Electronic Supplementary Material

Ultralong hydroxyapatite-based forward osmosis membrane for freshwater generation

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Preparation of GO by Hummer's method

GO was prepared using the modified Hummer's method [1 - 2] by oxidation of graphite. Graphite flakes (3.0 g) and $KMnO_4$ (18.0 g) were added to the mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) with slow stirring. The reaction was then heated to 50 °C and stirred for 12 h. After cooling to room temperature, the reaction was carefully poured onto ice (400 mL). About 6 mL of 30 % H_2O_2 was dropwise. After being washed with an additional 200 mL of ethanol, the remaining material d into the solution until the color turned yellow. The solution was centrifuged at 4000 rpm for 4 h, and the supernatant was decanted away. The remaining solid material was then washed in sequence with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol for 2 times. After being washed with an additional 200 mL of ethanol, the remaining material was vacuum-dried overnight at room temperature. The obtained solid was dispersed into

a certain amount of bi-distilled water to form the GO solution with a concentration of 1.0 mg mL^{-1}.

S1. Ultralong Hydroxyapatite (UHA) membrane

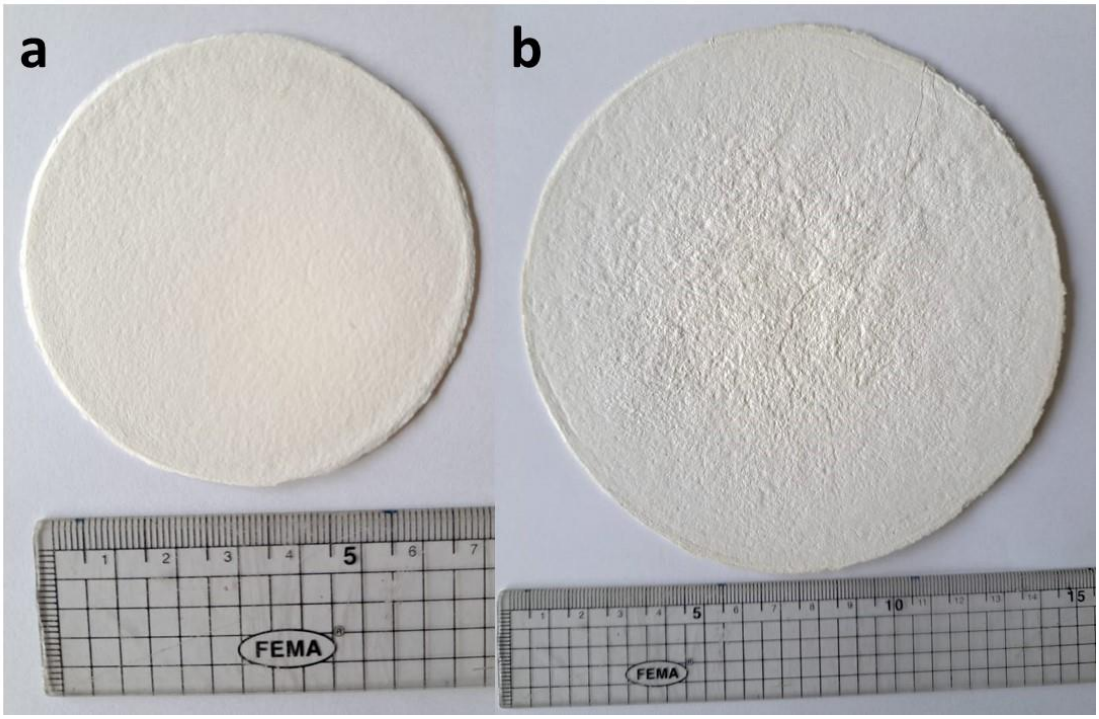

Fig. S1. Photo images of the prepared UHA membrane; (a) 7.0 cm, and (b) 13 cm.

S2. FO test

A laboratory-scale FO system (Fig. S2) was used to assess the water flux across the GO/UHA membrane. The feed solution was deionized water, and the draw solution was 2.0 M NaCl aqueous solution. The feed and draw solutions were circulated with peristaltic pumps. The feed side was equipped with a weight balance for recording the weight change and a conductivity meter for recording the conductivity change at the start and end of the run. The test temperature

was 25 ±1 °C (room temperature). A hydroxyapatite-only membrane with different concentrations of graphene oxide with hydroxyapatite was also tested under the same conditions. Before recording data, the leakage tests were conducted by eye and soaked in water. We found that making the assembly well sealed by Amire Alfa (commercial grade adhesives) for at least 1hr on both sides was critical. If the UHA nanowire membrane completes the leakage, these samples were then used for the following FO tests.

