

One Step Synthesis of Au Nanoparticles Supported on Graphene Oxide Using an Eco-Friendly Microwave-Assisted Process

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Microwave (MW) assisted processes become more and more used in the synthesis and alteration of graphene materials. This technique brings some various advantages compare to the classical ones because it is a green, low-cost, environmentally-friendly process. Moreover, no toxic solvent is necessary for the production of high-quality graphene-based materials. This eco-friendly process has recently received important attention as uniform, fast, energy efficient and scalable approach to synthesis noble metals supported on graphene oxide. A facile, rapid, low cost and efficient method to prepare gold supported on reduced graphene oxide (Au/rGO) is presented in this paper. The Au/rGO samples were produced using the microwave power of 800 W and two temperatures, 60 and 80°C, for 30 minutes only. The physical characterization showed that the Au nanoparticles were grafting on the graphene surface. Additionally, the nitrogen adsorption-desorption isotherms show a high pore volume and specific surface suggesting that a larger mesoporous volume have been achieved. The presence of interconnections between micropores and mesopores is beneficial to the mass transport process in PEMFC by creating a facile access of the reactants. Moreover, the accelerated stability tests (AST) of the catalysts showed that the catalysts are stable and no remarkable change in the shape of the voltammetry curve could be observed after 200 cycles.

Keywords: microwave irradiation, graphene, gold nanoparticles.

1. INTRODUCTION

The potential applications of nano-carbon materials as catalyst supports and electronic materials have attracted many interests due to their morphologies that can be designed as needed [1]. Many methods have been developed to synthesize nano-carbon materials, like chemical vapor deposition (CVD), arc-discharge, epitaxial growth and bottom-up synthesis [2, 3]. Anyhow, increased temperature treatment is generally necessary to obtain the desired crystallinity for these kinds of materials which is correlated with their characteristics [4]. Recently, microwave irradiation become more and more used in the synthesis and alteration of graphene materials [5–7] and in the conception of the graphene compounds in liquid phase [8–10].

Microwave (MW) heating is a technique that brings some advantages, like rapidity, regularity, clarity to obtain smaller and well dispersed nanoparticles [11]. This method has received significant attention as a novel, bright method to decrease the constitution of "re-graphitized" carbon zone of graphene [12, 13]. In a classical microwave reaction in liquid phase, the microwave irradiation ensures a reverse temperature variation. The effect of potential superheating and the selective wave-absorption of polar solvents or substrates cause this technique to be energy-efficient and time-saving [11, 14]. The heating produced by microwave irradiation and interfered by the dielectric relaxation or ionic conduction, assure a manner to heat homogeneously

a system and a very important factor is that the ability of the wave-absorption of the sample can heat selectively the substrates. Whereas the microwave irradiation is a sharp and adsorption-selective heating method [15], it is also adequate for solid phase reactions [16, 17]. During this technique no mechanical stirring or energy loss to the environment are observed. The materials that absorb microwave may be efficiently and homogeneously heated [15].

Microwave heating is estimated as an attractive way in organic compounds and inorganic materials synthesis for reducing the time of the reaction. Moreover, this technique eliminates secondary reactions improving the efficiency and the yield of a distinctive synthetic protocol [18]. Recently, some authors reported the synthesis of graphene through reduction of graphene oxide using microwave heating [19, 20].

Generally, the catalysts for fuel cells are synthesized through chemical reduction method using mainly the ethylene glycol (EG). NaBH₄ is a powerful reducing agent which might be efficient at low temperature and more exactly at room temperature, in spite of several some drawbacks since the particle size and dispersion of the metal nanoparticles cannot be controlled. In comparison with NaBH₄, ethylene glycol (EG) involve a superior reaction temperature, usually > 120 °C and increased reaction time (> 4 h). An alternative method to these can be utilization of a mixture of NaBH₄ and EG who put together the advantage of each one, like powerful reducing mediator of NaBH₄ and better dispersion assured by EG. Utilizing this alternative method smaller nanoparticles with superior dispersion can be obtained [21, 22].

