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Unconventional Electrode Material Prepared from Coir Fiber through Sputter Coating of Gold: A Study toward Value Addition of Natural Biopolymer

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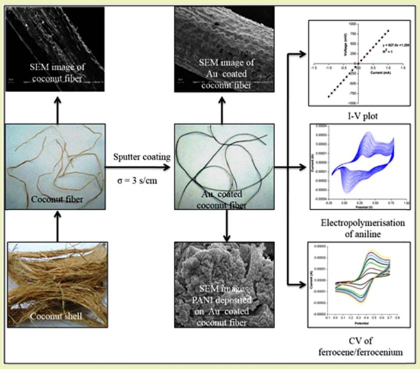
Ⓢ *Supporting Information*

ABSTRACT: The preparation and properties of a simple and cost-effective gold-coated coir fiber electrode are reported. The natural fiber [Young's modulus (Y) = 65.10 MPa], without any pretreatment, was sputter coated with gold to a thickness of 125 nm. The flexible and mechanically strong (Y = 83.84 MPa) composite fiber with electrical resistivity 4.4×10^{-4} Ω cm behaved normally as an electrode in well understood electrochemical processes such as cyclic voltammetry and electropolymerization. The electrode was evaluated both in aqueous and nonaqueous media. The results were comparable with the control data generated using a conventional gold wire electrode.



KEYWORDS: *Natural fiber electrode, Gold sputter coating, Bioelectrode, Cyclic voltammetry*

INTRODUCTION

The liquid metal, Hg, several metallic solids such as Pt and Au, and other conducting substrates such as graphite are well-known electrode materials. Semiconducting materials are also well studied as electrodes in photoelectrochemical processes.[1] Superconducting electrodes too have been reported.[2] Electrochemical processes are conducted on bare electrode surfaces or after various types of modifications such as direct chemical functionalization or through coating of conducting polymers,[3,4] clays,[5,6] zeolites,[7] silica,[8] and graphene.[9] The latter, in turn, are utilized to incorporate electro-active compounds, sensors, and electrocatalysts. Conducting coatings over nonconducting substrates are also reported, for example, indium−tin oxide coating on glass that serves as an optically transparent electrode.[10]

Although carbon electrodes such as graphite and carbon paste are well known, such carbon is derived either from a mineral resource or petroleum coke. With the growing interest in the value addition of discarded bioresources, tailor-made electrode materials fabricated from biomaterials will rise in demand.[11−14] Weavable fibers have been converted into electroactive textiles used in supercapacitors.[15] Twisting configurations of working and counter electrodes in dye-sensitized solar cells (DSCC) have also been studied.[16,17] A comprehensive review of wire-like flexible electrodes is available in the literature.[18] Reports on the use of bioresources as electrode material are scant. Coir or coconut fibers are inexpensive and abundantly available in many countries including India. Coir fiber is used extensively for making mats and ropes, while rubberized coir is used in mattresses. The fiber comprises a thick wall of cellulose over which lignin is deposited. It possesses important attributes such as nonperishable nature, durability, wire-like appearance, and excellent mechanical strength.[19,20] Carbon dip-coated coir fiber encapsulated in a glass capillary has been used in biosensing applications.[21,22] Metal-coated coconut fibers were manufactured by electroplating; in this procedure, pretreated coconut fiber was immersed in a solution of $SnCl_2$, $PdCl_2$, and other salts, and the coated fiber was used for water purification and electromagnetic shielding.[23] Fabrication of a gold-coated wire-like electrode made out of coir fiber is reported in the present work. An ultrathin layer of gold was deposited over the fiber without any pretreatment, and the composite was utilized as an electrode. Gold was selected as the coating material because of its noble nature, ease of sputter coating, and ample prior art on its application as an electrode material. The suitability of the electrode was demonstrated through common electrochemical experiments.

