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One-step synthesis of graphene/polyallylamine–Au nanocomposites and their electrocatalysis toward oxygen reduction

Qixian Zhang[a], Qiaoqiao Ren[b], Yuqing Miao[b,*,1], Junhua Yuan[b], Kaikai Wang[a], Fenghua Li[a], Dongxue Han[a,*,1], Li Niu[a]

[a] Engineering Laboratory for Modern Analytical Techniques, c/o State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
[b] Laboratory of Biomimetic Electrochemistry and Biosensors, Department of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, PR China

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ABSTRACT

A simple, inexpensive, one-step synthesis of graphene/PAA–Au nanocomposites was achieved by using polyallylamine (PAA) as a reducing and stabilizing agent. The synthetic process was carried out only in aqueous solution, which is versatile and environmentally friendly. The resulting nanocomposites could be dispersed into water stably without any additional protection by polymeric or surfactant stabilizers. The products were further characterized by UV–visible absorption spectroscopy, transmission electron microscopy (TEM), fourier transform infrared spectroscopy (FTIR) and photoelectron spectroscopy (XPS). The results indicate that graphene sheets played an important role as a support material to increase the active area of Au nanoparticles (AuNPs). And the resulting graphene/PAA–Au nanocomposites film exhibited good electrocatalytical activity towards reduction of both H_2O_2 and O_2, which showed potential application in electrochemical sensors.

1. Introduction

Since firstly reported in 2004, graphene has rapidly become a research focus of chemistry physics and materials science [1,2]. It has a lot of potential applications in the future Hi-Tech field, due to its peculiar mechanical properties, electronic, chemical and unique single-layered 2-D structure [3–5]. Researches on graphene were originally motivated by its peculiar electrical transport properties and the possibility of potential applications in nanoelectronics. Graphene sheets, owing to their exceptional thermal and mechanical properties and high electrical conductivity, are also of great interest to serve as new nanoscale building blocks to create unique macroscopic materials [6]. It has displayed a variety of applications including graphene-based nanoelectronic devices, composite materials, and gas sensors [3,7].

Different from carbon nanotubes, a key challenge in the synthesis and processing of bulk-quantity graphene sheets is the prevention of aggregations. At present, a variety of methods for the preparation of individual graphene or chemically-modified graphene sheets have been reported, including scotch tape method, non-covalent or covalent functionalization of reduced graphene oxide (GO) [8–12] and chemical reduction of GO suspensions [13–15]. Reduction of GO has readily produced agglomeration of the hydrophobic graphene sheets, which has relatively high surface area revealed by BET measurement [16]. The synthesis of graphene usually needs a soluble GO solution, a reducing agent and a stabilizing agent [17,18].

The high electrocatalytical activity of Au nanoparticles leads to its increasing applications in electrochemistry, electroanalysis and bioelectronics [19]. The catalytical activity of Au nanoparticles has been known to strongly depend on the gold oxidation state, nanoparticle size and surface properties [20]. Various synthetic methods of Au nanoparticles have been reported till now, but most of them are based on the reduction of Au ions by toxic reducing agents such as hydrazine and $NaBH_4$ [21]. Furthermore, reports on preparations of Au nanoparticles with narrow size distribution and long-term electrocatalytic activity are still very limited [22,23]. It is possible to use GO as a precursor to produce graphene/nanoparticles composites. The attachment of AuNPs onto graphene not only prevent the restack of these sheets during the chemical reduction process, but also lead to the formation of a new class of graphene-based nanocomposites.

PAA (Scheme 1) was previously studied for its stabilizing ability [24], however, its dual character both as a kind of reducing and stabilizing agent for the preparation of metal nanoparticles

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* Corresponding authors. Fax: +86 431 8526 2800.
E-mail addresses: yqmiao@zjnu.cn (Y. Miao), dxhan@ciac.jl.cn (D. Han).
[1] Equivalent contribution.

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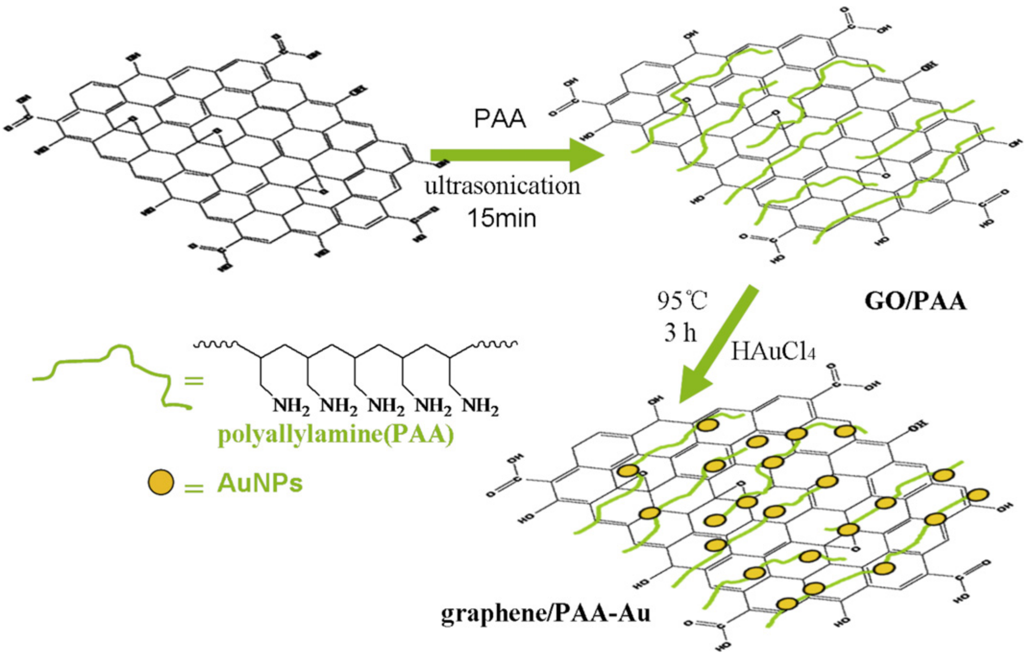

