Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Electrochemical detection of mercury using biosynthesized hydroxyapatite nanoparticles modified glassy carbon electrode without preconcentration

P. Kanchana[1], N. Sudhan[1], S. Anandhakumar[2], J. Mathiyarasu[2], P. Manisankar[3], C. Sekar[1*]

[1]Department of Bioelectronics and Biosensors, Alagappa University, Karaikudi-630 004, Tamilnadu, India.

[2] Central Electrochemical Research Institute, Karaikudi-630 006, Tamilnadu, India.

[3]Department of Industrial Chemistry, Alagappa University, Karaikudi-630 003, Tamilnadu, India.

*E-mail: Sekar2025@gmail.com

Phone: +91 9442563637

I. Synthesis of pristine HA using microwave method

In order to investigate the stability and reproducibility of the microwave method, pristine hydroxyapatite was prepared repeatedly by using a domestic microwave oven (Samsung-CE104VD, 6 power levels, 2450 MHz with input voltage of 230 V-50 Hz AC). Briefly, 100 mL of 0.4 M $(CaNO_3)_2.4H_2O$ solution (A) and 100 mL of 0.24 M $(NH_4)_2HPO_4$ solution (B) were prepared using deionized water. Subsequently, solution B was added to solution A slowly with constant stirring. During the reaction, pH of the solution was maintained at 10 using ammonia solution. The mixture was then exposed to microwave irradiation of 600 W for 20 minutes, washed with deionized water and dried at 80°C in a hot air oven and the resultant powder obtained in each experiment is white in colour. Fig. S1A shows powder XRD patterns of the pristine HA samples. The observed planes are exactly match with the powder diffraction file (ICDD PDF Card No. 09-0432 of hexagonal phase, space group $P6_3/m$) confirming the HA phase formation. There are no peaks corresponding to possible impurities, such as calcium hydroxide and other calcium phosphates and the average crystallite sizes of the as synthesized samples are nearly same (Table. S1). To further establish the reproducibility of the HA synthesise using microwave method, cyclic voltammograms (CVs) recorded at 50 mVs^{-1} for sample 1, 2 and 3 modified glassy carbon electrodes in 1 M KCl containing 1 mM of $[Fe(CN)_6]^{3-/4-}$ (Fig. S1B). The peak current (i_{pa}) values of the prepared samples are approximately equal and are shown in Table S1. These results indicate that the HA prepared by domestic microwave oven with the power 600 W has better stability and reproducibility. In our earlier studies, we have synthesized pristine hydroxyapatite by microwave irradiation method

and demonstrated the applicability of HA based electrodes for the determination of different analytes [1-3]. The obtained results are highly reproducible.

