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Green synthesis of Au coated on ZnO nanoparticles using orange peel extract and its application for electrochemical detection of formaldehyde

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We report the facile preparation of Au coated ZnO nanoparticles via a two-step green synthesis route. The aqueous of orange peel extract (OPE) was used both as biocomplexing and bioreducing agents, while the $Zn(NO_3)_2$ and $HAuCl_4$ were employed as precursors. Initially, OPE was prepared to synthesize the ZnONPs, followed by the reduction of $HAuCl_4$, generating Au coated on ZnO nanoparticles (Au/ZnONPs). The IR spectra at around 438.95 cm^{-1} confirmed the presence of Zn-O absorption in the nanoparticles, while it was not observed in the OPE. Further characterization using XRD and SEM-EDX indicated that the spherical of Au was successfully coated on the sponge-like structure of ZnO with the crystalline size of ZnONPs and Au/ZnONPs were 21.30 and 26.67 nm, respectively. The modified Au/ZnONPs on graphite paste electrode showed the excellent electrochemical detection of formaldehyde solution by the linearity range from 1 to 100 mM (R^2=0.9945) with LOD of 10.27 mM and RSD of 0.39%. In addition, the modified electrode showed high selectivity toward formaldehyde, instead of ethanol.

Keywords: ZnO nanoparticle; Au coating; green synthesis; orange peel extract; formaldehyde detection.

Introduction

Nowadays the preparation of nanoparticles through green synthesis methods using plant derivatives have gained attract many researchers due to its simplicity, using less chemical toxic reagents, low-cost, and could employ waste of many agricultural and domestic industries (Wicaksono *et al.*, 2020; Wicaksono and Hamidah, 2018; Ariyanta *et al.,* 2021). Among many plant derivates waste, orange (*Citrus sinensis*) peels waste has been extensively employed in nanoparticles synthesis, such as gold-palladium core-shell (Au@PdNPs) (Wicaksono *et al.*, 2020), silver (Ag) (Kahrilas *et al.*, 2014), and zinc oxide (ZnO) nanoparticles (Nava *et al.*, 2017; Luque *et al.*, 2018).

On the other hand, due to the large surface area and excellent charge transport (Zhao *et al.*, 2015), zinc oxide nanoparticles (ZnONPs) exhibited prospective performance as electrocatalysts for dyes (Ya *et al.*, 2017) and H_2O_2 electrochemical detection (Zheng *et al.,* 2016). To increase the sensing performance, the surface of ZnONPs could be modified by a noble metals coating (Zhao *et al.*, 2015). Gold (Au) has been extensively employed for many surface modification processes to increase the conductivity and electrocatalytic ability of the ZnONPs (Zhao *et al.*, 2015). Zao and co-workers have employed the Au nanoparticles coated on ZnO nanorods for electrochemical sensing of lactate (Zhao *et al.*, 2015). Thus, the performance of Au deposition on ZnONPs surface was also interesting to be more explored. To the best of our knowledge, the evaluation of green synthesized Au coated on ZnONPs (Au/ZnONPs) for the electrochemical sensing of formaldehyde is yet to be investigated. *Formaldehyde* (HCHO) is a carcinogenic chemical to humans that is illegally used for food preservatives, such as tofu, fish, and noodle (Zhou *et al.*, 2009; Weng *et al.*, 2009).

In this work, we reported the performance of the green synthesized Au/ZnONPs as the electrocatalyst in the electrochemical sensing of formaldehyde solution. The synthesized nanoparticles were characterized by Fourier-transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy-energy dispersive X-ray (SEM-EDX). The Au/ZnONPs was then modified to a graphite paste electrode (GPE) and employed as the working electrode. Furthermore, the evaluation of linearity range, limit of detection (LOD), precision, and selectivity was also thoroughly performed.

Experimental Section

Green synthesis and characterization of Au/ZnONPs

The preparation of ZnONPs follows the previous report by Luque and co-workers (Luque *et al.*, 2018). Initially, the orange peel was dried at 90 °C for 15 h followed by grinding to obtain a fine powder.

