Supporting information

Table.S1 Specificity and accuracy of each analyte obtained from the cross-validation model

Analytes	Abbr.	Sensitivity （%）	Specificity （%）	Accuracy （%）
Formaldehyde	ForA	100	100	100
Acetaldehyde	AceA	100	100	100
Butyraldehyde	ButA	100	100	100
isobutyraldehyde	iButA	100	100	100
Pentanal	PentaA	100	100	100
Glutaraldehyde	GluA	50	100	95
Caproaldehyde	CapA	100	100	100
Heptaldehyde	HepA	100	100	100
Furaldehyde	FurA	100	100	100
Benzaldehyde	BenzA	100	88	90

The leave-one-out method[1], as a kind of cross-validation model, was performed to calculate quantitatively the accuracy of the performance of sensor. The accuracy of recognition was one of the most important norms, and results were showed in table S1. To all the analytes, the accuracy of aldehydes is over 90%, and the specificity of aldehydes is over 88%.

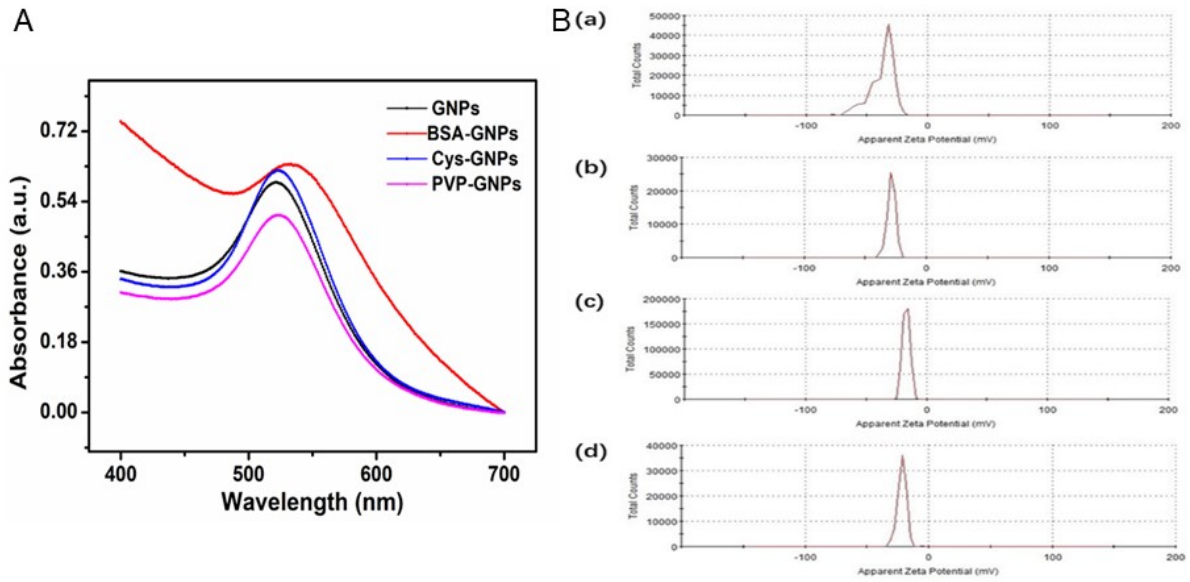

Fig.S1 (A) UV-Vis spectrum of gold nanoparticles modified with different ligands. (B) Zeta potential of gold nanoparticles modified with different ligands：(a) GNPs; (b) Cys-GNPs; (c) PVP- GNPs; (d) BSA- GNPs

All the absorption peaks of GNPs located in the range of 520~531 nm. The absorption peak of GNPs at 522 nm. The absorption peak of BSA-GNPs at 531nm. The absorption peak of Cys-GNPs at 523nm. The absorption peak of PVP-GNPs at 520 nm.The surface of GNPs shows negative charge when Cys, PVP, and BSA were chosen as the ligands.