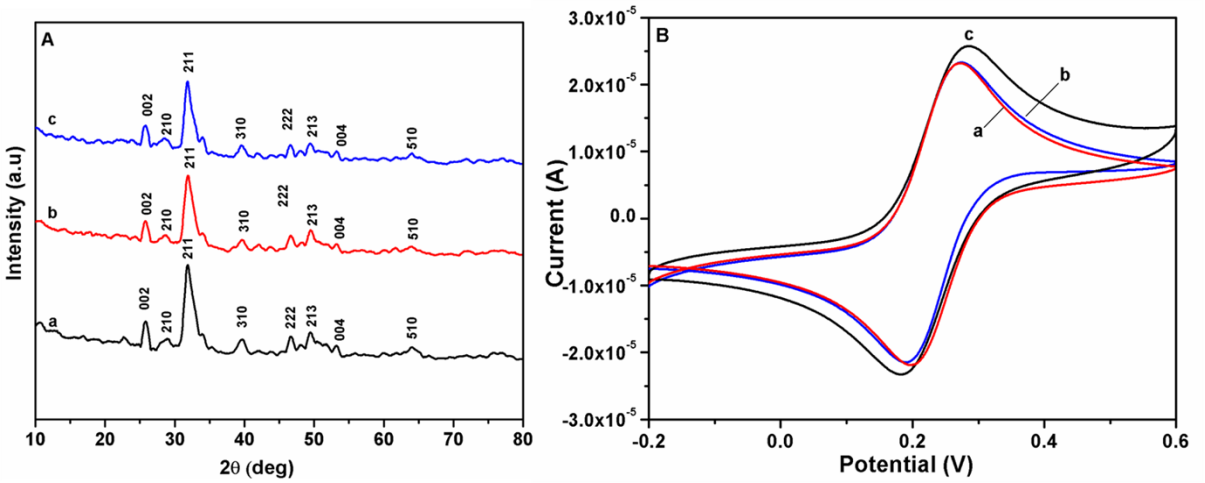

Fig. S1(A) XRD pattern of pristine HA; (B) CVs recorded for modified GCE in 1 M KCl solution containing 1 mM $[Fe(CN)_6]^{3-/4-}$ at a scan rate of 50 mVs^{-1}: (a) sample 1 (b) sample 2 and (c) sample 3.

Table 1 Crystallite size and CVs Peak Current (i_{pa}) values of pristine HA samples

HA samples	Crystallite size (nm)	CVs Peak Current (i_{pa}) (μA)
Sample 1	19.02 ± 2.06	23.01 ± 0.523
Sample 2	20.52 ± 1.583	23.52 ± 1.05
Sample 3	22.30 ± 1.03	25.80 ± 2.27

II. Electrochemical characterization of undoped HA and Av-HA

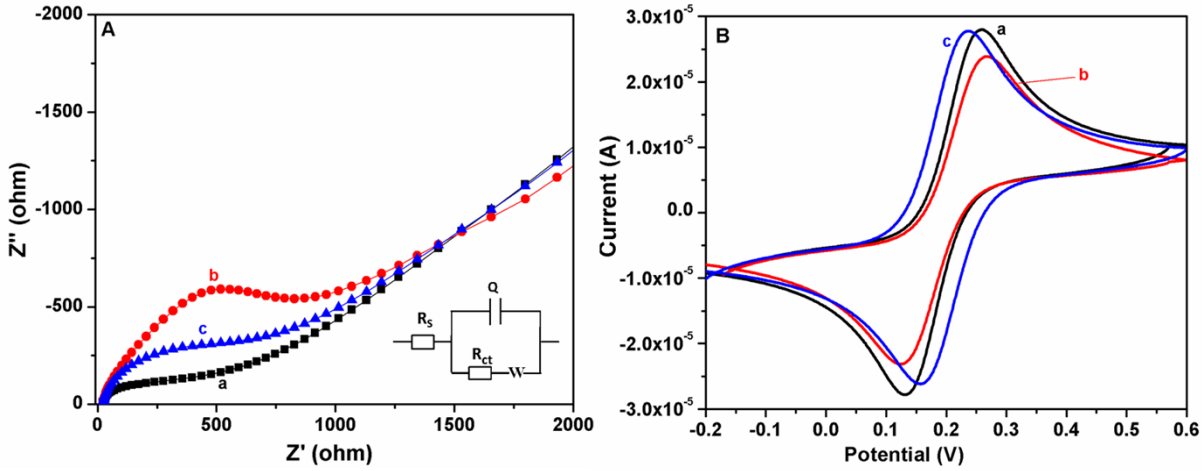

Fig. S2 (A) Electrochemical impedance spectra recorded in 1 M KCl solution containing 1 mM $[Fe(CN)_6]^{3-/4-}$; (B) CVs recorded in 1 M KCl solution containing 1 mM $[Fe(CN)_6]^{3-/4-}$ at a scan rate of 50 mVs^{-1} for (a) bare GCE, (b) HA and (c) Av-HA modified GCE.

References

1. P. Kanchana, N. Lavanya, C. Sekar, Mater. Sci. Eng. 35 (2014) 85-91.
2. P. Kanchana, C. Sekar, Mater. Sci. Eng. 42 (2014) 601-607.
3. P. Kanchana, C. Sekar, Spectrochim. Acta. A 137 (2015) 58-65.