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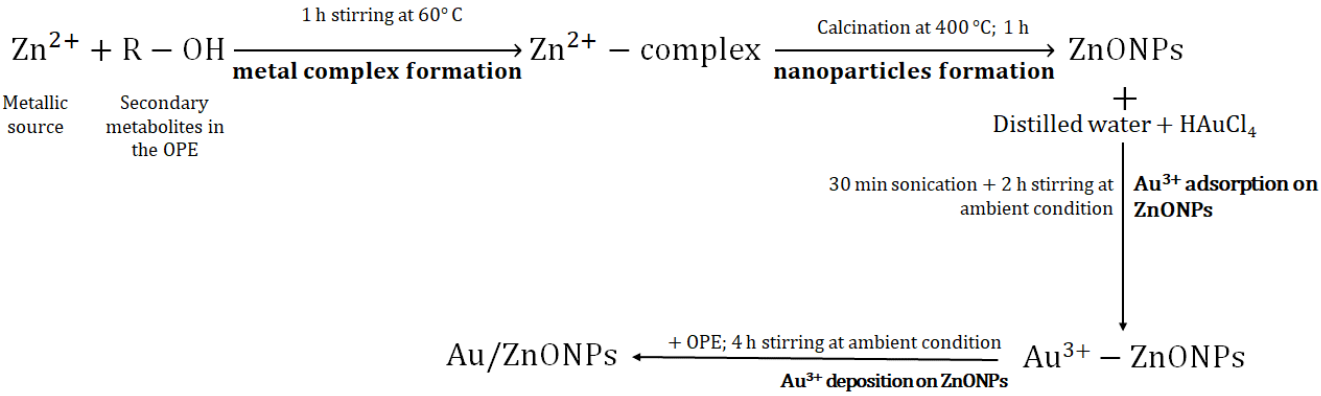
A 2% (w/v) orange peel extract (OPE) was diluted in distilled water followed by 3 h stirring under the ambient condition, then boiled at 90 °C for 1 h and filtered. Afterward, A 2 g of $Zn(NO_3)_2$ was added to the OPE, then heated at 60 °C, generating a thin deposit. Finally, the deposit was calcined at 400 °C for 1 h, generating a white powder of ZnONPs. Meanwhile, the deposition of Au on ZnONPs surface to form Au/ZnONPs based on the modified Fageria's work (Fageria *et al.,* 2014). Briefly, a 1% (w/v) of ZnO powder was diluted in distilled water and sonicated for 30 min. Afterward, 10 mL of 0.01 M $HAuCl_4$ was added to the mixture and stirred for 2 h until a deposit was formed. The deposit was washed then dispersed to 20 mL of distilled water, subsequently the addition of 0.2 mL of OPE and stirred for 4 h, generating a purple deposit of Au/ZnONPs. Finally, the deposit was washed with distilled water and dried to obtain a powder of Au/ZnONPs. The nanoparticles were then characterized by FTIR (Thermo Nicolet Avatar 360), XRD (Bruker D2 Phaser Cu Kα1 radiation, λ=1.54056 A°), SEM-EDX (Phenom Pro-X), and stored for further application in the electrode fabrication.

Fabrication of graphite paste electrode modified by Au/ZnONPs and its electrochemical performance for formaldehyde detection

GPE and its modification were fabricated following Likasari and co-workers' previous report (Likasari *et al.*, 2021). Briefly, paraffin oil was heated until reached 85 °C, then the graphite powder was added to form a paste (paraffin and graphite mass ratio was 7:3). Afterward, the paste was filled into a glass electrode casting containing Cu wire, then dried at ambient temperature overnight. To obtain the GPE modified by Au/ZnONPs, a 20% (w/v) of Au/ZnONPs powder was diluted in ethanol 96% and dropped into the GPE, then dried at ambient condition overnight before use. A cyclic voltammetry (CV) technique from -0.5 to 1 V with 3 system electrodes (Au/ZnONPs/GPE, Ag/AgCl, and Pt as working, reference, and auxiliary electrodes, respectively) and a scan rate of 0.1 V/s in 25 mM HCHO in 0.1M buffer phosphate pH 9 was used to evaluate the electrochemical sensing performance of the Au/ZnONPs/GPE electrode. The mass transfer mode and analytical parameters, such as linearity, LOD, precision, and selectivity were also evaluated.



Scheme 1. The proposed mechanism of Au/ZnONPs formation

Result and Discussion

Au/ZnONPs preparation and its characterizations

The synthesis of Au/ZnONPs follows the mechanism figured in **Scheme 1**, which mainly consists of Zn^{2+}-complex molecules formation, followed by ZnONPs formation, then deposition of Au^{3+} on the surface of ZnONPs to form Au/ZnONPs. Initially, Zn^{2+} from metallic sources reach with the OH functional group of the OPE, generating Zn^{2+}-complex. Afterward, the complex was then calcined to form ZnONPs due to the oxidation of Zn and decomposition of organic compounds by heating. Finally, the deposition of Au^{3+} on ZnONPs to form Au/ZnONPs was assisted by the OPE as a bioreducing agent, instead of using of hydrazine chemical reductor as reported by Fageria and co-workers (Fageria *et al.,* 2014). OPE mainly contains secondary metabolites group of flavonoids, citric and ascorbic acids which could act both as complexing and reducing agents in the Au/ZnONPs formation (Wicaksono *et al.*, 2020; Luque *et al.*, 2018).