EXPERIMENTAL PROCEDURE

All chemicals were of analytical grade and used as received. Potassium chloride and tetraethylammonium tetrafluoroborate were purchased from Spectrochem India, ferrocene carboxylic acid from Alfa Asear,

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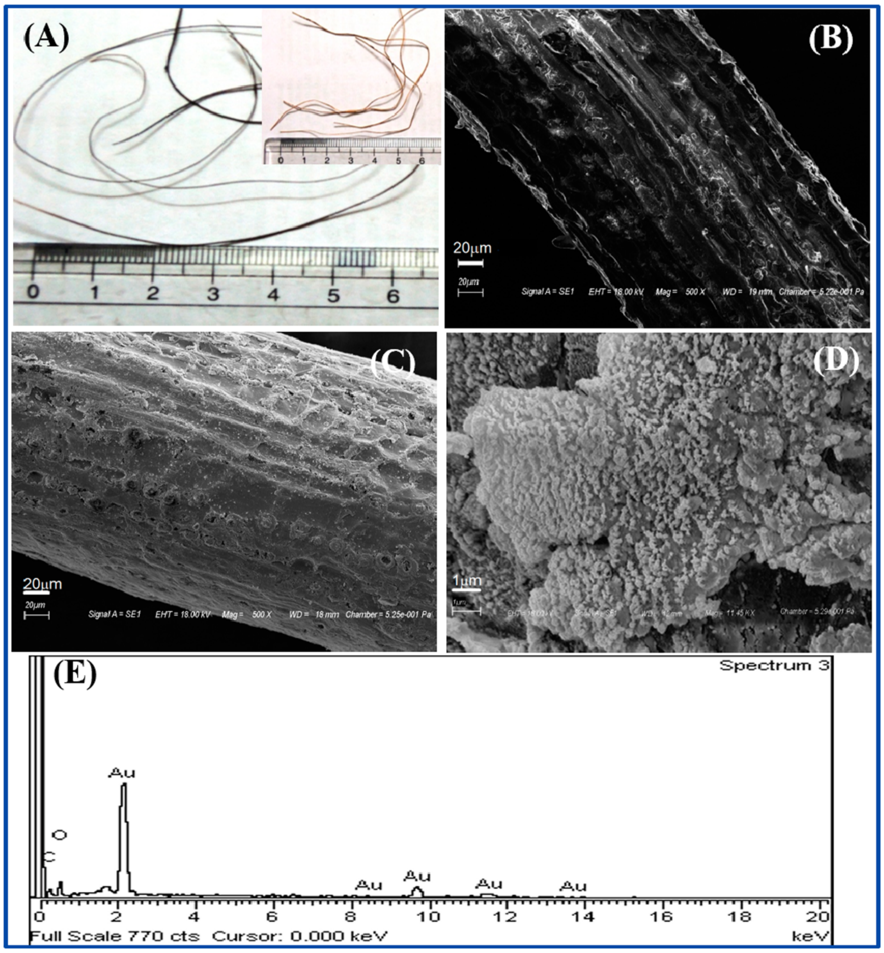

Figure 1. (A) Optical micrograph of gold-coated coir fiber (in-set: uncoated), (B) SEM image of uncoated coir fiber, (C) SEM image of gold-coated coir fiber (coir electrode), (D) SEM image of deposited polyaniline on coir electrode, and (E) EDX spectra of C.

and $Ru(bpy)_3Cl_2.6H_2O$ and aniline from Sigma Aldrich. Coir fiber obtained from fully matured healthy coconut fruit was used for the study and purchased from local market. HPLC grade solvents were used for the study. Au coating of coir fiber was performed using Polaron SC7620 mini-sputter at 8 Pascal pressure. SEM and EDX analyses were done using a LEO 1430 VP scanning electron microscope. Tensile strength testing was carried out for a specimen length of 10 cm and diameter 0.18 mm using a universal testing machine (Zwick Roell, type X force P, S/N 756324). A preload of 0.01 N was applied at a speed of 20 mm/min keeping grip to grip separation of 4.74 cm at the start position. Young's modulus (Y) was determined from the regression slope in the elastic region of the stress−strain curve. Current-voltage (I−V) measurements were performed using a Keithley 2635A source meter unit (SMU). Electrochemical experiments were performed using a Princeton applied research potentiostat (PAR-STAT 2273) at room temperature (24 ± 2 °C). A three-electrode assembly was used in all measurements in which Au-coated coir fiber or Au wire (in control experiment) was used as working electrodes, while platinum foil and Ag/AgCl (sat KCl) were used as auxiliary and reference electrodes, respectively. The contact in the working electrode was made through a spring-loaded clip, which was suitably modified.[24]