The FO cell hydraulic test also verified the assembly's seal character. Prior to each test, the system was washed with deionized water until it was clean on both sides. The water was then extracted before the tanks were refilled with the required solutions. The data recording of each test was started until the system was stabilized. The solute concentration of the feed solution was determined from the conductivity of the solution.

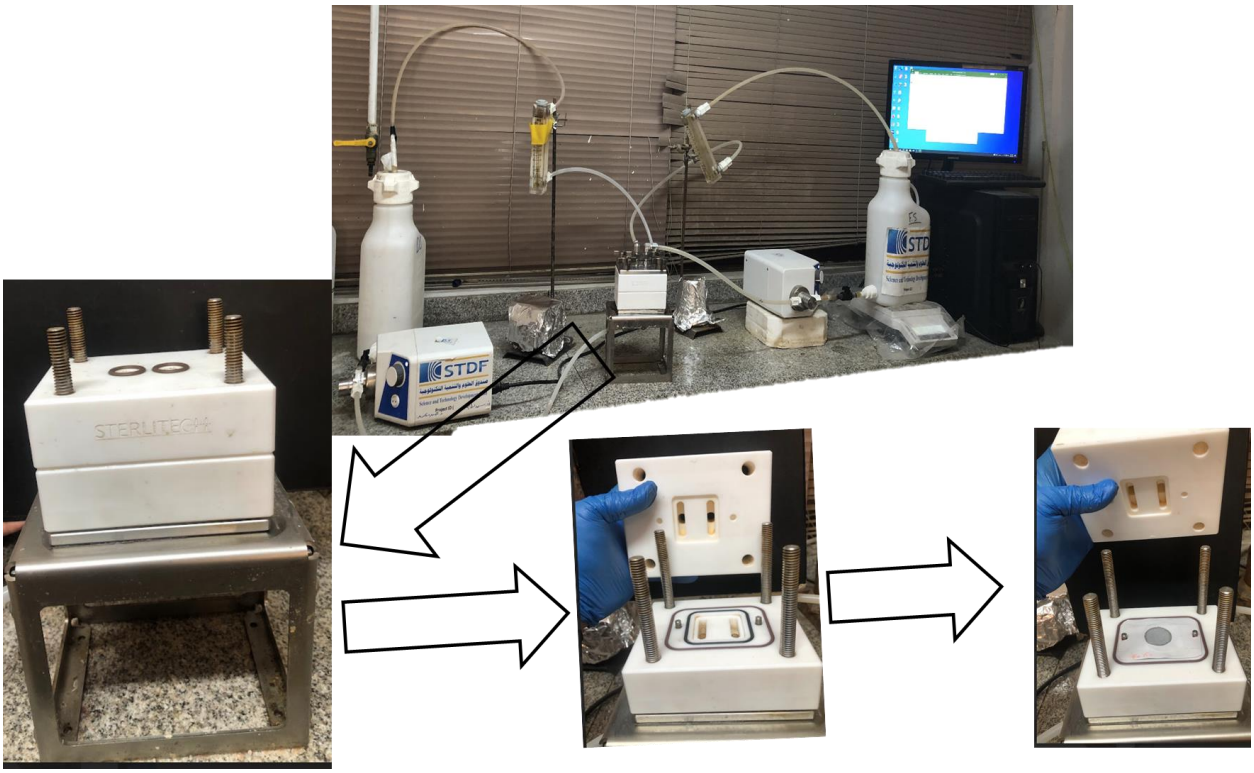

Fig. S2. FO setup used in this work. The UHA-based membrane was mounted with double-sided carbon tape to a plastic sheet covering the entire FO cell. The plastic sheet and carbon tape were previously drilled with an aperture, exposing the UHA-based membrane to feed and draw solutions.