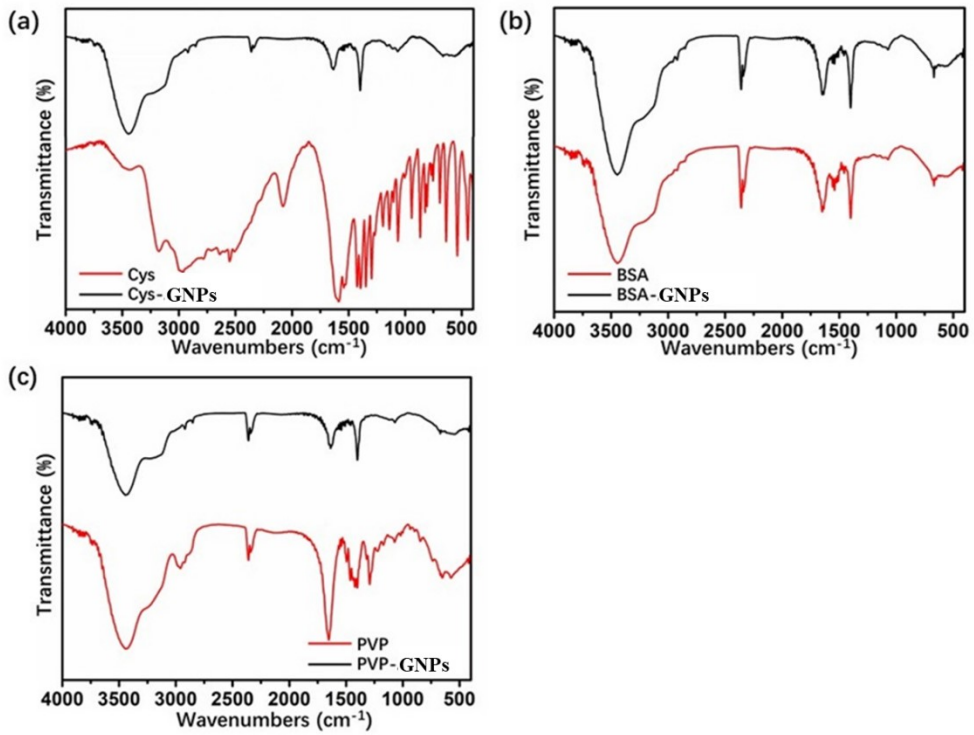

Fig.S2 FT-IR spectra of different ligands and GNPs modified with different ligands

The shows the FT-IR spectra for different ligands and GNPs modified with different ligands (Fig.S1). The main bands in BSA spectrum are in the range of 3000 cm^{-1} to 3400 cm^{-1} for the O-H stretching vibrations, 1647 cm^{-1} for C=O stretching vibrations and 1222 cm^{-1} for C–N stretching vibrations. Two main absorption peaks in PVP spectrum are 1650cm^{-1} for C=O stretching vibration and 1298 cm^{-1} which is due to and C–N stretching vibration[2]. The peaks at 1636 cm^{-1} and 1400 cm^{-1} are indicated the asymmetric and symmetric stretching vibrations of carboxylate. The broad band of Cys located in the range of 3000 to 3500 cm^{-1} shows the $NH3^{+}$ stretching vibration and a weak band near 2551 cm^{-1} corresponds to S-H vibrational band[3].

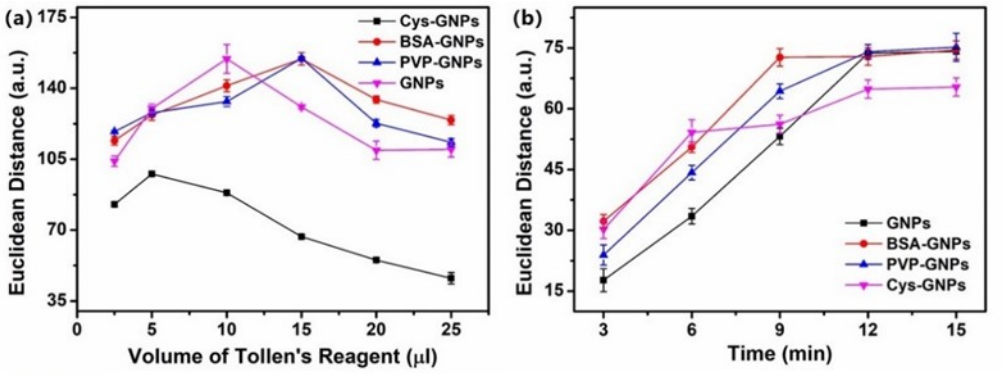

Fig.S3 Euclidean distance of the array under different volumes of Tollens' reagent (a) and incubation time (b)

The optimal volume of Tollens' reagent for GNPs modified with different ligands is showed in Fig.S2a. In order to shorten the reaction time, time was optimized when the Euclidean distance reached a plateau at 60 °C (Fig.S2b). After reaction more than 12 min, the reaction intensity is the largest and reaches a plateau. We chose 12 min as the time to achieve stability of sensor arrays for the subsequent experiments.