Au Coating on Coir Fiber and Estimation of Coating Thickness. Fibers were physically picked from the surface of the coconut shell [Figure S1 (A), Supporting Information] and manually separated into individual strands. Fibers of uniform diameter (130−200 μm) were selected for the study [Figure S1 (B), Supporting Information]. For coatings of Au, a bundle of fibers (75 to 100) without any pretreatment were placed into the chamber of a sputter coater (100 mm diameter × 100 mm height) (Figure S2, Supporting Information). The vapor pressure of gold was maintained uniformly in the chamber which facilitated uniform coating.[25,26] After 1 h of coating, the color of the fiber changed from yellow to dark brown (Figure 1A). The fibers were removed from the coater and characterized. The thickness of Au coating on the surface of the fiber was determined using the following equation.

$$d = KIVt \tag{1}$$

where d is the coating thickness in angstrom; K is an experimentally determined constant (for Au used with air, $K = 0.07$ approximately); I is the plasma current in mA (5 mA in present study), V is the bias voltage in kV (1 kV in present study), and t is the sputtering time in seconds (3600 s in present study).

Measurement of Current−Voltage Plot and Calculation of Specific Resistance (ρ). The contacts on the coir fiber electrode for measurement of I−V characteristics were made using conducting silver paste and copper wire. The copper wire was connected to the SMU with a crocodile clip. The bias current of ±1.0 mA was applied, and corresponding voltage was measured. The sweep was generated by the instrument, and 32 measured data points were averaged automatically. The averaged and stored data were collected and plotted to obtain the I−V curve. The electrical resistance of the coir fiber electrode was calculated from the slope of the curve. The specific resistance of the coating was calculated considering it as a sheet and applying the equations: Specific resistance $\rho = R \times (W \times L)/H$; wherein the width of the sheet (thickness of the coating) is $W = 125$ nm $= 1.25 \times 10^{-5}$ cm; length of the sheet (circumference of the coating, i.e., $2\pi r$) is $L = 2\pi(0.19)/2$ mm $= 5.97 \times 10^{-2}$ cm; height (length of the fiber between two contacts) is $H = 1.4$ cm; and measured resistance (from slope of

I–V curve) is $R = 8.27 \times 10^2$ ohm. From the above data, $\rho = 4.4 \times 10^{-4}$ ohm cm.

Cyclic Voltammetry (CV) of Ferrocene Carboxylic Acid in Aqueous Medium. A solution of ferrocene carboxylic acid (3 mM) in 0.1 M KCl was prepared using Milli Q water (resistivity ≥18 M Ω). The experiment was performed in a 10 mL open glass cell using the conventional three electrode configuration. CVs were recorded at different scan rates (10–150 mV/s) without any agitation. The gold-coated coir fiber electrode and an Au wire were used as working electrodes.

Cyclic Voltammetry Study in Acetonitrile Medium. CVs were recorded under N_2 atmosphere in an airtight cell. One mM solution of $[Ru(bpy)_3]Cl_2$ was prepared in dry acetonitrile in the presence of 0.1 M tetraethylammonium tetrafluoroborate (supporting electrolyte). N_2 was purged for 10 min before start of the experiment. CVs were recorded at various scan rates (25–300 mV/s) without any agitation.

Electrochemical Polymerization of Aniline on Coir Fiber Electrode. Anilinium sulfate monomer was prepared by dissolving 0.1 M aniline in 0.5 M H_2SO_4 followed by sonication for 5–8 min. Electro-polymerization on a coir fiber electrode in an open glass cell was carried out using 10 mL of freshly prepared monomer. A total of 35 potentiodynamic cycles were run in potential window of −0.2 to 0.8 V vs Ag/AgCl.

