Supporting Information

Oxygenated functional group-engaged electroless deposition of ligand-free sliver nanoparticles on porous carbon for efficient electrochemical non-enzymatic H_2O_2 detection

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The file includes Experimental Section, Figs. S1-S15 and Tables S1-S4.

Chemical and materials

Potassium citrate ($C_6H_5K_3O_7$), sodium chloride (NaCl), fructose (Fru), urea (Urea), uric acid (UA), ascorbic acid (AA), sucrose (Suc) and silver nitrate ($AgNO_3$) were obtained from Aladdin Industrial Inc., China. Nafion (5 wt%) was supplied by Sigma-Aldrich. Graphene oxide was purchased from Nanjing XFNANO Materials Tech Co., Ltd. $K_2HPO_4 \cdot 3H_2O$, $KH_2PO_4 \cdot 3H_2O$, and H_2O_2 were purchased from Chengdu Kelong Reagent Co., Ltd. Different kinds of milk, including Mengniu/250 mL (milk-M, Inner Mongolia), Ely/250 mL (milk-E, Inner Mongolia) and Trenwith/250 mL (milk-T, Inner Mongolia), and orange juices, such as Master Kong/250 mL (juice-M, Tianjin), President/500 mL (juice-P, Shanghai) and Coca/500 mL (juice-C, Shanghai) were purchased from Wal-Mart supermarket, China. Bovine serum obtained from Shanghai Hyclone. All of the above chemicals were of analytical grade and used without further purification. De-ionized (DI) water was used for preparing samples. Double distilled water was used throughout the electrochemical measurement.

Syntheses of PC: Typically, 1.5 g potassium citrate was calcined in a tube furnace under argon at 800 ℃ for 1 h [1]. The resulting solid was rinsed by an aqueous HCl solution (1.0 M) for 24 h. Subsequently, the black power was isolated through centrifugation, washed with water, and dried at 70 ℃ for 10 h.

Characterization

X-ray diffraction (XRD) was recorded using a Regaku D/Max-2500 (Rigaku Co., Japan) diffractometer with a Cu Kα radiation to determine the crystal structure. The

morphologies of the obtained samples were characterized using a scanning electron microscope (SEM) (FE-SEM, JSM-7500, Japan) and a transmission electron microscopy (TEM) (JEM-2100F, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) spectra and ultraviolet photoelectron spectrum (UPS) were recorded on a Thermo ESCALAB 250 Axis Ultra spectrometer (VG Scientific, UK) using an Al Kα radiation. Fourier transform infrared spectroscopy (FTIR) spectrum was performed on NEXUS 670 infrared spectrophotometer (Thermo Nicolet, USA). The spectrum was recorded in the range from 400 to 4000 cm^{-1} by using pressed KBr tables. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis was carried out on SPECTRO ARCOS spectrometer. The Brunauer–Emmett–Teller (BET) surface area and pore volume of the samples was analyzed by an ASAP 2020 Micromeritics instrument.

The calculation of ΔE

The driving force for the SIED is the positive ΔE between the reduction potential of Ag^+ ($\varphi_{Ag^+/Ag}$) and the oxidation potential of PC ($\varphi_{R-PC/O-PC}$). According to Eq. (1), the value of ΔE can be calculated. The oxidation potential of $\varphi_{R-PC/O-PC}$ was calculated to be -0.25 V on the basis of the work function from the UPS result. Additionally, the reduction potential of $\varphi_{Ag^+/Ag}$ was calculated to be 0.779 V according to the Nernst equation Eq. (2). Therefore, the value of ΔE was calculated to be 1.029 V, indicating that the spontaneous redox reaction for the synthesis of Ag/PC was thermodynamically feasible.

$$\Delta E = \varphi_{Ag^+/Ag} - \varphi_{R-PC/O-PC} \quad (1)$$

$$\varphi_{Ag^+/Ag} = 0.779 + \frac{0.059}{1}\log\frac{[Ag^+]}{[Ag]} \quad (2)$$

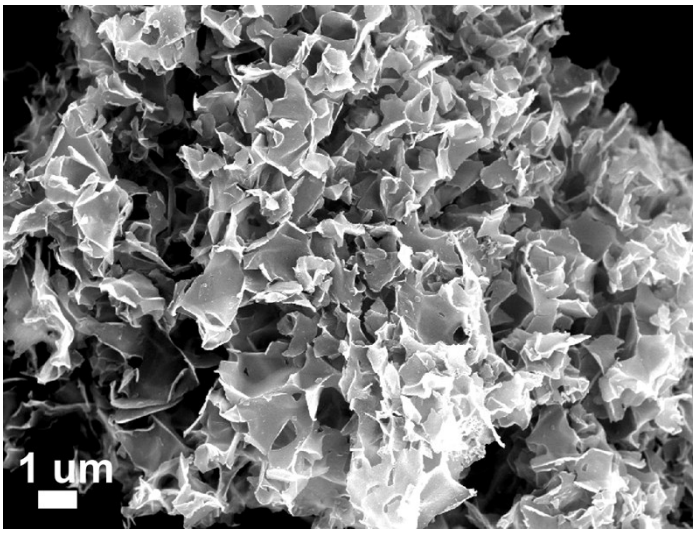

Fig. S1 Low-magnification SEM image.