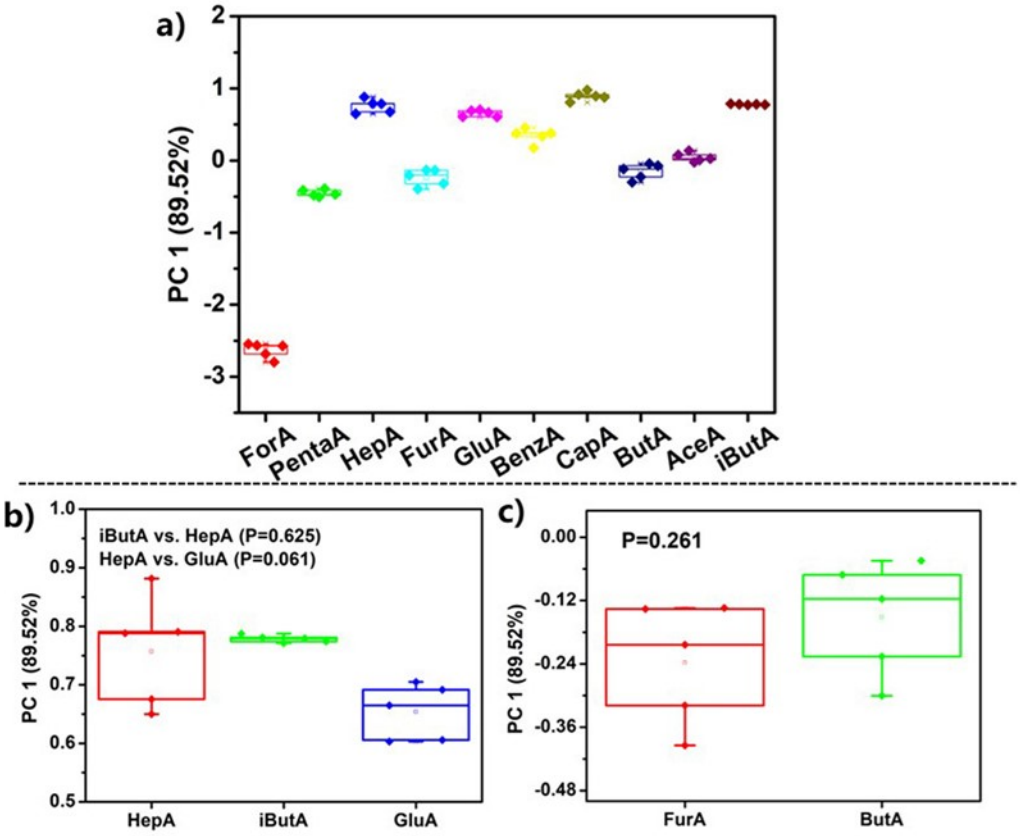

Fig.S4 (a) Distribution of scores of the first-dimension principal components of ten aldehydes: Significant difference analysis based on the scores of the first-dimension principal components: (b) Isobutyraldehyde vs. heptaldehyde vs. glutaraldehyde; (c) Furfural vs. butyraldehyde

The PCA score plot of the ten aldehydes on the first-dimensional principal component was showed in Fig.S3a. Most of the aldehyde samples could be accurately discriminated based on the PC1. Therefore, t - test of independent sampler was evaluated to these aldehydes that was overlapped with others. But a significant difference analysis was not performed between isobutyraldehyde and heptaldehyde ($p=0.625>0.05$), as well as heptaldehyde and glutaraldehyde ($p=0.061>0.05$). Similarly, the significant difference between furfural and butyraldehyde were non-existent. Hence, better-optimized classification techniques, LDA was adopted to distinguish them in our consequent work.

Since the value of the variance of principal components provides information about contribution of a certain chemical property to discriminate samples[4]. The detection principle of our sensor to distinguish aldehydes is designed according to the reducibility

of aldehydes. Thus, we infer that the first PC indicates the diverse reducibility of different aldehydes.

