Enhanced Electrochemical performance at high temperature of Cobalt Oxide/Reduced Graphene Oxide Nanocomposites and its application in lithium-ion batteries

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We report a microwave irradiation method for the preparation of reduced graphene oxide (RGO) based Co$_3$O$_4$ nanocomposites as anodes for lithium-ion (li-ion) batteries. The Co$_3$O$_4$/RGO nanocomposites displayed good electrochemical behavior as anodic materials for li-ion batteries when compared to pure Co$_3$O$_4$. The Co$_3$O$_4$/RGO nanocomposites with low RGO content resulted in stable electrochemical performance with 100% coulombic efficiency at a high current density of 500 mA/g for 50 cycles. The enhanced capacity of the Co$_3$O$_4$/RGO nanocomposites is due to the incorporation of RGO, which resulted in a four times larger surface area than that of Co$_3$O$_4$. This increased surface area could facilitate the absorption of more lithium ions, resulting in excellent electrochemical performance. Interestingly, the novelty of this work is that the designed li-ion batteries showed stable electrochemical performance even at a high temperature of 100 °C, which might be useful for rechargeable battery applications in a wide temperature range.

Lithium-ion batteries have a number of applications as energy storage units mainly in electric vehicles and electronic devices owing to their high capacity, long cycling life, and environmental friendliness. There is an urgent need to improve these batteries to meet energy demand requirements. One method to enhance li-ion batteries performance is to design alternative negative or anode materials, including transition metal oxides, and replace the conventional anode material, graphite, which has a theoretical capacity of only 372 mAh/g.

Currently, transition metal oxides have received considerable attention as anodic materials for use in li-ion batteries because of their superior theoretical capacity, with approximately three times the capacity of the commercial graphite that have a capacity of 372 mAh/g, making these materials good candidates for energy storage systems. Among the transition metal oxides, Co$_3$O$_4$ is the most frequently used as anode materials because of its high theoretical capacity (890 mAh/g).

Generally, cobalt oxides, that include binary oxides such as Cobalt (II) oxide (CoO), Cobalt (III) oxide (Co$_2$O$_3$) and Cobalt (II, III) oxide (Co$_3$O$_4$), have been widely explored for applications in li-ion batteries. However, Co$_3$O$_4$ is synthesized more easily than the other two oxides, as it can be prepared from different cobalt salts by heating in air at 300 to 400 °C. However, one limitation of Co$_3$O$_4$ nanoparticles as anodic material for li-ion batteries is that they experience poor cycling stability and irreversible capacity loss due to the volume expansion/contraction and agglomeration of the Co$_3$O$_4$ nanoparticles.

One way to solve the above issues is to synthesize Co$_3$O$_4$ nanoparticles with carbon, such as graphene, which can also improve the conductivity of Co$_3$O$_4$. Graphene has a high surface area, good mechanical properties, and high electrical conductivity, which helps in improving the electrochemical properties of metal oxides.

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Many synthetic routes to prepare Co$_3$O$_4$ nanoparticles have been reported, such as co-precipitation, hydrothermal synthesis, thermal decomposition, and reduction$^{13-15}$. Whereas, in situ reduction of cobalt salt in the presence of graphene oxide is commonly followed to prepare Co$_3$O$_4$/RGO nanocomposites$^{16}$. The structural properties of a material, which includes porosity and surface area, strongly affects their performance as electrodes in li-ion batteries making it challenging to design electrode materials.

In contrast to the above mentioned conventional synthesis methods, microwave-assisted techniques of electrode materials for li-ion batteries can provide easy, fast and large-scale synthesis of nanomaterials, in addition to, controllable parameters and energy saving characteristics$^{17}$. In microwave irradiation technique, heating occurs via two mechanisms namely, polarization and conduction. In polarization process, materials are directly heated by radiation, and the radiation or external electric field interacts with the polar molecules that possess a dipole moment and are forced to reorient by rotation which leads to collision and heat generation. However, to generate heat, a substance must possess a dipole moment such as a water molecule this is because external electric fields are sensitive to dipole. In conduction mechanism, heat is generated via the collision of ions in the sample with the neighboring atoms or molecules$^{17,18}$.