S3. SEM analysis of the GO/UHA membranes

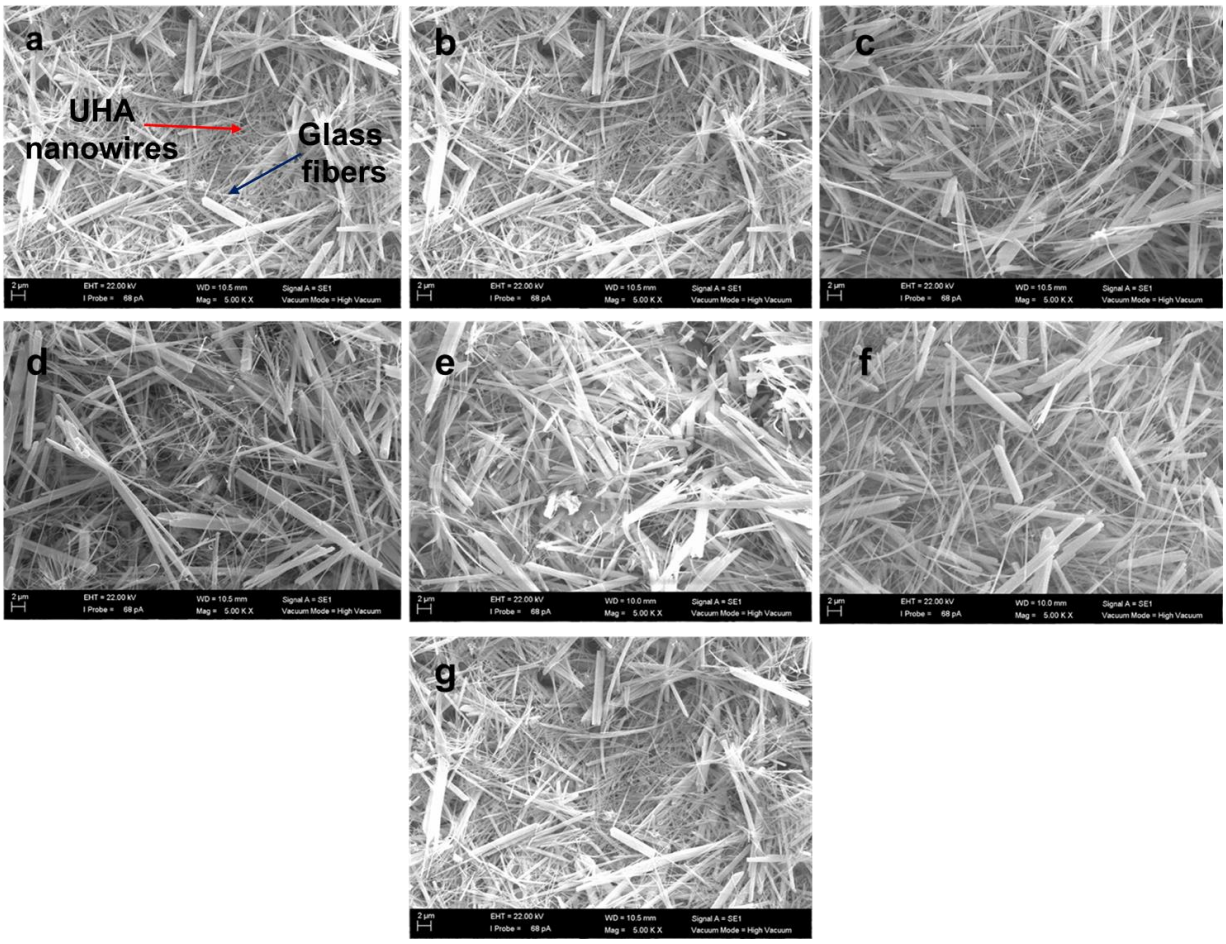

Fig. S3. The top surface analysis of UHA and GO/UHA membranes by SEM: (a) 0 mg GO/UHA, (b) 10 mg GO/UHA, (c) 20 mg GO/UHA, (d) 30 mg GO/UHA, (e) 40 mg GO/UHA, (f) 50 mg GO/UHA and (g) 60 mg GO/UHA membranes.

Relationship between roughness and surface wettability:

Wenzel [3] established a simple relationship between the roughness and the contact angle:

$$\cos\theta^* = r\ \cos\theta$$

where θ* is the measured contact angle, and r is called the roughness coefficient and indicates the ratio of the total surface area to the surface geometrically projected onto a plane.