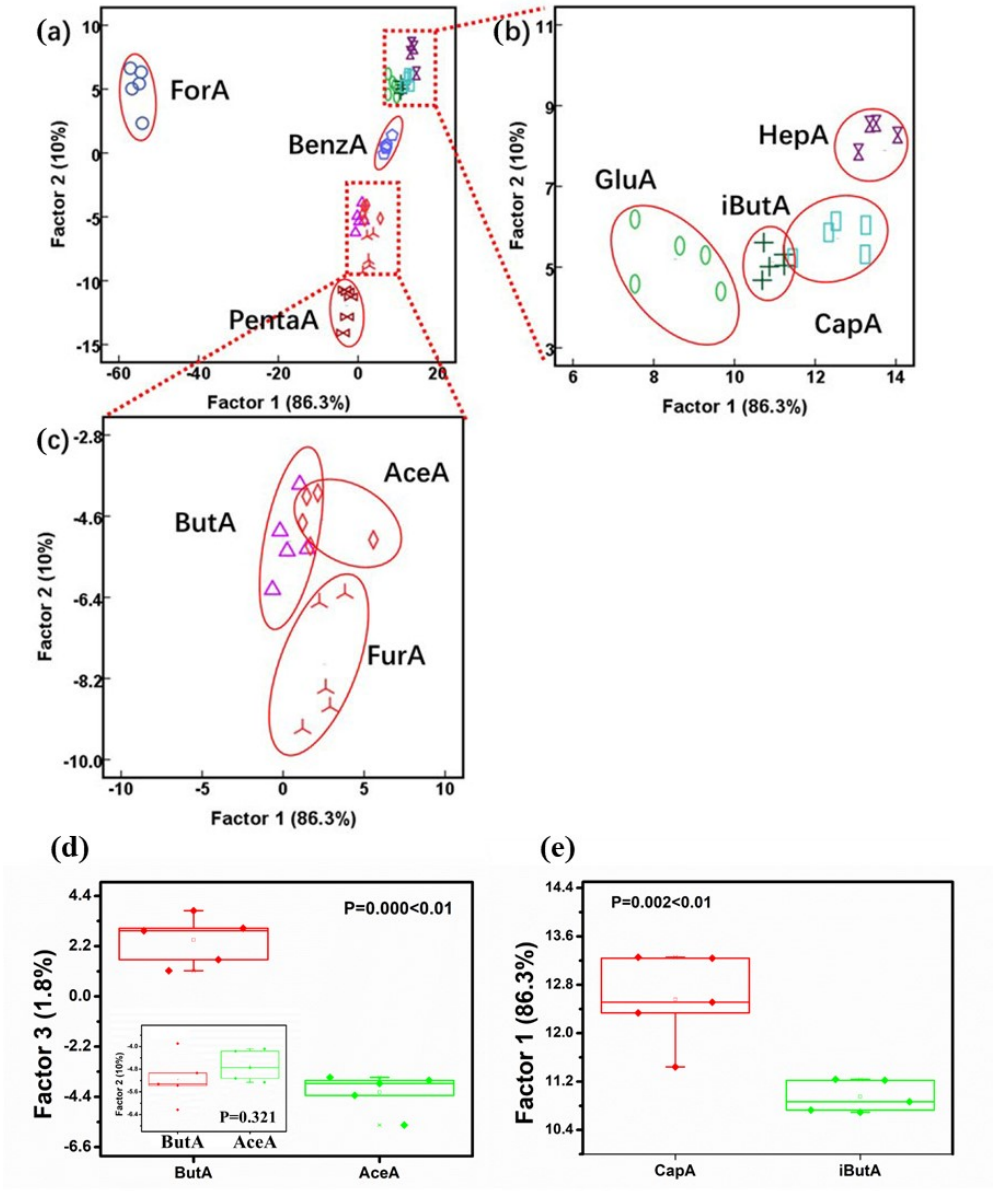

Fig.S5 LDA discrimination results of ten aldehydes based on the first two-dimensional discrimination factors((a)(b) and (c)). Significant difference analysis of the discriminant scores of butyraldehyde and acetaldehyde in the second dimension and third dimension (d); significant difference analysis of the discriminant scores of hexanal and isobutyraldehyde in the first dimension (e)

As a dimensional reduction method, LDA makes an excellent discrimination among analytes by generating several optimized orthogonal dimensions. Remarkably, most experimental samples were respectively classified into a single cluster accurately without any overlap (Fig.S4a). Unfortunately, there was still some mild overlapping that were two groups of butyraldehyde and acetaldehyde (Fig.S4c) as well as

caproaldehyde and isobutyraldehyde(Fig.S4b). There are two groups of analytes that show extreme significant differences respectively according to the t-test of the dimension of factor 3 ($p=0.00<0.01$) and the dimension of factor 1 ($p=0.002 < 0.01$), valeraldehyde and butyraldehyde (Fig.S4d) as well as, caproaldehyde and isobutyraldehyde (Fig.S4e). Hence, all each analyte could be discriminated by LDA.

References

1. Y. Wang, X. Zhong, D. Huo, Y. Zhao, X. Geng, H. Fa, X. Luo, M. Yang and C. Hou, *Talanta*, 2019, **192**, 407-417.
2. V. A. Dhumale, R. K. Gangwar, S. S. Datar and R. B. Sharma, *Materials Express*, 2012, **2**, 311-318.
3. S. Aryal, B. K. C. Remant, N. Dharmaraj, N. Bhattarai, C. H. Kim and H. Y. Kim, *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.*, 2006, **63**, 160-163.
4. J. R. Askim, M. Mahmoudi and K. S. Suslick, *Chemical Society reviews*, 2013, **42**, 8649-8682.