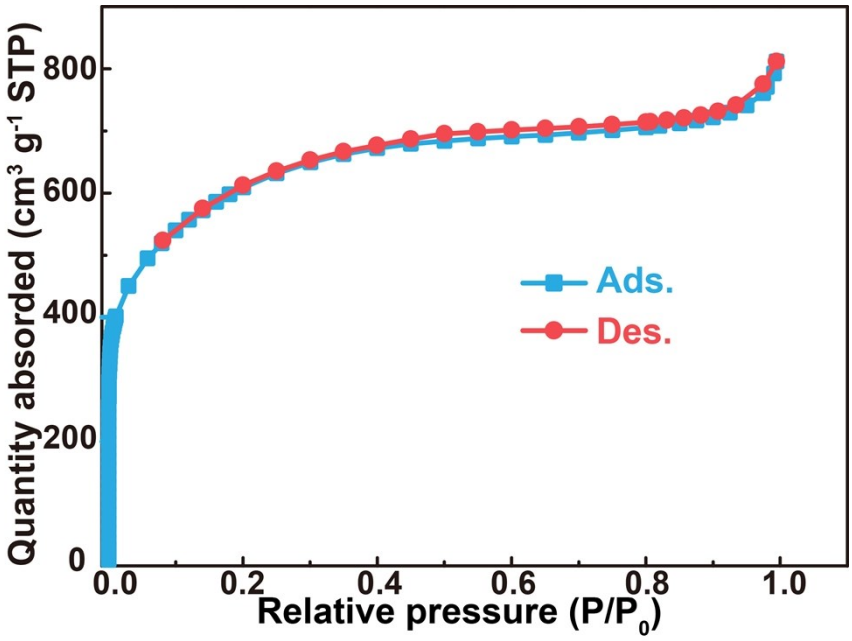

Fig. S2 N_2 sorption isotherm curve of PC.

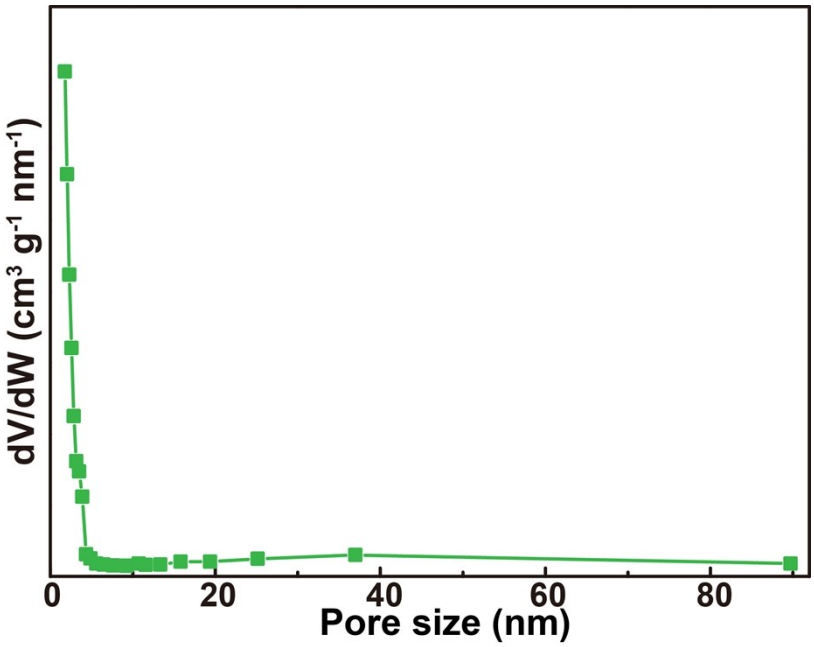

Fig. S3 The pore size distribution of PC.