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Through actual methods of synthesis, using of microwaves has attracted considerable attention, due to extremely easy handling, as well as to its various applications in preparation of nanostructured materials. The main advantages of this synthesis processes is connected especially to low cost and high efficiency, since microwave energy is absorbed directly by the reactants instead of being absorbed by the vessel or reactor, as in conventional techniques. Using microwaves synthesis, the uniform heating could provide more homogeneous nucleation and shorter crystallization times. Moreover, the microwave hydrothermal processes has recently obtained a significant recognition due to the feasibility of controlling the materials structure and the reaction selectivity by simply controlling temperature, reaction pressure and reaction time.

This paper reports the synthesis, using microwave-assisted hydrothermal synthesis, of Au nanoparticles (AuNP). The novelty of this work is the synthesis method itself, meaning the application of microwave for obtaining of Au nanoparticles supported on graphene oxide, instead taking into account the conventional methods up to date.

2. EXPERIMENTAL

2.1. Materials

Graphene oxide was purchased from Abalonyx (Norway), Sodium Borohydride, 98%, powder, from Alfa Aesar, Hydrogen tetrachloroaurate (III) hydrate (chloroauric acid), Premion ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$), crystalline, from Alfa Aesar, Distilled water.

2.2. Methods

Synthesis starts from graphene oxide. 250 mg of graphene oxide powder was dispersed in distilled water – using 4 wt.% graphene. Sodium borohydride, (aqueous solution 8.1 wt.%) in distilled water was added on the graphene oxide dispersion, then the mixture was homogenized for 30 minutes in the ultrasonic bath. Chloroauric acid (solution 1 wt.%) was then added in the obtained dispersion and treated again in ultrasonic bath for 30 minutes. After the second ultrasonic step, the dispersion was heated at microwave oven at 100 °C and 800 W power for 30 minutes. The synthesis product was cooled down, washed on fritted disk funnel with a mixture of 1:1 in volume water to ethyl alcohol, until the washing solution was free from chloride ions, then the slurry was dried in a laboratory freeze dryer.

2.3. Physical characterizations

Fourier-transform infrared spectroscopy (FT-IR) was carried out on Agilent Cary 630 FTIR system. This spectrometer is versatile, innovative, and intuitive, providing superior quantitative and qualitative information for routine analysis of solids, liquids, and gases. With a wide range of sample interfaces and high performing optics, the compact Agilent Cary 630 FTIR gave accurate results. The system includes standard transmission Diamond ATR. The chemical composition of the samples was determined using Flash 2000/Thermo Scientific equipment. Samples are placed in tin nails (1–3 mg). For

the quantification of C, N and H it was used the combustion method at 950 °C. For oxygen determination, the equipment uses the pyrolysis method at $T = 1050$ °C. The gas is separated on the SM5A column (molecular sieve) and also detected by the TCD. Au content (wt.%) and trace metals (K, Mn) analysis were performed with an atomic absorption spectrometer VARIAN AA 240 FS after sample mineralization in a microwave digestion system MILLESTONE 1200 MEGA. The standard addition method was used as calibration method. 0.1 g sample was weighed in the crucible of modified Teflon. Over the samples the following reactive were added: 2 ml conc. HF, 2 ml conc. HClO_4 and 2 ml conc. H_2SO_4 . A blank control was run for purity reagents. The power program chosen was: 50/250 W – 50/400 W – 100/500 W.

The specific surface areas of the samples were determined using the BET method by performing nitrogen sorption measurements using a Quantachrome Autosorb IQ equipment. The adsorption and desorption experiments were done at 77 K after initial pre-treatment of the samples by degassing at 115 °C for 4 h.

2.4. Microwave setup

The Microwave heating was performed with a MARS 6 system which delivers approximately 1800 watts of microwave energy at a frequency of 2450 MHz. All reagents were added to the microwave reactor, without any previous treatment, and were heated at 60 °C (obtained sample was encoded Au/rGO-60) and respectively 80 °C (obtained sample was encoded Au/rGO-80). The obtained sol was centrifuged and washed several times with deionized water and dried at 80 °C. The as-prepared materials were characterized as materials with potential electrocatalytic activity.

2.5. Electrode preparation

Catalyst ink was prepared by dispersing 5.0 mg of Au/rGO-60 and Au/rGO-80 catalysts, isopropyl alcohol (Sigma-Aldrich), deionized water and 26 μl of 5 wt.% Nafion solution (Ion Power), dispersed and sonicated in cold-water for 45 min. Thin catalyst film was obtained by dropping 10 μl of the catalyst ink onto the polished gold disk electrode (4 mm diameter) followed by drying at 40 °C.