■ RESULTS AND DISCUSSION

Preparation of Gold-Coated Coir Fiber. Dry coir fibers of uniform dimension were gold coated using a sputter coater. The thickness of the gold layer was estimated to be 126 nm using eq 1 in the Experimental section. SEM was also recorded for the standalone gold coating after thermal decomposition of the coir fiber at 700 °C (Figure S3, Supporting Information). As shown in Figure S3 (A) of the Supporting Information, the surface revealed an agglomeration of many individual gold particles forming a somewhat rough surface. Further, it was deduced from Figure S3 (B) of the Supporting Information that the thickness of the gold coating was fairly uniform. Figure 1A shows a representative optical micrograph of the gold-coated fiber (inset shows the uncoated fiber). It is shown in the scanning electron micrographs of Figure 1B and C that the surface roughness of the uncoated fiber manifested in the coated fiber also. The EDX spectra of the as-coated surface predominantly showed the peaks due to Au (Figure 1E).

Mechanical Properties of Gold-Coated Coir Fiber. The stress–strain curve recorded during tensile testing of the uncoated and gold-coated coir fibers is given in Figure 2.[27] Two slopes corresponding to elastic and inelastic deformation regions and the failure point "C" are shown in the plot. The elastic limit reduced from a strain value of 2.75% to 1% upon coating. However, the trends were opposite in the inelastic region (section "bc" of the curve). The failure point (point "c") rose from a strain limit of 9.5% to 14.0% when the fiber was coated. Y was calculated from the stress–strain curves and found to be 65.10 and 83.84 MPa for uncoated and coated coir, respectively.

The Current–Voltage (*I*–*V*) Profile of Gold-Coated Coir Fiber. The I–V profile of the coated fiber was ohmic ($R^2 = 1$) between ±1.0 V bias voltage window (Figure 3). The electrical resistivity of the coating was measured from the cross-sectional area (thickness of coating 125 nm and circumference of fiber 5.97×10^{-2} cm) of the coating and length of the fiber (1.4 cm). The value was estimated to be 4.4×10^{-4} Ω cm (see Experimental section for details). The electrode thus prepared was used in various electrochemical processes in aqueous as well as nonaqueous media.

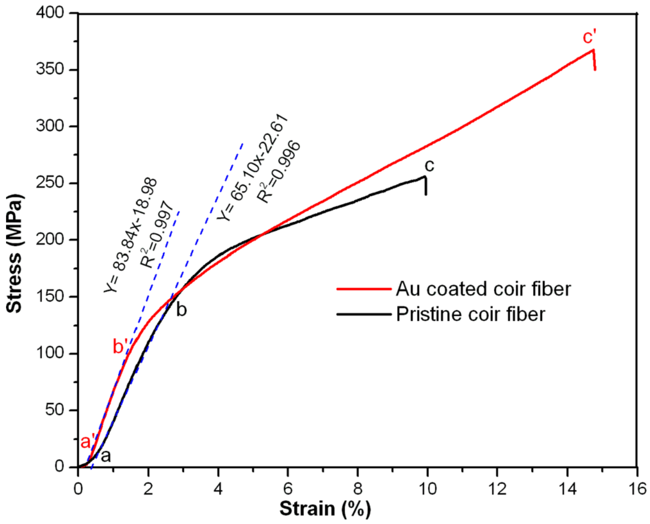

Figure 2. Stress–strain plot of pristine (black) and Au-coated (red) coir.

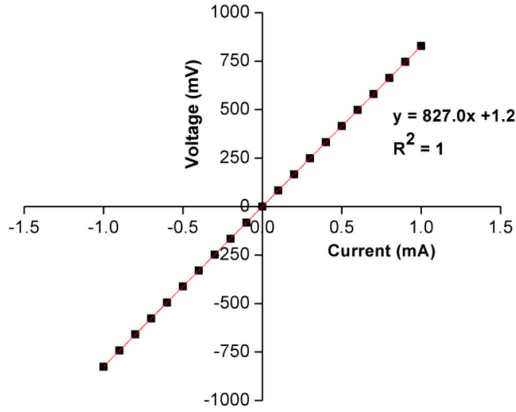

Figure 3. Current–voltage (I–V) plot of the coir electrode using silver contacts.