This is called the *apparent contact angle* for a rough surface because it is the angle of the droplet contour with an apparently straight profile line. θ is the contact angle that would exist on a smooth surface of the same material and corresponds to the ideal contact angle according to Young's equation.

Based on the Wenzel equation, it can be seen why the critical angle for the transition from wetting enhancement to reduction is 90°. Since cos θ assumes negative values above 90°, the apparent contact angle becomes larger. However, the Wenzel equation can then be applied only to a limited extent because, at low wetting, not all the depressions of the rough surface are usually filled with liquid. Cassie and Baxter [4] have formulated the following relationship for a condition where only parts of the entire surface are in contact with the liquid:

$$\cos\theta^* = rf\cos\theta + f - 1$$

Where f is the proportion of the area actually wetted.

S4. XRD of the synthesized GO

GO was prepared using the modified Hummer's method by oxidation of graphite. The XRD pattern of GO shows the sharp diffraction peak at 10° corresponds to the basal spacing of GO (8.97 Å)[1], as shown in Fig.S4.

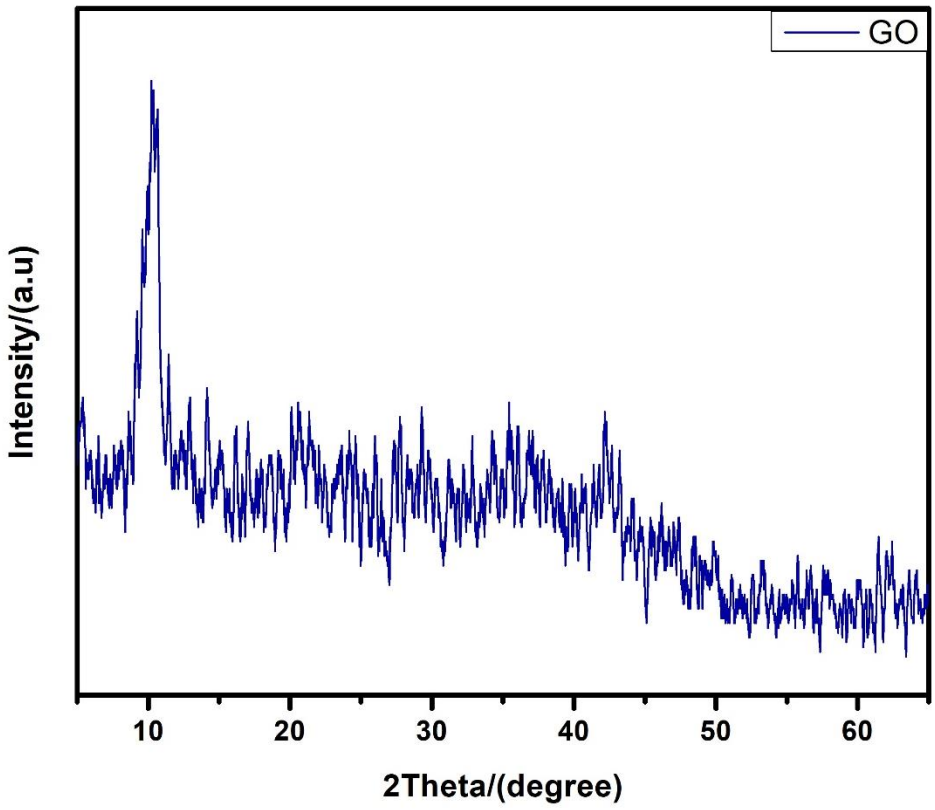

Fig. S4. XRD of the modified GO nanosheets.