2.6. Electrochemical measurements

The electrochemical measurements were performed using a VersaSCAN electrochemical workstation including two potentiostats VersaSTAT F and 3F from Princeton Applied Research and the supplied electrical devices, software, and gold disk electrode, was used.

A classical three electrodes cell was used for the cell measurements, using an Ag/AgCl electrode and a Pt wire as the reference and counter electrodes, respectively. The prepared electrodes were tested on a solution of 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ in distilled water, using KCl as indifferent electrolyte so that the concentration was 100 mM. The cyclic voltammograms (CV) experiments were performed for the gold disk electrode between -0.35 and 0.8 or 1 V vs Ag/AgCl with a sweep rate of 50 mVs^{-1} .

The electrochemical surface area was evaluated from Randles-Sevcik equation:

$$I_p = 2.69 \times 10^5 \times z^{3/2} \times S \times D^{1/2} \times c \times \nu^{1/2} \quad (1)$$

where I_p is the peak current (A); z is the number of exchanged electrons; S is electrochemical surface area (cm^2); D is the diffusion coefficient of the electroactive species ($\text{cm}^2 \cdot \text{s}^{-1}$), c is the concentration of the electroactive species ($\text{mol} \cdot \text{L}^{-1}$) and ν is the scan rate ($\text{V} \cdot \text{s}^{-1}$).

3. RESULTS AND DISCUSSION

3.1. Structural and chemical analysis

In order to investigate the structure and to characterize the porosity of doped graphene, the nitrogen adsorption-desorption isotherms were recorded using Brunauer-Emmett-Teller (BET) method. The adsorption/desorption isotherm of Au/rGO sample are presented in Fig. 1. The N_2 isotherms show characteristics of type IV with a uniform H1 hysteresis loop at a relative pressure range of 0.45–0.95, with steep adsorption/desorption branches, suggesting that there are good transport properties among the micropores and mesoporous channels in Au/rGO sample. The hysteresis loop is mainly due to the several mechanisms that take place in pores between capillary condensation and evaporation processes.

The BET surface area was estimated of $244.3 \text{ m}^2 \cdot \text{g}^{-1}$ (corresponding to Au/rGO-60) and $177.8 \text{ m}^2 \cdot \text{g}^{-1}$ (corresponding to Au/rGO-80). The obtained BET surface area of prepared Au/rGO samples indicates a decrease of specific surface area during the proposed technologies, comparatively to our results obtained in the case of graphene sheets ($795 \text{ m}^2 \cdot \text{g}^{-1}$) (Table 1).

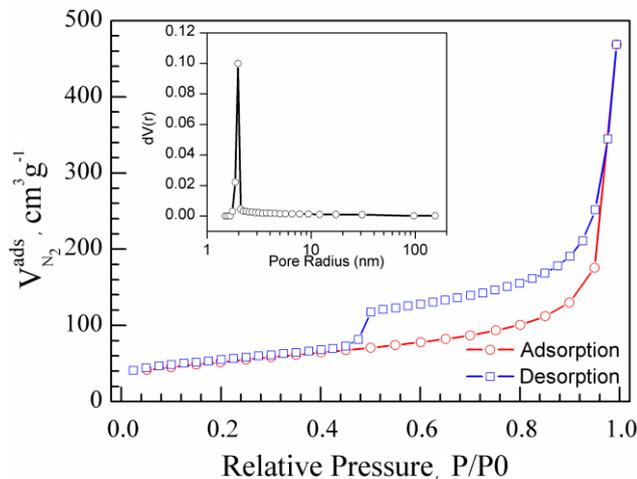


Fig. 1. Nitrogen sorption isotherms of Au/rGO-60 sample

The pore size distribution curve was estimated from desorption branches of isotherm using Barrett-Joyner-Halenda (BJH) method and was presented as inserted plot. BJH desorption average pore radius of Au/rGO-80 shows a unimodal peak (19.693 \AA) slightly higher to the pore radius of Au/rGO-60 (19.676 \AA). At the same time the total pore volume of Au/rGO-60 ($1.049 \text{ cm}^3 \cdot \text{g}^{-1}$) is much bigger than Au/rGO-80 ($0.74 \text{ cm}^3 \cdot \text{g}^{-1}$), suggesting that, for the last one, a part of mesopores were blocked during the grafting process. The analysis of pore size distribution also confirmed the coexistence of micro and mesopores, providing a hierarchical porous structure in prepared catalysts. The existence of the mesopores and

interconnections are important for the mass transport process in PEMFC by creating a facile access of the reactants, and a more favorable path for break and conveyance of water product through graphene structure.