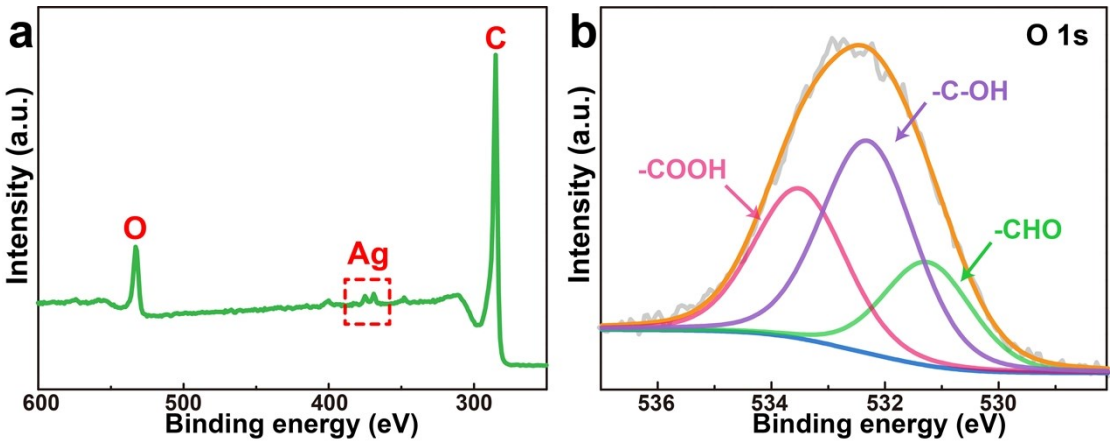

Fig. S4 (a) XPS full scan spectra and (b) O 1s high resolution XPS spectra for Ag/PC-6.

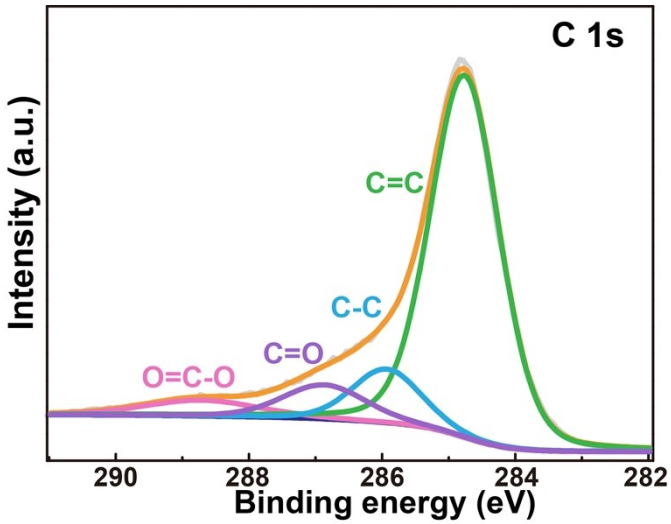

Fig. S5 C1s high resolution XPS spectra for Ag/PC-6.

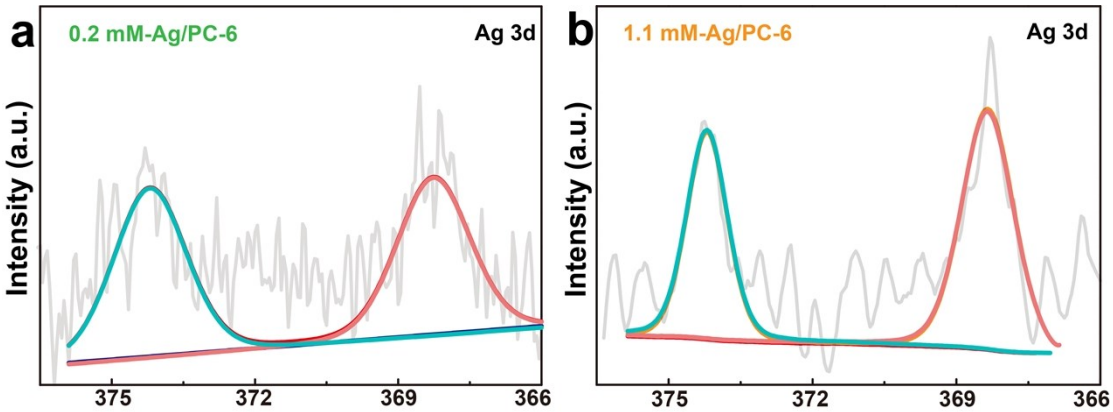

Fig. S6 Ag 3d high resolution XPS spectra for 0.2 mM-Ag/PC-6 (a) and. 1.1 mM-Ag/PC-6 (b).