Cyclic Voltammetry of Gold-Coated Coir Fiber in Aqueous and Nonaqueous Media. Ferrocene carboxylic acid was taken as an electroactive species for characterization of the coir fiber electrode in aqueous medium. The cyclic voltammograms of the ferrocene/ferrocenium couple obtained at different scan rates (10–150 mV/s) in 0.1 mM aqueous KCl are shown in Figure 4. The expected performance was observed.[28] The plot of (I_p) versus $\nu^{1/2}$ was linear both for cathodic and anodic peak potentials (inset of Figure 4). However, the peak-to-peak separation of 90 mV suggested deviation from the Nernstinian behavior for a 1-electron transfer process. The linear variation of I_p versus $\nu^{1/2}$ indicates that the process is diffusion limiting. Moreover, a small intercept in the I_p versus $\nu^{1/2}$ plot is indicative of nonfaradaic current.

A control experiment was carried out with the same redox couple in aqueous solution using gold wire of comparable diameter as the working electrode. It is shown in Figure 5 that the peak current density was higher in the case of the coir fiber electrode, despite the fact that the peaks were broader. This observation was consistent with the evidently higher roughness of the coir electrode surface as revealed by the SEM images in Figure 1C and Figure S1 of the Supporting Information.

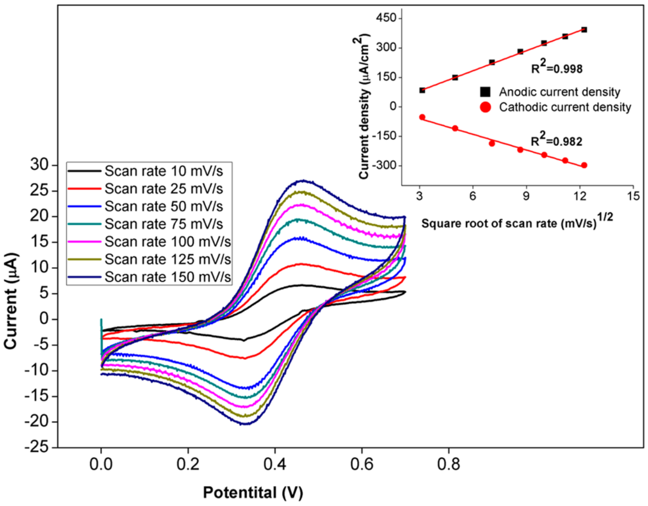

Figure 4. Cyclic voltammograms of 3 mM ferrocene carboxylic acid in aqueous medium on a coir electrode having 0.1 M KCl as the supporting electrolyte. Scan rate 10−150 mV/s. [Insert: plot of cathodic (at 0.35 V) and anodic peak (at 0.44 V) current density vs square root of scan rate.].

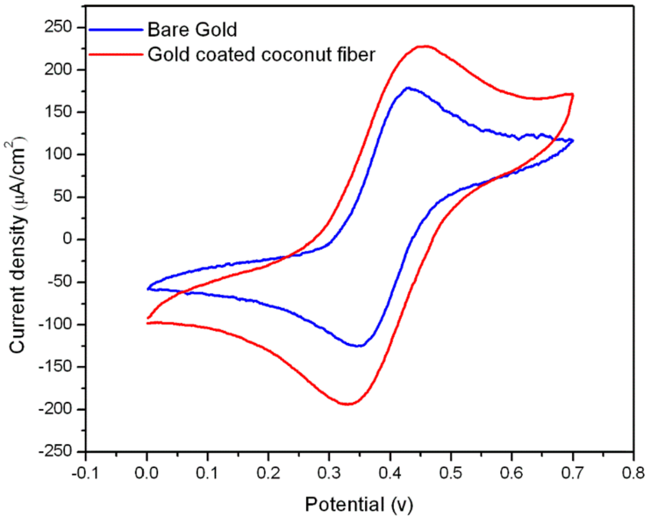

Figure 5. Cyclic voltammograms of ferrocene/ferrocenium redox on conventional gold wire electrode and coir electrode recorded in aqueous media. The scan rate was 50 mV/s.