Table 1. Textural properties of Au/rGO samples

Sample	$S_{\text{BET}}, \text{m}^2 \cdot \text{g}^{-1}$	Pore volume, $\text{cm}^3 \cdot \text{g}^{-1}$	$Dv(r), \text{\AA}$
Au/rGO-60	244.3	1.049	19.676
Au/rGO-80	177.8	0.74	19.693

The chemical composition of rGO and Au/rGO samples are presented in Table 2. The analysis were performed using atomic absorption and elemental analysis. The higher concentration of Au obtained could be explained taking into account the different reaction temperature used for the sample preparation.

Table 2. Chemical compositional analysis

Sample	Elemental analysis %					Atomic absorption %
	C	H	N	S	O	Au
rGO	72.25	0.64	0.49	—	16.41	—
Au/rGO-60	55.10	1.01	0.37	0.47	10.29	15.71
Au/rGO-80	47.95	0.95	0.36	0.27	8.70	23.56

The FT-IR spectra of Au/rGO-60 and Au/rGO-80 samples gave similar curves (Fig. 2). The spectrum presents the C–O stretching vibration that originates from the remaining oxygen functionalities at 1250 cm^{-1} , C=C stretching vibrations assigns to the carbon atoms of the graphene layer at 1590 cm^{-1} , C=O stretching vibration, significantly weakened after graphene reduction at 1723 cm^{-1} , and at $\sim 3450 \text{ cm}^{-1}$ due to the O–H stretching mode of intercalated water.

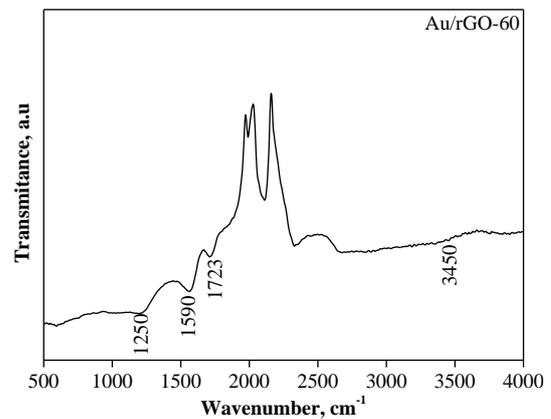


Fig. 2. FT-IR spectra of Au/rGO-60

3.2. Electrochemical studies of Au/rGO catalysts

In order to observe the redox activity of Au based catalysts, cyclic voltammetry measurements using the prepared electrodes were performed. The electrochemical performance of the electrodes is achieved to measure their efficiency using electrochemical redox couple ferro/ferricyanide and electroactive zones, respectively.

The accelerated stability test (AST) of Au based catalysts is performed by using CV measurement. The CV are evaluated from 1 to 200 cycles with a potential window of $-0.35 - 0.8 \text{ V}$ and $-0.35 - 1.0 \text{ V}$ vs. Ag/AgCl [23].

In Fig. 3 and Fig. 4 are presented the cyclic voltammograms of Au/rGO-60 and Au/rGO-80 catalysts after 200 cycles in the potential field of $-0.35-0.8$ V vs Ag/AgCl.