Sun et al., conducted a survey on microwave irradiation’s effect and the size and shape of graphene based nanocomposites on their electrochemical performances$^{17}$. Of the different morphologies, graphene based 2D transition metal oxides is a favorable morphology as it assists in facilitating li-ion diffusion and other$^{17}$. Microwave irradiation is favorable for the 2D growth of inorganic nanocrystals, and as reported in our previous study, porous 2D Co$_3$O$_4$/RGO nanocomposites were obtained via microwave-assisted method making it potential candidate for li-ion batteries$^{19,20}$.

Many research groups have reported the application of graphene-based Co$_3$O$_4$ nanocomposites as anodic materials in li-ion batteries, and in most of the reported studies, the designed li-ion batteries displayed high specific capacity and stable performance only with high RGO content$^{21}$ and low current densities at room temperature or in a narrow operating temperature range.

In this study, to overcome the issue of the narrow operating temperature range of li-ion batteries, Co$_3$O$_4$/RGO nanocomposites with a low RGO content were prepared through a microwave irradiation-assisted solution route and used for high-temperature rechargeable batteries with high electrochemical performance and good thermal stability.

**Experimental Details**

**Preparation of Co$_3$O$_4$ nanoparticles and Co$_3$O$_4$/RGO nanocomposites.** Co$_3$O$_4$ nanoparticles and Co$_3$O$_4$/RGO nanocomposites were synthesized by a microwave irradiation-assisted solution method following the procedures described in our previous work$^{22}$.

**Material characterization.** The chemical compositions of the samples were determined using Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet-iS10) recorded in the range of 4000–400 cm$^{-1}$. A thermogravimetric analyzer (TGA, STA7200) was used to determine the thermal stability of the materials from ambient to 500°C at a heating rate of 5°C/min under nitrogen atmosphere. A transmission electron microscopy (TEM, JEOL JEM-2100F) was used to study the morphology of the materials. The Brunauer–Emmett–Teller (BET) was used to obtain the specific surface area through a surface area analyzer (Micromeritics ASAP 2020) by N$_2$ adsorption-desorption while the pore size distribution was determined by the Barrett–Joyner–Halenda (BJH) method.

**Electrochemical characterization.** To fabricate the working electrode, the active material (80%) was mixed with a conductive agent carbon black (10%) and a binding agent polyvinylidene fluoride (PVDF) (10%) in 50:50 ethanol:dimethylsulfoxide (DMSO) to form a homogenous slurry followed by casting them onto copper substrates and drying at 80°C under vacuum to remove the solvent. The resulting material was then punched to form disks of ~15 mm with an electrode thickness of 50 µm. The specific capacity and current density were obtained based on the mass of the electrodes which is approximately 1 mg. Polypropylene membrane Celgard 2325 was employed as the separator, 1 M LiPF$_6$ was used as the electrolyte and lithium as the counter electrode which were then assembled into CR2032 coin-type cells in an argon-filled glove box. Charge/discharge measurements, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were all studied using an electrochemical workstation (Gamry 3000). CV was performed in the voltage window from 0 to 3 V at 50 mV/s scan rate. EIS was performed by using a sine wave of 10 mV in a frequency range of 1 Hz – 100 kHz. Galvanostatic charge/discharge tests were evaluated in the voltage window from 0 to 3 V. For high temperature testing; the cell was kept inside a bomb calimeter vessel by connecting the positive and negative terminal of the coin cell battery to the two electrodes of the vessel. The cell was then left inside the vessel at the specified testing temperature for several hours to reach thermal equilibrium. The measurements were performed at 100°C and were tested by the Gamry potentialstat/galvanostat connected to the bomb calimeter vessel. The batteries were cycled in a range of 0 and 3 V at 500 mAh/g for 50 cycles. CV was also performed in the potential window from 0 to 3 V and at a scan rate of 50 mV/s. EIS was conducted at a frequency range of 1 Hz – 100 kHz by using a sine wave of 10 mV.