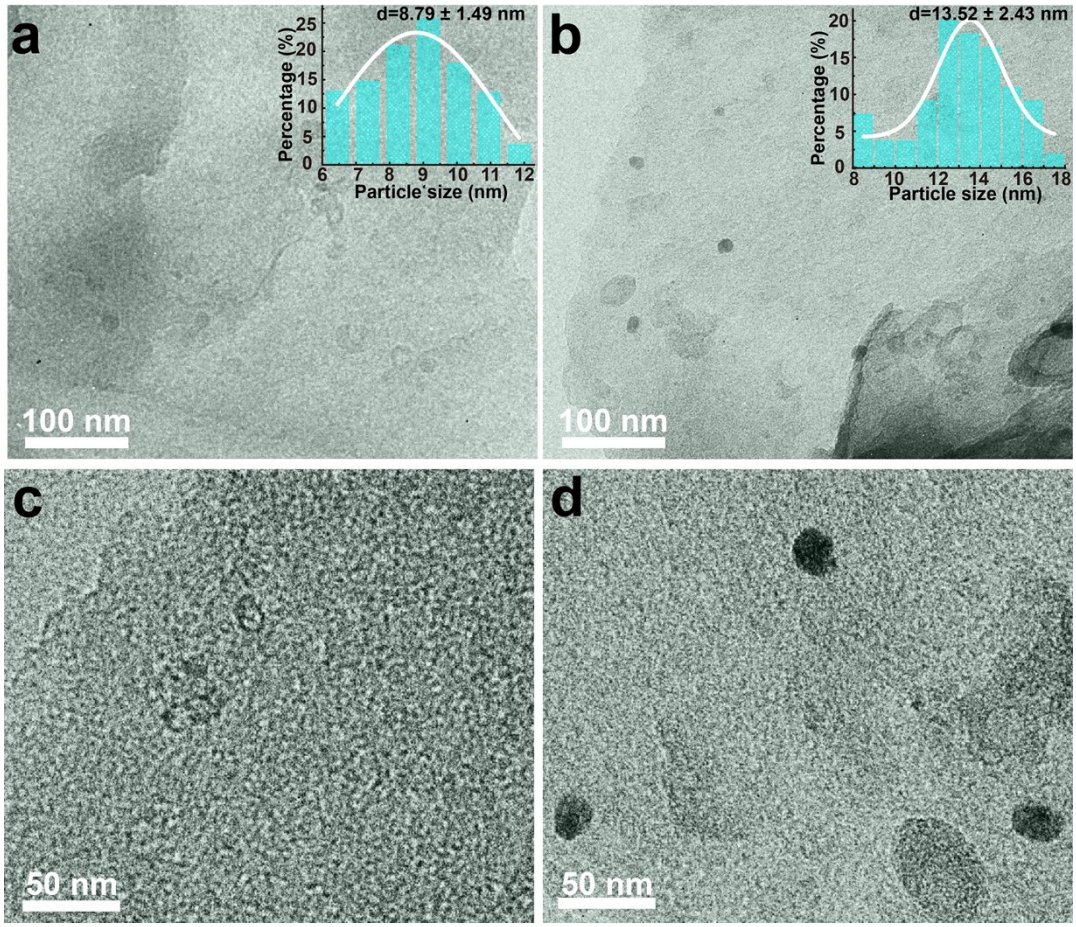

Fig. S7 TEM images of 0.2 mM-Ag/PC-6 (a, c) and 1.1 mM-Ag/PC-6 (b, d).

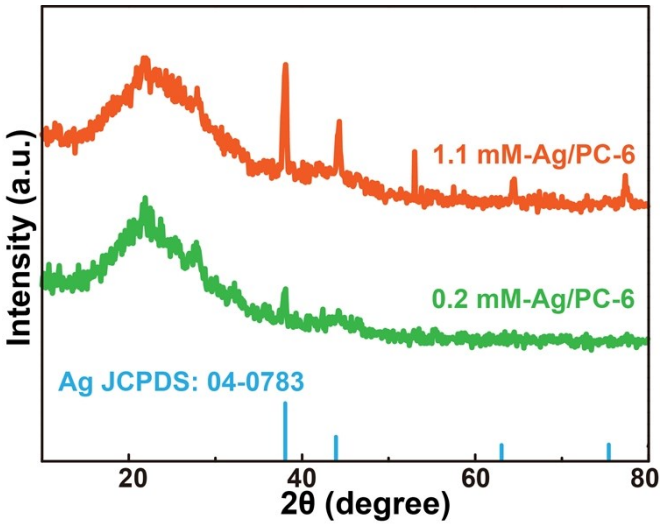

Fig. S8 XRD patterns of 1.1 mM-Ag/PC-6 and 0.2 mM-Ag/PC-6.