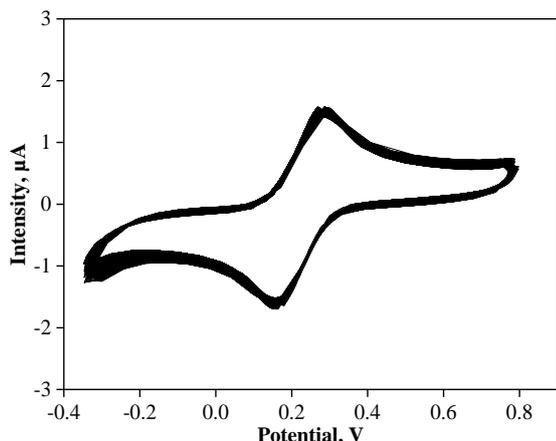


Fig. 3. The cyclic voltammograms of Au/rGO-60 catalyst after 200 cycles at 50 mV s^{-1}

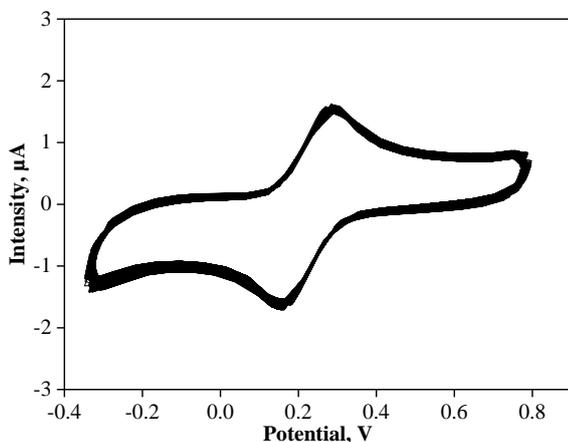


Fig. 4. The cyclic voltammograms of Au/rGO-80 catalyst after 200 cycles at 50 mV s^{-1}

It can be observed that well defined and reproducible anode and cathode peaks related to $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox couple with a quasi-reversible behaviour are obtained after 200 cycles. Moreover, for both catalysts the adsorption and desorption of hydrogen can be observed at 0.18 and 0.325 V. Similar values were obtained in ref [24].

In Table 3 the electrochemical surface areas (ECSA) for our catalysts in the potential range $-0.35-0.8$ V are shown. Increasing the synthesis temperature a slight difference is observed in the ECSA. In the same time no significative differences are distinguished after 200 cycle.

Table 3. The S_{ECSA} of the of Au/rGO prepared samples

Sample	Electrochemical surface area, cm^2	
	First cycle	200 cycle
Au/rGO-60	9.288×10^{-3}	9.607×10^{-3}
Au/rGO-80	9.694×10^{-3}	9.867×10^{-3}

Fig. 5 presents a comparison between gold disk electrode, rGO, Au/rGO-60 and Au/rGO-80 at 50 mV s^{-1} scan rate. As we can easily observe, in the case of gold

disk electrode (black line) there is no charge accumulation due to the presence of a smooth and flat surface. In the presence of the reduced graphene (red line), the electric double layer is caused to a non-uniform surface that leads to charge accumulation at different levels on the sample.

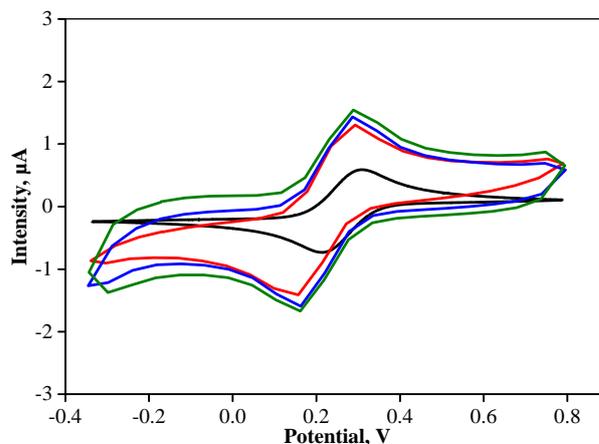


Fig. 5. The cyclic voltammograms of the gold disk electrode (black line), rGO (red line), Au/rGO-60 catalyst (blue line) and Au/rGO-80 catalyst (green line) at 50 mV s^{-1} scan rate

In Table 4, the ECSA was calculated for the potential range $-0.35-1$ V. It can be observed that Au/rGO-60 sample has a higher ECSA than Au/rGO-80 due to a higher pore volume and a specific surface.