**Results and Discussion**

FTIR was used to demonstrate the effect of RGO on the chemical structure of the Co$_3$O$_4$ nanoparticles. Fig. 1(a) shows the FTIR spectra of Co$_3$O$_4$ nanoparticles and Co$_3$O$_4$/RGO nanocomposites. The absorption bands at 586.61 cm$^{-1}$ and 671.05 cm$^{-1}$ are assigned to Co–O stretching vibrations and O–Co–O bridging vibrations, respectively. For the pure Co$_3$O$_4$ nanoparticles, the weak absorption bands at 1052.41 cm$^{-1}$ and 1251.76 cm$^{-1}$, are assigned to C–O stretching vibrations, the band at 1649.67 cm$^{-1}$ and the C–H bands near 2980.64 cm$^{-1}$ are due to the presence of cobalt acetate (Co(CH$_3$COO)$_3$) residues. However, the presence of the O–H band at 3526.79 cm$^{-1}$
suggests the possibility of adsorbed water. For the RGO-based nanocomposites, some functional groups were still detected. Although the peaks decreased and almost disappeared after the reduction of GO to RGO due to the deoxygenation process, in this case, many peaks were detected due to the partial reduction of GO. Two peaks at 856.9 cm$^{-1}$ and 1118.05 cm$^{-1}$ are attributed to the alkoxy and epoxy (C-O) groups, respectively, of GO. The peaks at 1636.34 cm$^{-1}$ and approximately 2932.70 cm$^{-1}$ are assigned to the bending of the C=C aromatic rings of RGO and aliphatic C-H groups, respectively. The existence of the C=C peak in the spectra of all the RGO-based samples suggests that the sp$^2$ structure of the carbon atoms was retained. The strong C=C peak observed for Co$_3$O$_4$/RGO indicates a stable graphene structure. Furthermore, the peak centered at approximately 3533.27 cm$^{-1}$ is attributed to the hydroxyl (OH) groups of GO, as GO is considered to be hydrophilic$^{23–25}$.

The weight percentage of RGO in the Co$_3$O$_4$/RGO nanocomposites and the thermal properties were investigated using TGA. The TGA curves of the Co$_3$O$_4$ nanoparticles and their RGO nanocomposites from ambient to 550 °C are shown in Fig. 1(b). The TGA plot for the Co$_3$O$_4$ nanoparticles shows a weight loss of only 0.6% in a single step. This loss might be due to dehydroxylation of the β-Co(OH)$_2$ species generated during the synthetic process. This result indicates that the Co$_3$O$_4$ nanoparticles are thermally stable with no dramatic mass loss. Based on the weight losses, the TGA curve of the RGO based nanocomposites can be divided into three. In the region from ambient to 100 °C, a clear minor loss of 0.3% is observed for Co$_3$O$_4$/RGO, which is caused by the desorption of physisorbed water. In the second region from 100 to 300 °C, an additional weight loss of 0.7% is observed. The loss in this region results from the decomposition of labile oxygen groups, which includes carboxylate, anhydride, lactone, and epoxy or hydroxyl groups, present in RGO. In the region beyond 300 °C, a weight loss of 0.5% is observed, which results from the decomposition of more stable groups, including carbonyl, phenol, and quinone groups. The total loss of 1.5% shows that all the oxygen-containing groups of GO were converted to RGO during the reduction process. According to the mass remaining after 500 °C, the weight percentage of Co$_3$O$_4$ in the Co$_3$O$_4$/RGO nanocomposites was estimated to be 99%$^{26}$.

Morphological studies were performed on both the Co$_3$O$_4$ nanoparticles and Co$_3$O$_4$/RGO nanocomposites using TEM, as shown in Fig. 1(c,d), respectively. Previously, we reported that the Co$_3$O$_4$ nanoparticles exhibited nanoporous structures$^{27}$. Using TEM, detailed structures of the Co$_3$O$_4$ nanoparticles and Co$_3$O$_4$/RGO nanocomposites were observed; although pores were not clear, the presence of Co$_3$O$_4$ incorporated on the RGO sheets was observed. In addition to the morphology, the d-spacing of the nanostructures could also be obtained using TEM. The TEM image of a single pure Co$_3$O$_4$ nanoparticle reveals that it has a spherical shape, as shown in Fig. 1(c). Atomic-resolution TEM of the Co$_3$O$_4$/RGO nanocomposites clearly shows the Co$_3$O$_4$ nanoparticles and RGO sheets, as shown in Fig. 1(d). The TEM shows a clear interlayer distance of 0.24 nm, that matches to the (311)
plane of fcc Co\(_3\)O\(_4\) crystals. Also, the interlayer spacing of 0.35 nm, indexed to the (002) plane of RGO, is observed in the TEM image of Co\(_3\)O\(_4\)/RGO, which matches the results obtained from X-ray diffraction (XRD)\(^{28}\).