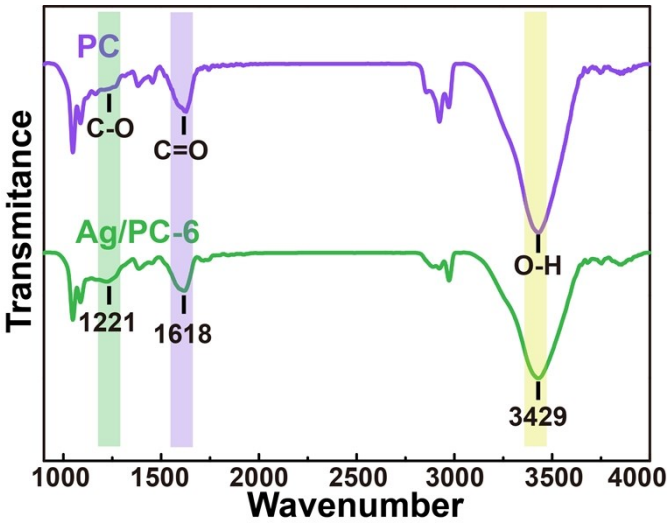

Fig. S9 The FTIR characterization of PC and Ag/PC-6.

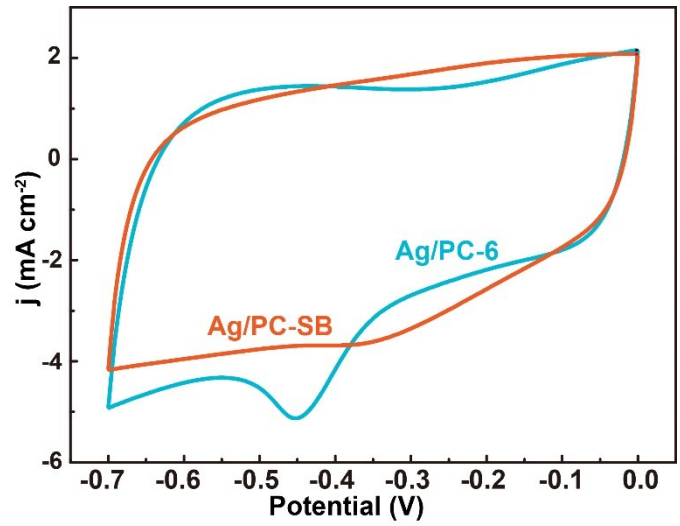

Fig. S10 CVs of Ag/PC-6 and Ag/PC-SB in 0.1 M PBS with 5 mM H_2O_2 (Scan rate: 50 mV s^{-1}).

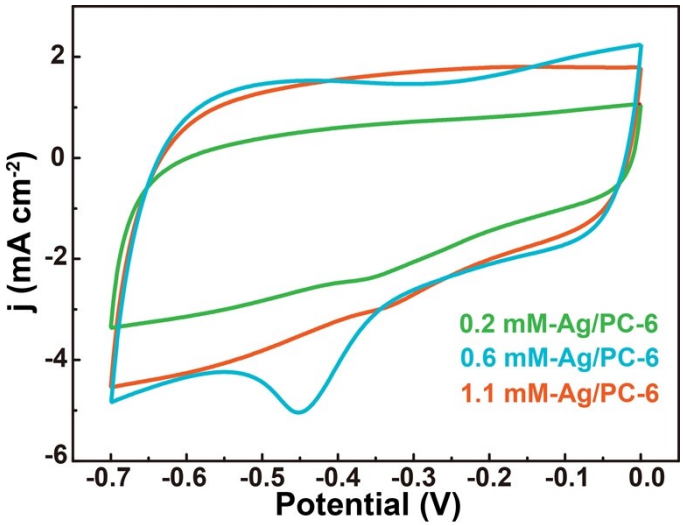

Fig. S11 CVs of Ag/PC-6 with different Ag ions concentration (0.2, 0.6 and 1.1 mM) in 0.1 M PBS in the presence of 5 mM H_2O_2 (Scan rate: 50 mV s^{-1}).

