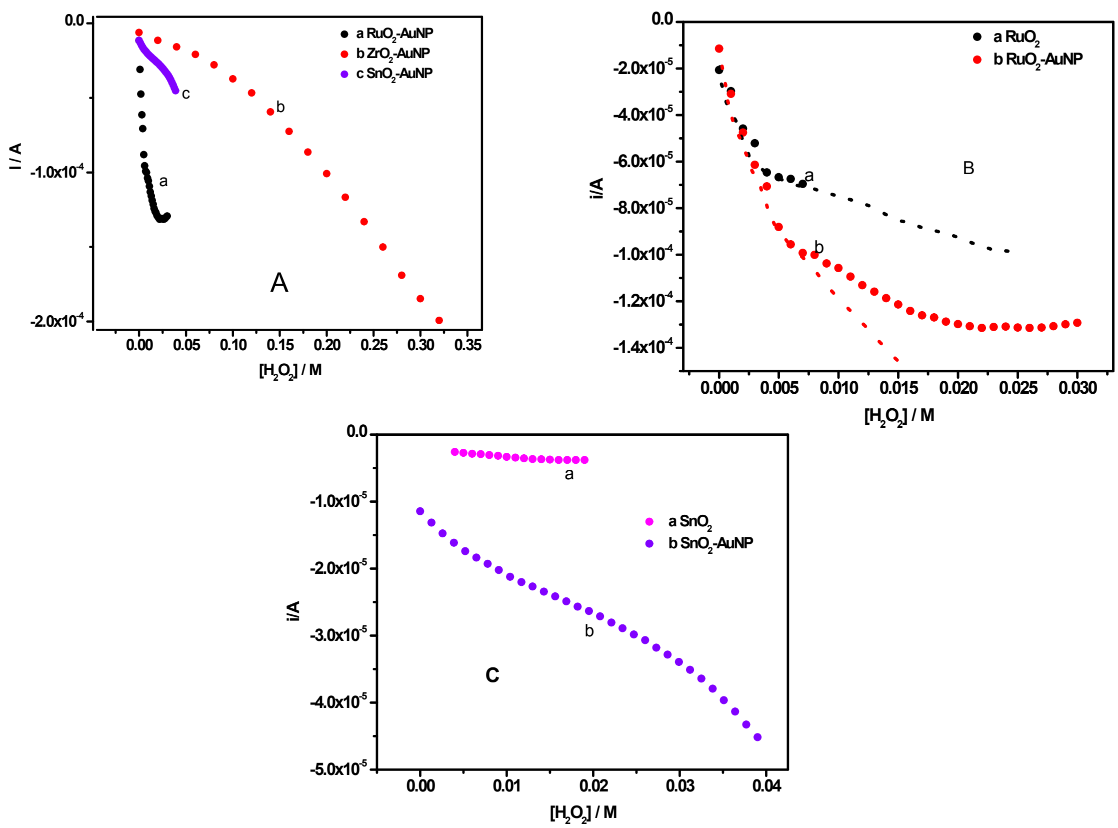


Fig. S7. CV behaviors of RuO_2-AuNP (curve a,b), ZrO_2-AuNP (curve c,d), SnO_2-AuNP (curve e,f), modified GCEs in antiseptic (A) and commercial milk (B) in phosphate buffer measured at a scan rate 5 mVs^{-1}. Solid lines indicate the CV behaviors in the absence (curves, a,c,e) and the dotted lines represent the CV behaviors (curves b, d, f) in presence of commercial samples

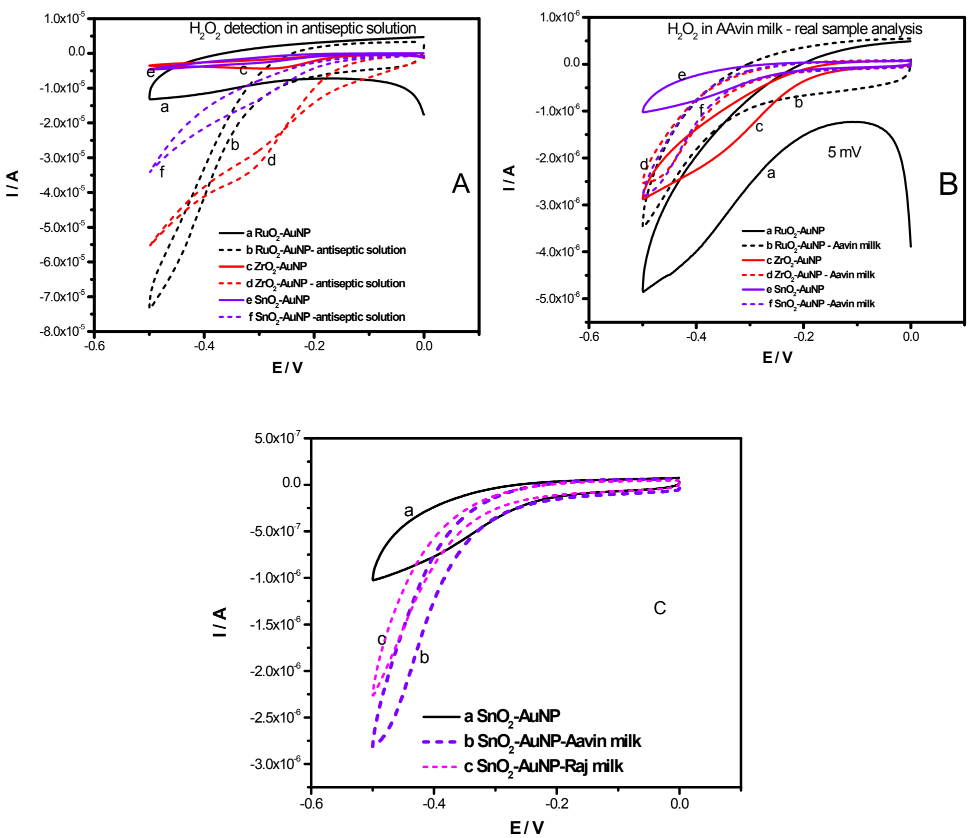


Table S3. Michealis-Menten kinetic parameters obtained for different metal oxide and metal oxide-AuNP used in this study for the reduction of H_2O_2 in phosphate buffer