The specific surface area was obtained from the BET isotherms that is a plot of the amount of gas adsorbed as a function of the relative pressure. On the other hand, a plot of pore volume versus pore size gives the pore size distribution and can be calculated using the BJH method. Both the Co\(_3\)O\(_4\) nanoparticles and Co\(_3\)O\(_4\)/RGO nanocomposites exhibited adsorption–desorption isotherms with typical type IV hysteresis loops, a characteristic of mesoporous materials that have different pore sizes as shown in Fig. 2. Co\(_3\)O\(_4\)/RGO nanocomposites displayed a high BET specific surface area of 57 m\(^2\)/g, which is four times higher than Co\(_3\)O\(_4\) nanoparticles with a BET specific surface area of only 14 m\(^2\)/g; this increase in the specific surface area is attributed to the addition of RGO to the Co\(_3\)O\(_4\) nanoparticles. Furthermore, BJH calculations showed that the pore size distributions of the Co\(_3\)O\(_4\) nanoparticles and Co\(_3\)O\(_4\)/RGO nanocomposites were found to be in the range of 80–90 nm.

To study the electrochemical behavior of the Co\(_3\)O\(_4\) nanoparticles and Co\(_3\)O\(_4\)/RGO nanocomposites, CV was first performed in a range of 0 and 3.0 V at a scan rate of 50 mV/s for 3 cycles, as shown in Fig. 3. A cathodic or reduction peak appeared at approximately 0.87 V for the Co\(_3\)O\(_4\) nanoparticles and at 0.67 V for the Co\(_3\)O\(_4\)/RGO nanocomposites in the first scan. These peaks resulted from the reduction of Co\(_3\)O\(_4\) to Co metal, the formation of clusters between Co and Li\(_2\)O, the insertion of lithium into RGO in the case of the Co\(_3\)O\(_4\)/RGO nanocomposites and the formation of a solid electrolyte interphase (SEI) layer on the active material\(^9\). In the anodic or oxidation scan, two peaks at 1.26 V and 2.28 V for the Co\(_3\)O\(_4\)/RGO nanocomposites were observed after the first cycle; these peaks are due to the de-insertion of lithium ions from RGO and the reversible oxidation of Co metal to Co\(_3\)O\(_4\)\(^{29,30}\), respectively. However, a weak or almost nonexistent oxidation peak was observed for Co\(_3\)O\(_4\), which could be due to the high scan rate. No significant drop in the peak intensity in subsequent cycles was observed for either the Co\(_3\)O\(_4\) nanoparticles or Co\(_3\)O\(_4\)/RGO nanocomposites, suggesting the good reversibility of lithium storage and a high stability\(^{11}\). The electrochemical conversion reaction of Co\(_3\)O\(_4\)-based anodes can be described as\(^{30}\):

\[
\text{Co}_3\text{O}_4 + 8 \text{ Li} \rightarrow 4 \text{ Li}_2\text{O} + 3\text{Co}
\]

Also, the Co\(_3\)O\(_4\)/RGO nanocomposite displayed a higher current than the Co\(_3\)O\(_4\) nanoparticles, which was due to the incorporation of conductive RGO sheets.

Typical charge/discharge cycling of the prepared Co\(_3\)O\(_4\) nanoparticles and Co\(_3\)O\(_4\)/RGO nanocomposites was performed at a current density of 500 mA/g for five cycles, as shown in Fig. 3. The initial charge/discharge capacities were approximately 66/55.5 mAh/g and 47/42.7 mAh/g for the Co\(_3\)O\(_4\) nanoparticles and Co\(_3\)O\(_4\)/RGO nanocomposites, respectively, at the same current density. The Co\(_3\)O\(_4\)/RGO nanocomposites exhibited stable cycling performance with 85% capacity retention after the 5\(^{th}\) cycle and charge/discharge capacities of 39/36.5 mAh/g, while the Co\(_3\)O\(_4\) nanoparticles showed a dramatic capacity loss with only 48% capacity retention after 5 cycles, evidencing the positive effect of the RGO sheets that led to an enhanced electrochemical response.