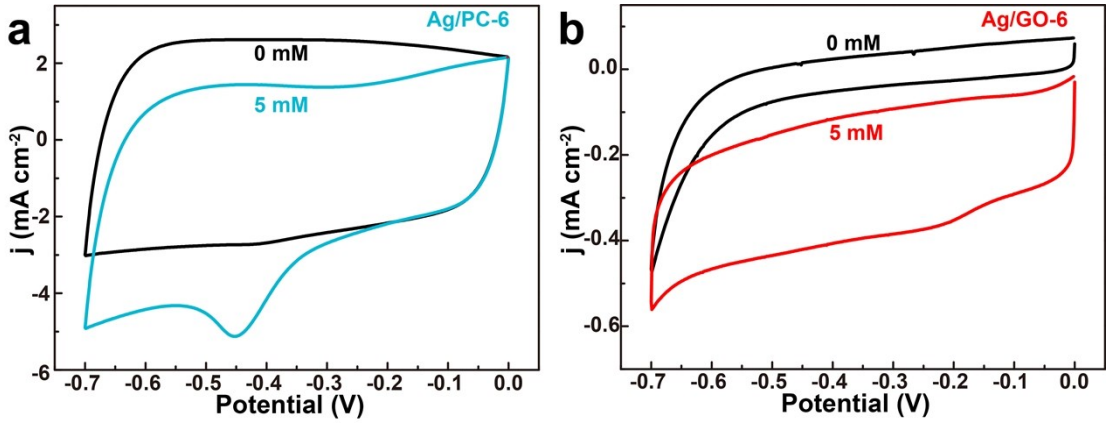

Fig. S12 CVs of Ag/PC-6 (a) and Ag/GO-6 (b) in 0.1 M PBS in the absence and presence of 5 mM H_2O_2 (Scan rate: 50 mV s^{-1}).

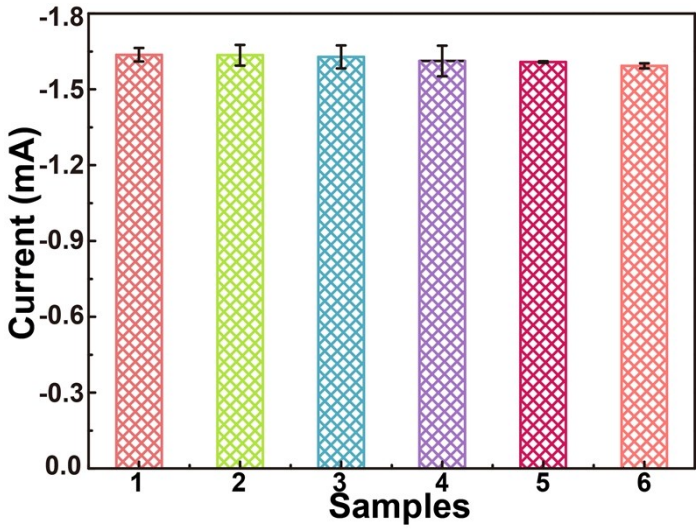

Fig. S13 Cathodic peak currents of the six successive tests with the same Ag/PC-6 in 9 mM H_2O_2 (n=3).

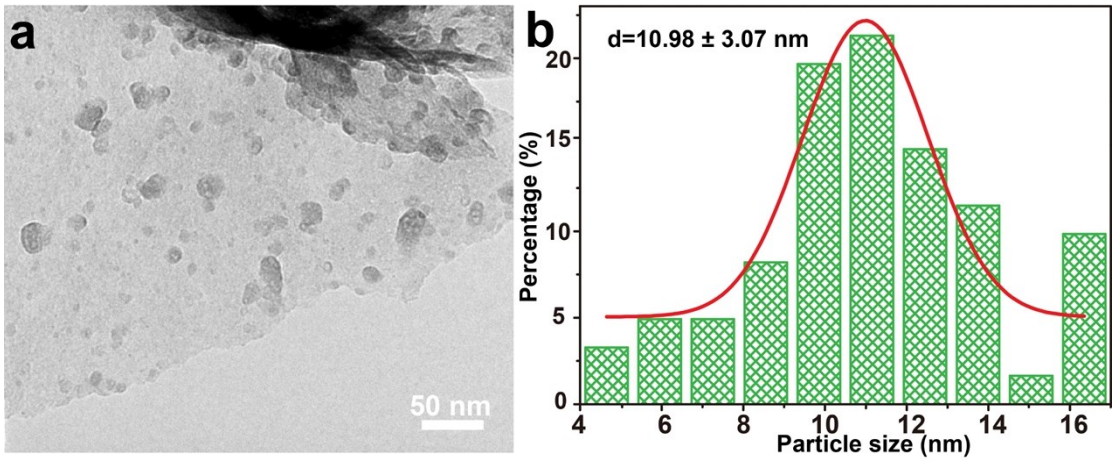

Fig. S14 TEM image (a) and the particle size distribution (b) of Ag/PC-6 after the electrochemical H_2O_2 detection about 5000s.