Surfaces	K_m / M	K_c / s	Γ_t / moles cm^{-2}
RuO_2	2.12×10^{-3}	4.8×10^{4}	1.42×10^{-13}
RuO_2-AuNP	10.1×10^{-3}	1.18×10^{8}	3.2×10^{-17}
ZrO_2	7.16×10^{-5}	8.47×10^{3}	1.38×10^{-13}
ZrO_2-AuNP	1.48	5.32×10^{6}	9.53×10^{-15}
SnO_2	3×10^{-3}	5.4×10^{3}	5.9×10^{-14}
SnO_2-AuNP	2.3×10^{-3}	2.9×10^{5}	7.9×10^{-15}

Table S4. H_2O_2 detection at different metal oxide /metal nanoparticle modified electrodes.

Electrode materials	Linear range and LOD	Effect of inteferences with name	Real samples studied	Reference
AgNPs/ZnO/GCE	2µM to 5.5mM	Dopamine Ascorbic acid, Acetaminophen	--	QiWang.Microchim Acta (2010)169:361-365
AgNPs-MWCNT/Au electrode	0.05 to 17	AA,UA,	--	W. Zhao Talanta 80 (2009) 1029.
CPE/MWCNT/ RuO_2	0.5 to 50mM	Glu,AA,UA	--	Ramin M.A. Biosesnors and Bioelectronics (2012)
GCE/MnO_2/ Nafion	10.0×10^{-6} to 15.0×10^{-5}	UA.Dopamine,L-cysteine,AA	--	Li Zhen,Zhen Fang, Int.J.Electrochem. Sci.,4(2009)407-413
GC/MnO_2/GO nano composite	5 to 600 µM	Glu, citric acid,$cu2^{+}$	Classical$KMnO_4$ titration method	Limiao Li, Talanta 82(2010)1637-1641
CPE/NiO	1-110 µM	AA, UA	Diluted juice sample	Ying Mu, Biosensors and Bioelectronics 26(2011)2948-2952
GC/MWCNT/NiO	2.0×10−4mol/L to 1.2 × 10−2mol/L	AA, UA	Blood human serum sample	Shamsipur etal.Bioelectrochemistry 77(2010)120-124
GC/CuO/MWCNT	Upto 3.0mM	Dopamine, AA,UA,lactose, Citricacid	Blood human serum sample	Jiang Yang, Talanta 82(2010)25-33
Pt/CuO/nafion	0.15 µM to 9mM	AA,Dopamine, Glucose Ethanol, L-cysteine	--	Xiang –Min, Electroanalytical chemistry 612(2008) 157-163
GCE/β-MnO2 nanorods	2.45 µM to 42.85 mM	L-glycine, glucose, L-glutamic acid,AA,UA, L-Ala	--	Ai-Jun Wang & Pei-Pei Zhang. Microchim Acta (2011) 175:31–37
GCE/ PPy-Pt hollow spheres nanocomposite.	3.5 µM to 9.9 mM	acetic acid, l-cysteine, AA,glucose, ethanol	--	Jingjing Li & Ruo Yuan. Microchim Acta (2010) 171:125–131
GCE/PTBO/ZrO_2/GCNT/ H_2O_2	0.05mM to .25mM	--	Antiseptic solution	Int. J. Electrochem. Sci., 6 (2011) 4188 – 420
Hb/ZrO_2chitosan/GCE/ H_2O_2	1.5 to 30.2M	--	--	Biosensors and Bioelectronics 19 (2004) 963–969
Au Electrode/ZrO_2/Hb – H_2O_2 sensor	1.75 µM to 4.9 mM	l-Cysteine Tyrosine Ethanol, Glucose, Acetic acid, Ascorbic acid		Microchim Acta (2010) 169:181–186
C@SnO2/PtNPs/GCE/ H_2O_2	1–170 µM	AA and UA	milk	Colloids and Surfaces B: Biointerfaces 101 (2013) 106–110
Au–chitosan/HRP/ITO/ H_2O_2	0.01 to 0.5 mM	--	--	Analytical Biochemistry 360 (2007) 288–293
AuNP aarays/ITO/ H_2O_2	1×10^{-6}–5×10^{-4}M	--	--	Analytica Chimica Acta 540 (2005) 299–306

HRP/nano-Ni–SnO_2 /GCE/ H_2O_2	1.0×10^{-7} to 3.0×10^{-4} M	--	--	Biosensors and Bioelectronics 36 (2012) 41–47
RuO_2-Nafion-AuNP/GCE/ H_2O_2	0.1nM to 30mM	AA, UA and CA	Antiseptic solution	Present work
SnO_2-Nafion-AuNP/GCE/ H_2O_2	1.3 mM to 39 mM	AA, UA and CA	Milk	Present work
ZrO_2-Nafion-AuNP/GCE/ H_2O_2	1 nm to 1000 mM	AA, UA and CA	Milk	Present work