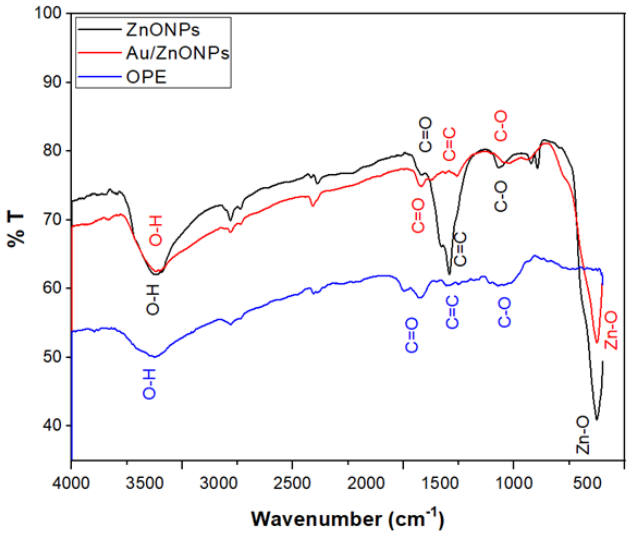


Figure 1. FTIR spectra of ZnONPs, Au/ZnONPs, and orange peel extract (OPE)

Figure 1 depicts the FTIR spectra of OPE and the green synthesized ZnONPs and Au/ZnONPs. The peak at 3434, 1638, 1442, and 1106 cm^{-1} are corresponded to -OH, C=O, C=C aromatics, and C-O of the secondary metabolites, similar to the previous report (Wicaksono *et al.*, 2020; Luque *et al.*, 2018). A peak at 438 cm^{-1} that attributable to the Zn-O groups was appeared in both ZnONPs and Au/ZnONPs, confirming the successful formation of ZnO and Au/ZnO (Azizi *et al.*, 2014). Moreover, no peak Au is observed in the FTIR spectra of Au/ZnONPs, similar to another report (Kumar *et al.,* 2014).

Figure 2A represents the XRD pattern of the ZnONPs and the Au/ZnONPs. The peaks at 31.69˚, 34.30˚, 36.14˚, 47.44˚, 56.47˚, and 67.81˚ which are corresponded to (100), (002), (101), (102), (110), and (103) planes of hexagonal wurtzite structure of ZnO (JCPDS No. 36-1451), while the additional peaks at 38.20˚, 44.41˚, and 62.87˚ are attributable to (111), (200), and (220) crystal planes of Au (JCPDS No. 04-0784), indicating the presence of Au on the ZnONPs which is confirming the Au/ZnONPs was successfully formed (Fageria *et al.,* 2014). The crystalline size of the nanoparticles was also calculated by the Debye-Scherrer equation (Equation 1) using the highest peak of ZnO (101) with D as the crystalline size (nm), K is Scherrer constant (0.9), λ is the X-ray wavelength from Cu-Kα used (1.541Å), β is the full width at half maxima of the (101) plane (FWHM, rad), and θ is Bragg diffraction angle (rad), resulting in the crystalline size of ZnONPs and Au/ZnoNPs were 21.30 and 26.67 nm, respectively. The increased crystalline size of the Au/ZnONPs compared to the ZnONPs may be due to the presence of Au adsorbed on the ZnONPs.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Moreover, the SEM images were also confirmed the porous sponge-like morphology of ZnO (**Figure 2B**) (Yu *et al.*, 2013), while the spherical Au adsorbed on the surface of ZnO (**Figure 2C**)(Fageria *et al.,* 2014). The structure of Au/ZnONPs was also confirmed by elemental analysis shown in **Figure 2B and C** showing the high content of Au that indicates the presence of Au on the surface of ZnONPs.