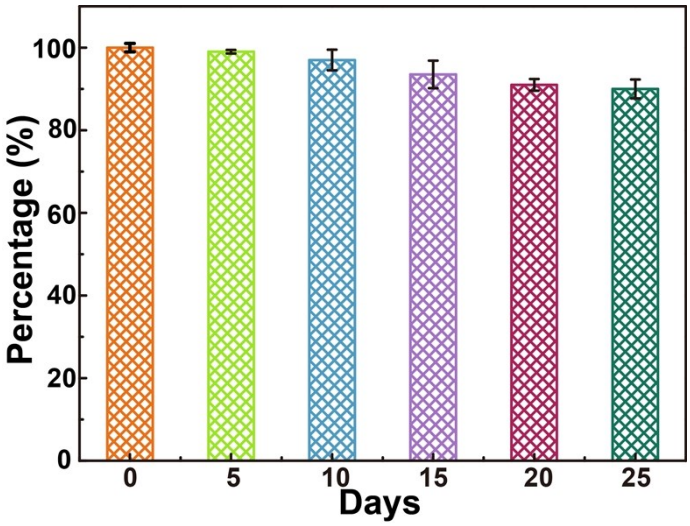

Fig. S15 Six tests with same Ag/PC-6 electrode to H_2O_2 monitoring in 25 days (n=3).

Table S1. ICP characterization results of Ag/PC-1, Ag/PC-6, and Ag/PC-10.

Materials	Ag NPs content by ICP (wt%)
Ag/PC-1	0.91
Ag/PC-6	1.24
Ag/PC-10	1.28

Table S2. XPS characterization results of PC and Ag/PC-6.

Materials	O element content [a] (at%)	-C-OH group content (at%)	-CHO group content (at%)
PC	13.42	7.1	3.2
Ag/PC-6	10.58	4.8	1.9

[a] The content of Co element is collected by full scan spectrum of XPS.

Table S3. Comparison of electrochemical performance of previous reported sensors for H_2O_2 detection.

Electrodes	Linear range (mM)	LOD (μM)	Sensitivity (μA mM^{-1} cm^{-2})	Refs.
Ag NPs/porous silicon	0.0016-0.5	0.45	-	[2]
Ag NS/ITO	0.2-4	1	-	[3]
Ag NPs/3DG	0.03-16.21	16.21	-	[4]
Ag NPs/DNA	0.004-16	1.7	-	[5]
AgNPs/GN/GCE	0.1-40	28	-	[6]
Ag/MnO/CNTs/GCE	0.005-10.4	1.7	82.5	[7]
LSG-Ag	0.100-10	7.9	-	[8]
Inkjet printed Ag electrode	0.1 - 6.8	5.0	287	[9]
Ag/NCNFs	0.020–20	0.15	142.2	[10]
Cu_2O/AuCu/Cu	0.010-9	0.14	127.98	[11]
Au@Ag@C	0.005-4.75	0.14	-	[12]
AgCo/MWCNT/GCE	-	0.74	57.14	[13]
N-graphene-Ag NDs/ITO	0.1 - 80	0.26	88.47	[14]
Ag nanosheets	0.005-6	0.17	320.3	[15]

Ag–HNTs–MnO_2	0.002-4.71	0.7	119	[16]
Au-SiO_2-MTs	0.01-1	0.6	-	[17]
Pt-N-graphene/ITO	0.001-1	0.34	61.23	[18]
Pt-PVA-CNT/GCE	0.002–3.8	0.7	122.63	[19]
ZnO_3-CuO_7/CPE	0.003-0.53	2.4	1.11	[20]
PdCu/CB nanohybrid	0.0004-5.0	0.054	-	[21]
AuPd@GR	0.005-11.5	1	186.86	[22]
Mn@FeNi-S/GO	-	0.0088	8.929	[23]
Co@MOF-808	0.01-0.45	1.3	382.27	[24]
CC/Co@C-CNTs	0.0004-7.2	0.27	388	[25]
Nanorough Ag layer	0.01-22.5	6	-	[26]
AgNPs-rGO	0.1-60	1.8	-	[27]
MWCNT/Ag	0.05-17	0.5	1.42	[28]
Ag nanowire	0.1-3.1	29.2	266	[29]
Ag NP/PC-6	**0.001-20**	**0.729**	**226.9**	**This work**

Table S4. Real-time detection of H_2O_2 in real samples.

Food Samples	Added (μM)	Recovery rates (%)	RSD (%) (n=3)
juice-M	10	91.2	1.6
juice-P	10	96.0	2.1
juice-C	10	90.6	5.4
milk-M	10	86.4	3.5
milk-E	10	97.0	2.9
milk-T	10	80.0	2.2
scrum	10	99.0	2.0