Table 4. The S_{ECSA} of Au/rGO prepared samples

Sample	Electrochemical surface area, cm^2	
	First cycle	200 cycle
Au/rGO-60	10.828×10^{-3}	11.998×10^{-3}
Au/rGO-80	8.35×10^{-3}	10.099×10^{-3}

In Fig. 6 and Fig. 7 are presented the accelerated degradation test (AST) in the potential field of $-0.35-1.0$ V vs Ag/AgCl.

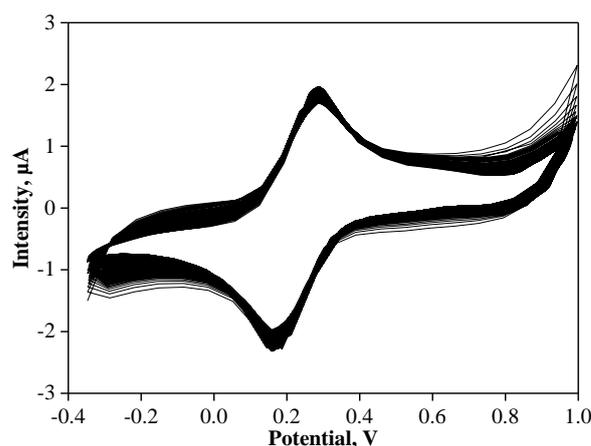


Fig. 6. The cyclic voltammograms of Au/rGO-60 catalyst after 200 cycles at 50 mV s^{-1} scan rate

It is seen that the voltammograms obtained using Au based catalysts are almost identical and the recorded data became stable after tenth cycle [25]. After 200 cycles, the CV measurement show very good stability, proving a good repeatability of Au based catalysts. It can be observed that

wider peaks are presented in the potential range 0.8–1.0 V and are assigned to the formation of gold hydroxide and oxide in the anodic scan as well as the corresponding reduction of gold oxide in the return sweep [24].

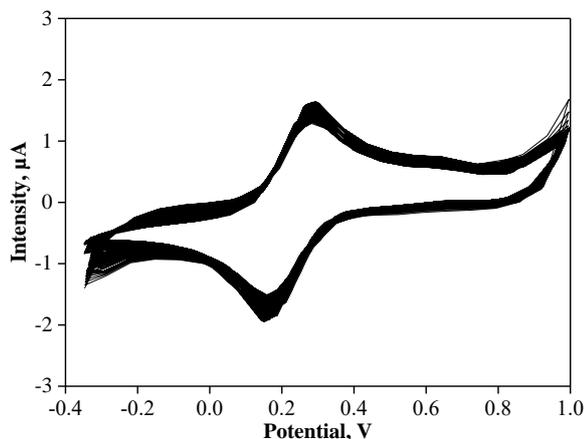


Fig. 7. The cyclic voltammograms of Au/rGO-80 catalyst after 200 cycles at $50 \text{ mV} \cdot \text{s}^{-1}$ scan rate

4. CONCLUSIONS

The using of microwave irradiation for synthesize graphene composites could be an advantage for many technologies in the energy domain such as fuel cells. Moreover, this technique proved to have some advantages being simple, quick, inexpensive and uniform, advantages that could be used more and more in the next future in order to synthesize various materials with controlled size and shape for the energy application.

In this work we have developed a facile, low time consuming, low cost and efficient method to prepare gold supported on reduced graphene oxide (Au/rGO). Au/rGO samples were synthesized at microwave power of 800 W and two different reaction temperatures, 60 and 80 °C, for 30 minutes only. The physical characterizations of the samples have indicated the grafting of Au nanoparticles on the surface of graphene sheets. Additionally, the nitrogen adsorption–desorption isotherms show that at 60 °C a higher pore volume and a specific surface were obtained suggesting that a larger mesoporous volume and interconnections are presented in this sample, which favored the mass transport process in PEMFC by creating a facile access of the reactants. The stability of prepared materials was evaluated by accelerated electrochemical stability test using a protocol involving multiple CV in potential range of $-0.35 \div 0.8$ and $0.35 \div 1.0 \text{ V vs. Ag/AgCl}$.

The good electrocatalytic activities of the samples were assigned to a mixture of benefits arising both from reduced graphene and the gold nanoparticles deposited on the support. The strong interactions between gold nanoparticles and rGO help to disclose the catalytically active sites, thus enhancing the charge transport through the rGO layers.

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