S5. FTIR analysis

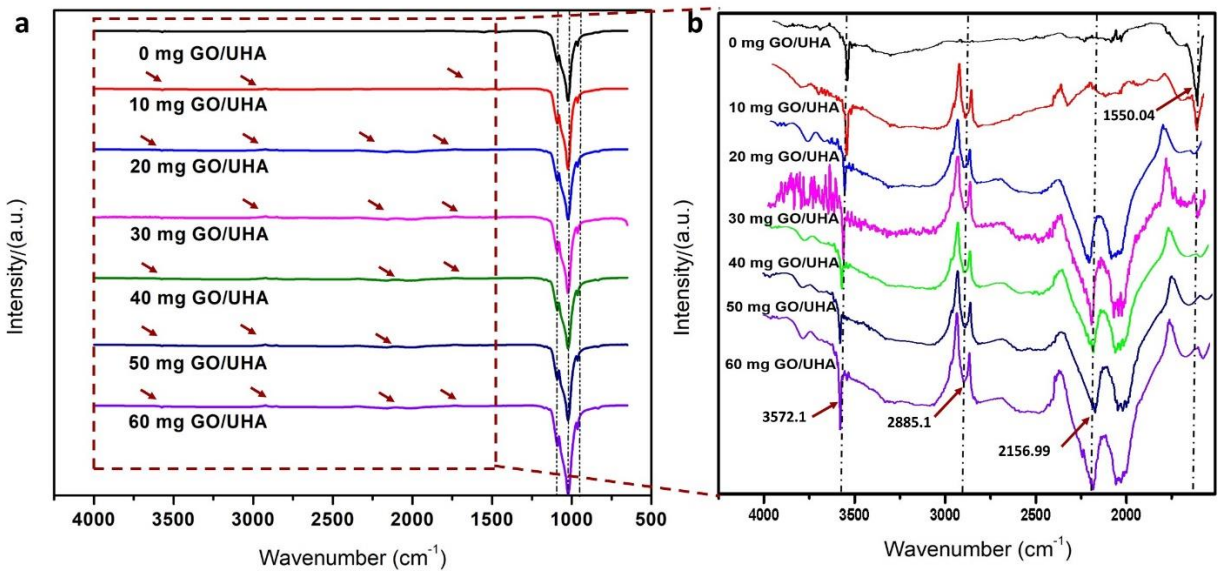

Fig. S5. FTIR spectra of the prepared UHA-based membranes. (a) 0 mg GO/UHA membrane, (b) 10 mg GO/UHA membrane, (c) 20 mg GO/UHA membrane, (d) 30 mg GO/UHA membrane, (e) 40 mg GO/UHA membrane, (f) 50 mg GO/UHA membrane and (g) 60 mg GO/UHA membrane.

S6. Control Test

When the membrane was soaked in water for 2 h it was observed that no air bubbles were released when the membrane was placed on a water surface.