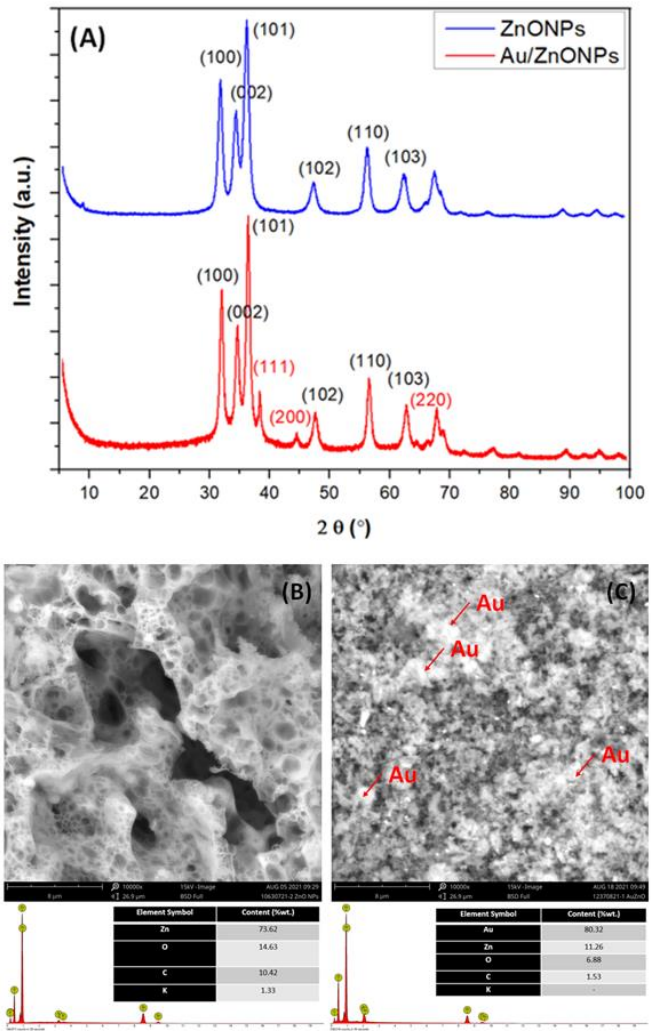


Figure 2. (A) XRD pattern; (B) and (C) SEM-EDX profile of ZnONPs and Au/ZnONPs, respectively

Electrochemical sensing of formaldehyde using Au/ZnONPs/GPE electrode

Figure 3A shows the cyclic voltammograms of HCHO on the Au/ZnONPs/GPE compared to the ZnONPs/GPE and the bare GPE electrode. A higher peak at -0.18 and 0.36 V on Au/ZnONPs/GPE electrode should be attributable to the oxidation peak of HCHO (Beltowska-brzezinska, 1985), indicating the increased conductivity and sensitivity due to the presence of Au on ZnONPs compared to the ZnONPs/GPE and GPE electrode. This was in agreement with the other report (Fang *et al.*, 2017; Hussain *et al.*, 2016). The electrooxidation reaction of HCHO on the basic medium through 2 step reaction follows the Equation 2 (Beltowska-brzezinska, 1985).

$$2HCHO + 4OH^- \rightarrow H_2(g) + 2HCOO^-(aq) + H_2O(l) + 2e^- \quad (2)$$

Moreover, a linear correlation of the square root of scan rate against the anodic peak at 0.36 V (**Figure 3B**) confirmed that the mass transport of HCHO on the Au/ZnONPs/GPE was mainly controlled by diffusion (Elgrishi *et al.*, 2018). The good analytical performance was also shown by a linearity range from 1 to 100 mM (R^2=0.9945) with the LOD was down to 10.27 mM (**Figure 3C and D**). Additionally, the modified electrode exhibited good precision with %RSD of 5 independent analytes was 0.39% and good selectivity towards 25 mM HCHO with the 2.2 times anodic current than 25 mM ethanol. This result was comparable with the previous report that employed the green synthesized CuO/Cu_2ONPs using Gum Arabic (Momeni and Sedaghati, 2018).