References

1. M. Sevilla and A. B. Fuertes, *ACS Nano*, 2014, **8**, 5069-5078.
2. A. A. Ensafi, F. Rezaloo and B. Rezaei, *Sens. Actuators, B* 2016, **231**, 239-244.
3. M. Amiri, S. Nouhi and Y. Azizian-Kalandaragh, *Mater. Chem. Phys.*, 2015, **155**, 129-135.
4. B. Zhan, C. Liu, H. Shi, C. Li, L. Wang, W. Huang and X. Dong, *Appl. Phys. Lett.*, 2014, **104**, 243704.
5. K. Cui, Y. Song, Y. Yao, Z. Huang and L. Wang, *Electrochem. Commun.*, 2008, **10**, 663-667.
6. L. Jia, J. Liu and H. Wang, *Electrochim. Acta* 2013, **111**, 411-418.
7. Y. Han, J. Zheng and S. Dong, *Electrochim. Acta* 2013, **90**, 35-43.
8. E. Aparicio-Martínez, A. Ibarra, I. A. Estrada-Moreno, V. Osuna and R. B. Dominguez, *Sens. Actuators, B* 2019, **301**, 127101.
9. L. Shi, M. Layani, X. Cai, H. Zhao, S. Magdassi and M. Lan, *Sens. Actuators, B* 2018, **256**, 938-945.
10. H. Guan, Y. Liu, Z. Bai, J. Zhang, S. Yuan and B. Zhang, *Mater. Chem. Phys.*, 2018, **213**, 335-342.
11. X. Liang, W. Li, H. Han and Z. Ma, *J. Electroanal. Chem.*, 2019, **834**, 43-48.
12. Y. Li, Y. Zhang, Y. Zhong and S. Li, *Appl. Surf. Sci.*, 2015, **347**, 428-434.
13. H. C. Kazici, F. Salman, A. Caglar, H. Kivrak and N. Aktas, *Fuller. Nanotube Car. N*, 2018, **26**, 145-151.
14. M. T. Tajabadi, W. J. Basirun, F. Lorestani, R. Zakaria, S. Baradaran, Y. M. Amin, M. R. Mahmoudian, M. Rezayi and M. Sookhakian, *Electrochim. Acta* 2015, **151**, 126-133.
15. B. Ma, C. Kong, X. Hu, K. Liu, Q. Huang, J. Lv, W. Lu, X. Zhang, Z. Yang and S. Yang, *Biosens. Bioelectron.*, 2018, **106**, 29-36.
16. S. Zhang, Q. Sheng and J. Zheng, *RSC Adv.*, 2015, **5**, 26878-26885.
17. S. Liu, B. Yu, F. Li, Y. Ji and T. Zhang, *Electrochim. Acta,* 2014, **141**, 161-166.
18. M. T. Tajabadi, M. Sookhakian, E. Zalnezhad, G. H. Yoon, A. M. S. Hamouda, M. Azarang, W. J. Basirun and Y. Alias, *Appl. Surf. Sci.*, 2016, **386**, 418-426.
19. Y. Fang, D. Zhang, X. Qin, Z. Miao, S. Takahashi, J.-i. Anzai and Q. Chen, *Electrochim. Acta* 2012, **70**, 266-271.
20. S. Daemi, S. Ghasemi and A. Akbar Ashkarran, *J. Colloid Interface Sci.*, 2019, **550**, 180-189.
21. Y. Liu, H. Li, S. Gong, Y. Chen, R. Xie, Q. Wu, J. Tao, F. Meng and P. Zhao, *Sens. Actuators, B* 2019, **290**, 249-257.
22. T. D. Thanh, J. Balamurugan, S. H. Lee, N. H. Kim and J. H. Lee, *Biosens. Bioelectron.*, 2016, **85**, 669-678.
23. S. Manavalan, J. Ganesamurthi, S.-M. Chen, P. Veerakumar and K. Murugan, *Nanoscale*, 2020, **12**, 5961-5972.
24. Y.-S. Chang, J.-H. Li, Y.-C. Chen, W. H. Ho, Y.-D. Song and C.-W. Kung, *Electrochim. Acta,* 2020, **347**, 136276.
25. L. Long, H. Liu, X. Liu, L. Chen, S. Wang, C. Liu, S. Dong and J. Jia, *Sens. Actuators, B* 2020, **318**, 128242.
26. W. Lian, L. Wang, Y. Song, H. Yuan, S. Zhao, P. Li and L. Chen, *Electrochim. Acta,* 2009, **54**, 4334-4339.
27. X. Qin, Y. Luo, W. Lu, G. Chang, A. M. Asiri, A. O. Al-Youbi and X. Sun, *Electrochim. Acta,* 2012, **79**, 46-51.
28. W. Zhao, H. Wang, X. Qin, X. Wang, Z. Zhao, Z. Miao, L. Chen, M. Shan, Y. Fang and Q. Chen, *Talanta*, 2009, **80**, 1029-1033.
29. E. Kurowska, A. Brzózka, M. Jarosz, G. D. Sulka and M. Jaskuła, *Electrochim. Acta,* 2013, **104**, 439-447.