To further investigate the stability of the Co\(_3\)O\(_4\) nanoparticles and Co\(_3\)O\(_4\)/RGO nanocomposites, the cyclic performance and rate capability were evaluated, as shown in Figs 4 and 5. The Co\(_3\)O\(_4\)/RGO nanocomposites showed a more stable cyclic performance than Co\(_3\)O\(_4\) with a reversible charge/discharge capacity of 26 mAh/g after the 50\(^{th}\) cycle, while the discharge capacity of Co\(_3\)O\(_4\) dropped continuously with each cycle, giving a reversible capacity of only 1.6/1.2 mAh/g after the 50\(^{th}\) cycle. Fig. 4 also shows the columbic efficiency of the Co\(_3\)O\(_4\)/RGO nanocomposites. During the first cycle, the Co\(_3\)O\(_4\)/RGO nanocomposites exhibited a coulombic efficiency above 100% due to the occurrence of a reverse reaction that involved the embedding of Li\(_2\)O in the metal particles, which enhanced the electrochemical activity as a result of Li\(_2\)O decomposition and metal–oxygen bond formation\(^{31,32}\). Thus, this metal could be oxidized to higher valence states, causing the delithiation capacity to be higher than the lithiation capacity, which resulted in a coulombic efficiency above 100%. The coulombic efficiency of the Co\(_3\)O\(_4\)/RGO nanocomposites was 100% after 50 cycles (Fig. 4), while the Co\(_3\)O\(_4\) nanoparticles exhibited a coulombic efficiency of 75% after 50 cycles (Fig. S1).
The rate capability of the Co$_3$O$_4$/RGO nanocomposites is shown in Fig. 5. At a low current density (100 mA/g), the Co$_3$O$_4$/RGO nanocomposites displayed initial charge/discharge capacities of 358/363 mAh/g, and when a higher current density was used (1000 mA/g), the charge/discharge capacities were 82.5/77.7 mAh/g.

EIS studies were performed for both the Co$_3$O$_4$ nanoparticles and Co$_3$O$_4$/RGO nanocomposites, as shown in the Nyquist plots in Fig. 6. The semicircle in the high-medium frequency region is due to the charge-transfer resistance. The diameter of the semicircle for Co$_3$O$_4$/RGO is smaller than that for Co$_3$O$_4$, which indicates that Co$_3$O$_4$/RGO is capable of faster charge transfer and that it exhibits less internal electrochemical resistance than Co$_3$O$_4$. The sloped lines in the low-frequency region can be attributed to the mass transfer process or the Warburg

Figure 3. Cyclic voltammetric (CV) and galvanostatic charge-discharge curves of Co$_3$O$_4$ and Co$_3$O$_4$/RGO nanocomposites.

Figure 4. Cycling performance of Co$_3$O$_4$ nanoparticles and Co$_3$O$_4$/RGO nanocomposites at 500 mA/g for 50 cycles.
resistance. The steeper tail for the Co$_3$O$_4$/RGO nanocomposites indicates a lower ion diffusion resistance and enhanced mass transport compared to Co$_3$O$_4$. Thus, the Co$_3$O$_4$/RGO nanocomposites showed high electrical conductivity and rapid charge and mass transfer, which play critical roles in the overall battery performance. Microwave-assisted techniques have been widely used for the synthesis of graphene-based metal oxides as electrodes in lithium-ion batteries which includes Co$_3$O$_4$-graphene, Mn$_3$O$_4$-graphene, SnO$_2$-graphene, ZnO-graphene nanocomposites. As compared with the results shown in Table 1, the Co$_3$O$_4$/RGO nanocomposites displayed a good reversible capacity of 96.36 mAh/g at 100 mA/g after 100 cycles with the addition of only 1% graphene content as shown in Fig. 7 which
was conducted for a new coin cell with Co₃O₄/RGO nanocomposites as electrodes. Also, CV at low current and EIS after 100 cycles were also performed as shown in Figs S2 and S3.