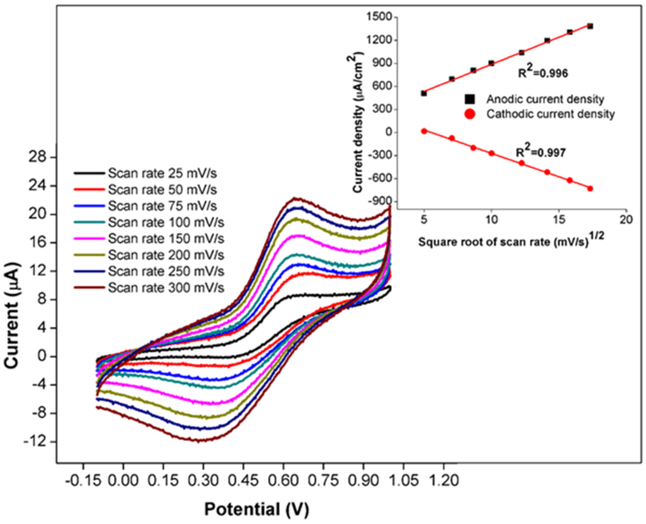

Figure 6. Cyclic voltammograms of 1 mM $[Ru(bpy)_3]Cl_2$ in nonaqueous medium (acetonitrile/0.1 M tetraethylammonium tetrafluoroborate) on coir electrode. Scan rate 25−300 mV/s. [Insert: plot of cathodic (at 0.39 V) and anodic (at 0.62 V) peak current density vs square root of scan rate.].

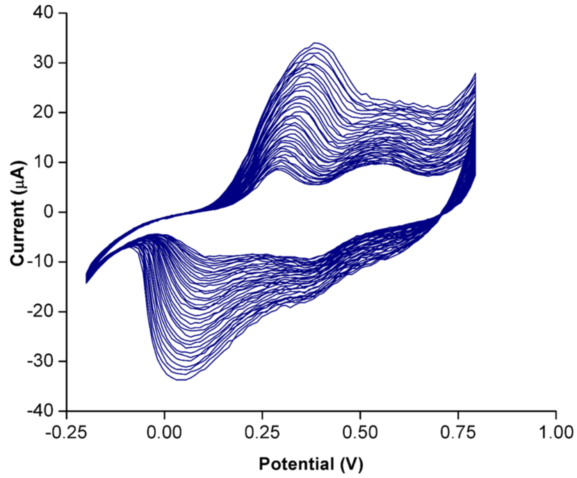

Figure 7. Potentiodynamic cycles (−0.2 to 0.8 V; 50 mV/s scan rate) showing growth of polyaniline on gold-coated coir electrode from a monomer solution containing 0.1 M aniline in 0.5 M H_2SO_4.

Similar redox cycling in nonaquous (acetonitrile) medium was also performed for $[Ru(bpy)_3]^{3+/2+}$ (Figure 6). Tetraethylammonium tetrafluoroborate (0.1 M) was taken as the supporting electrolyte. Although the peak-to-peak separations were large, the plots of $(I_p)_a$ and $(I_p)_c$ versus $v^{1/2}$ were linear, and the reversible nature of the redox process was self-evident. Thus, the electrode may have utility both in aqueous and nonaqueous media.

Electropolymerization of Aniline on the Surface of Gold-Coated Coir Fiber. The coir fiber electrode was subsequently used in electropolymerization application, using the polymerization of aniline as an example. The voltammograms recorded over 35 cycles in 0.5 M H_2SO_4 containing 0.1 M aniline are reproduced in Figure 7. The profile bore resemblance to that reported in the literature,[29] albeit with some differences. The peak attributed to the transformation of the leucoemeraldine form to the emeraldine form in the anodic cycle gradually shifted from around +240 mV in the initial cycles to +350 mV toward the end, whereas a near constant potential of about +150 mV has been observed on the conventional gold electrode.[30] The observed shift in anodic peak has been attributed previously to the irreversible cross-linking of the polyaniline in the anodic cycle,[29,31] although in the present case, substantial non-Faradaic effects cannot be ruled out.

■ CONCLUSIONS

In conclusion, an electrode was developed by sputter coating of gold over pristine coir fiber, a waste material, and it was used successfully in various aqueous and nonaqueous electrochemical applications. Future research will attempt to improve its performance and extend the work to other natural fibers—particularly banana and sisal fibers—and metal coatings. It is further proposed to study anodic stripping voltammetry for analysis of Hg, Pb, and other heavy metals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Optical images of the pristine and cleaned fibers used in the present study, photograph of the sputter-coating setup, and SEM images of self-standing gold coating remaining after calcination of gold-coated coir fiber. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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