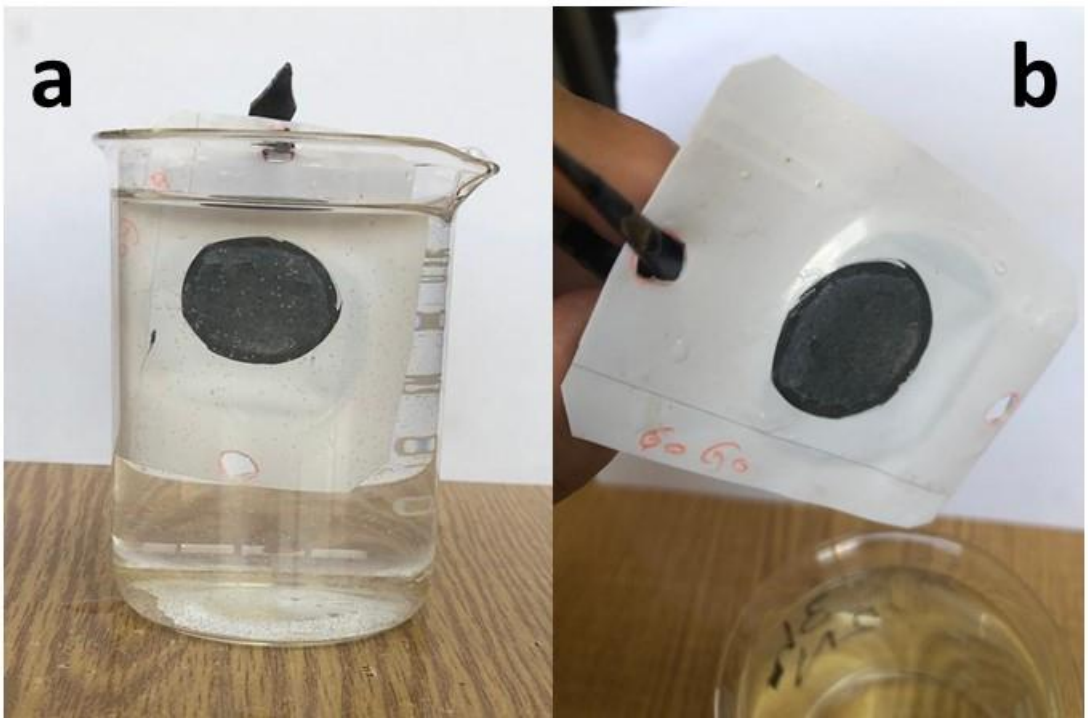

Fig. S6. Membrane soaking. (A) during the soaking of the membranes for 2 h. (B) after soaking the membranes and leaving them out of the water.

S7. A typical image of the prepared UHA-based membranes

Some pictures of the membranes on the ground before the process of preparation and cutting in the plastic stick (carbon tape) and put them in the mold and the forward osmosis unit.

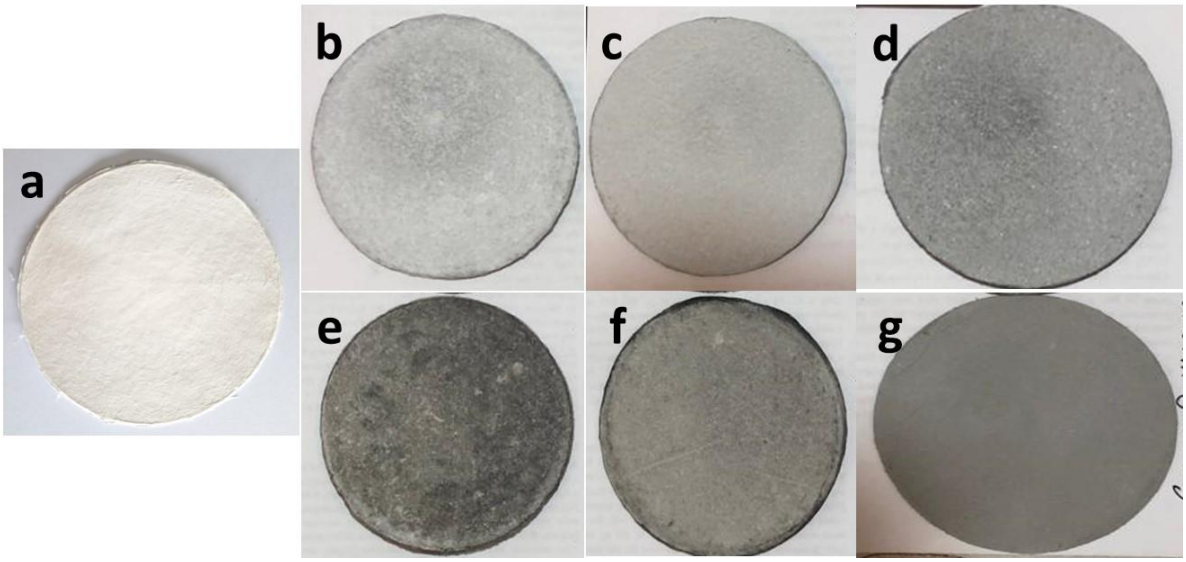

Fig. S7. some photos for deferent concentration membranes with diameter 9 cm. (a) 0 mg GO/UHA membrane, (b) 10 mg GO/UHA membrane, (c) 20 mg GO/UHA membrane, (d) 30 mg GO/UHA membrane, (e) 40 mg GO/UHA membrane, (f) 50 mg GO/UHA membrane and (g) 60 mg GO/UHA membrane.

References

1. Wang Y, Ou R, Wang H, Xu T. Graphene oxide modified graphitic carbon nitride as a modifier for thin film composite forward osmosis membrane. Journal Membrane Science, 2015, 475: 281–289
2. Hummers W S, Offeman R E. Preparation of graphitic oxide. Journal American Chemistry Society,1985, 80 (6): 1339
3. Wenzel R N. Resistance of solid surfaces to wetting by water. In Industrial Engineering. Chemistry,1936, 28 (8): 988-994

4. Cassie A B D, Baxter S. Wettability of porous surfaces. Transactions of the Faraday Society, 1944, 40: 546-551