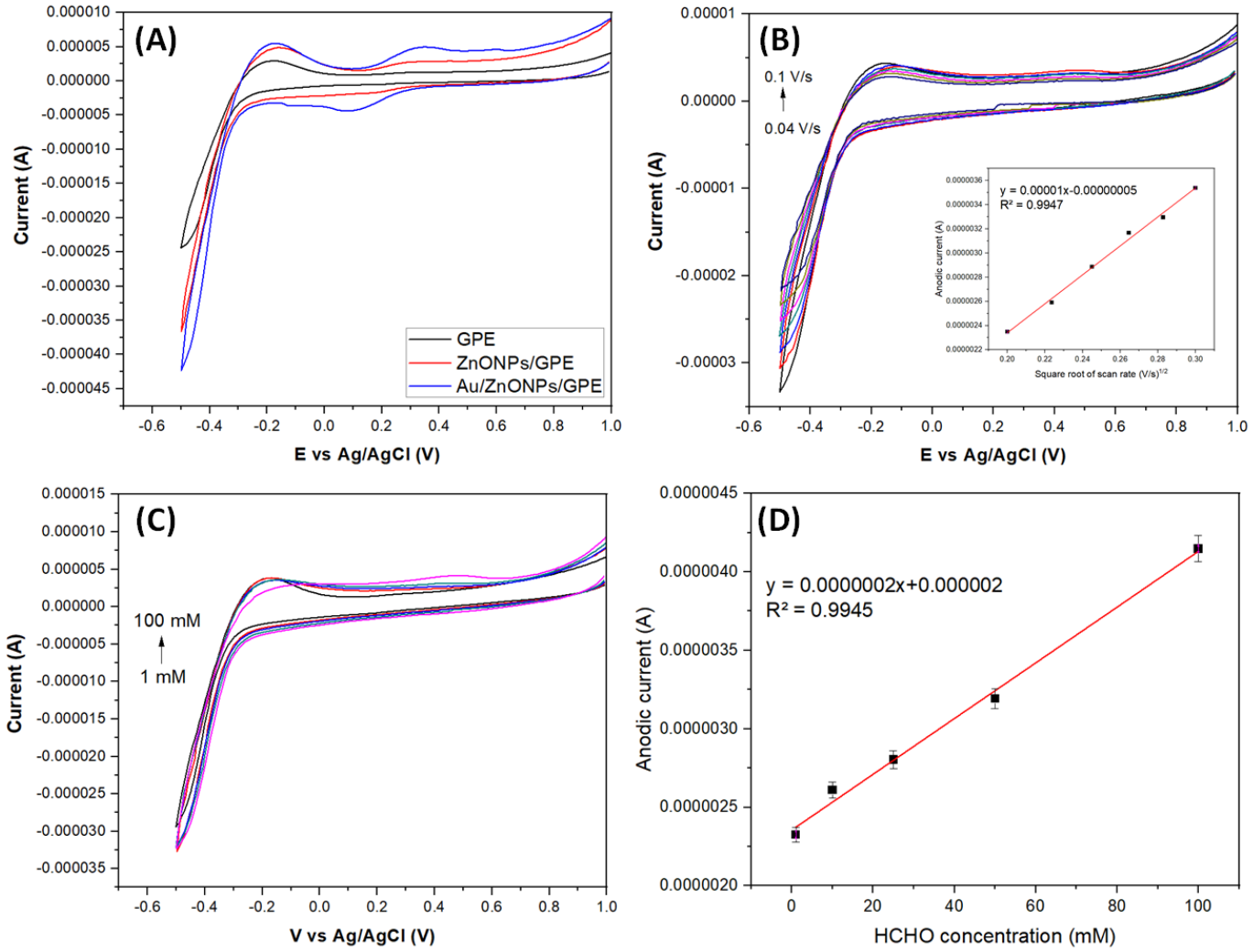


Figure 3. (A) The Cyclic voltammograms of 25 mM formaldehyde in 0.1 M phosphate buffer pH 9 on Au/ZnONPs/GPE compared to ZnONPs/GPE and bare GPE electrode; (B) the effect of scan rate against the CVs profile of the formaldehyde on Au/ZnONPs/GPE; (C) the effect of formaldehyde concentrations and (D) its linear correlation against the anodic current at 0.36 V extracted from (C)

Conclusion

In summary, the Au coated on ZnO nanoparticles through facile green synthesis route using orange peel extract as complexing and reducing agents was successfully prepared. The prepared ZnONPs have an irregular sponge-like shape, while the Au is evenly absorbed on the pore of ZnONPs with the increased crystalline size of Au/ZnONPs compared to the ZnONPs. The IR, XRD, and SEM-EDX characterizations confirmed that Au/ZnONPs were formed. Furthermore, from the CV analysis, the presence of Au on ZnONPs/GPE significantly increased the anodic current of HCHO compared to both ZnONPs/GPE and bare GPE electrodes. This study also revealed that the mass transfer mode of HCHO on Au/ZnONPs/GPE was mainly controlled by diffusion. Finally, the green synthesized Au/ZnONPs successfully enhanced the performance of HCHO electrochemical sensing with the wide linearity range concentration, high precision and sensitivity, as well as selectivity, and open the gate for further sensing application for various small organic molecule analytes.

Conflict of Interest

We have no conflict to declare.

Acknowledgements

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