Further electrochemical investigations were performed to test the electrochemical performance of the Co₃O₄/RGO nanocomposites at a higher operating temperature of 100 °C. Figure 8 shows the CV curve of the Co₃O₄/RGO nanocomposites performed at 100 °C in the range between 0 and 3.0 V at a scan rate of 50 mV/s for 3 cycles. The Co₃O₄/RGO nanocomposites exhibited an ideal CV curve of a Co₃O₄-based anode at 100 °C, with two reduction peaks at 0.86 V and 1.45 V in the first scan. These peaks resulted from the reduction of Co₃O₄ to Co metal, the formation of clusters between Co and Li₂O, the insertion of lithium into RGO and the formation of an SEI layer on the active material. Two peaks were observed at 1.45 V and 1.96 V in the anodic scan after the first scan, and these peaks are due to the de-insertion of lithium ions from RGO and the reversible oxidation of Co metal to Co₃O₄. The overlap between the second and the third cycles indicates the enhanced cycling stability of the Co₃O₄/RGO nanocomposites. Furthermore, the current response of Co₃O₄/RGO increased with stronger and sharper peaks when the operating temperature was 100 °C, which indicates the role of the high temperature in enhancing the CV performance of the Co₃O₄/RGO nanocomposites.

The galvanostatic charge/discharge capacities of the Co₃O₄/RGO nanocomposites measured at an operating temperature of 100 °C with a current density of 500 mA/g for 5 and 50 cycles are shown in Fig. 8. No decrease of charge/discharge capacity was observed when the operating temperature was increased from ambient (Fig. 4) to 100 °C (Fig. 8) at a constant current density, with 100% capacity retention for 50 cycles and a coulombic efficiency of 100%. Note that a coulombic efficiency above 100% was observed, which was due to the reversible insertion of Li₂O into the metal particles.

To further investigate the electrochemical behavior of the Co₃O₄/RGO nanocomposites at high operating temperature, EIS tests were conducted, as shown in Fig. 8. Comparing the Nyquist plots of Co₃O₄/RGO (Fig. 6) at room temperature and 100 °C (Fig. 8), the semicircle decreased in the high-mid frequency region following the

Table 1. Comparison of graphene content and electrochemical performance of Co₃O₄/RGO nanocomposites with Co₃O₄/graphene and other metal oxides/graphene reported.
increase of temperature to 100 °C, exhibiting a reduction in the electrochemical resistance, which was due to the larger amount of charges that could overcome the activation energy, thereby reducing the internal electrochemical resistance. In addition, the increase in the slope of the straight line of Co3O4/RGO in the low frequency region of the spectrum measured at 100 °C (Fig. 8) relative to that measured at room temperature (Fig. 6) is an indication of faster mass transport. This suggests the occurrence of excellent electrochemical behavior at high temperatures, which matches with the above CV and charge/discharge tests performed at a high temperature of 100 °C.

Conclusions

We successfully prepared Co3O4 nanoparticles and Co3O4/RGO nanocomposites via a microwave-assisted route. FTIR spectroscopy confirmed the formation of graphene-based Co3O4 nanoparticles. Co3O4/RGO nanocomposites’ thermal stability was determined using TGA. Morphological studies using TEM further confirmed the formation of Co3O4 nanoparticles in addition to Co3O4 nanoparticles supported on RGO. The prepared Co3O4/RGO nanocomposites showed excellent electrochemical behavior as anodes in li-ion batteries. A superior electrochemical response which includes enhanced charge/discharge capacity and cycling stability was observed. The enhanced electrochemical performance relative to that of the pure Co3O4 nanoparticles, even when high current densities are applied, is attributed to the incorporation of 2D graphene, which resulted in a surface area almost four times larger than that of pure Co3O4, and to the exfoliation and good integrity of the RGO sheets in the Co3O4/RGO nanocomposites, as determined from chemical and thermal studies. Furthermore, increasing the operating temperature from ambient to 100 °C further enhanced the electrochemical performance, making the prepared nanocomposites potential for high temperature li-ion batteries.

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**Author Contributions**
E.A. implemented the concept and contributed to the design of the experiment. Y.M. performed all the experiments and the electrochemical tests. F.A. and H.A. contributed to the electrochemical tests. Y.M. and F.A. wrote the manuscript and prepared the figures. Y.M., F.A., M.A., and E.A. discussed the results, commented, and reviewed the manuscript.

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