Scheme 1. Illustration of the preparation of graphene/PAA–Au composites and chemical structure of PAA.

has rarely been reported. To the best of our knowledge, till now only Shumaker-Parry has reported a method of Au nanoparticles synthesis using PAA as reducing and stabilizing agent [25].

Recently, Ruoff and co-workers reported a solution based approach to prepare graphene nano-composites in which GO was cross linked by PAA in solution [26]. It is also speculated to be possible to use GO as a precursor to produce graphene/metallic nanoparticles composites. The attachment of noble metal nanoparticles onto graphene not only prevented the graphene sheets from restacking during the chemical reduction process, but also led to the formation of a new class of graphene-based nanocomposites. In this work, we reported a facile and environmental friendly method for preparation graphene/PAA–Au nanocomposites for the first time. PAA have been successfully employed in preparations of graphene/PAA–Au nanocomposites as an efficient reductant and stabilizer. In this nano-composite, the homogeneously distributed Au nanoparticles on graphene sheets had an average diameter of 4.2 nm without other protection. The resulting nanocomposites showed excellent electrocatalytical activity towards reduction of H_2O_2 and O_2. This simple method provided a low-cost and “green” approach to process graphene based materials, which proposed promising opportunities for many technological applications.

2. Experimental details

2.1. Preparation of GO

GO was synthesized from natural graphite powder (spectral requirement, Shanghai Chemicals, China) according to a modified Hummers method [27,28]. Then GO was subjected to dialysis for 3–4 days in order to completely remove metal ions and acids. Finally, the product was dried in air at room temperature.

2.2. Synthesis of graphene/PAA–Au nanocomposites

10 mg dried GO was exfoliated in 20 mL distilled water to form a colloidal suspension through a 15 min ultrasonic treatment. Subsequently, 400 μL of 0.01 M $HAuCl_4{\cdot}3H_2O$ (Sigma–Aldrich) and 10 mL of 0.08 M PAA (Sigma–Aldrich, 20 wt% aqueous suspension, $M_w = 17{,}000$) were added dropwise to the aqueous suspension of GO with constant stirring. The mixture was then continually stirred at 95 °C for 3 h. The resulting graphene/PAA–Au nanocomposites were collected by centrifugation and washed with distilled water for three times. After the re-suspension into distilled water, the samples were stable for several months without any observable aggregation. As a controlled experiment, the PAA-protected Au nanoparticles (AuNPs) without GO were synthesized according to the above-mentioned method. Briefly, 400 μL of 0.01 M $HAuCl_4$ solution was dispersed into 20 mL water, and then 10 mL of 0.08 M PAA solution was added to the mixing solution. The resulting PAA-protected AuNPs were centrifugated and washed with water for three times. Scheme 1 shows the chemical structure of PAA and a schematic of the process to prepare graphene/PAA–Au composites.

2.3. Fabrication of graphene, graphene/PAA–Au nanocomposites and PAA–Au nanocomposites modified electrode

The glassy carbon (GC, 3 mm in diameter) electrodes were polished subsequently with 1.0, 0.3 and 0.05 μm alumina slurry, and then sonicated in water for several times. To prepare graphene, graphene/PAA–Au and PAA–Au modified GC electrodes, an aliquot of 8 μL 2.0 mg mL^{-1} graphene, graphene/PAA–Au or PAA–Au aqueous solution was dropped onto the surface of the GC electrode using a microsyringe, respectively. The dried films can be obtained after 9 h at 4 °C. Then the electrode was rinsed by distilled water for several times and further dried in air before use.

2.4. Instruments and measurements

The UV–vis absorption spectra were collected using a CARY 500 Scan UV/vis/NIR spectrophotometer. Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker Vertex 70 spectrometer (2 cm^{-1} spectral resolution). Transmission electron microscopy (TEM) micrographs were obtained using a JEOL 2000 transmission electron microscopy operating at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB MK II X-ray photoelectron spectrometer. Cyclic voltammetry (CV) was performed using a conventional three-electrode cell with a platinum wire as auxiliary electrode and

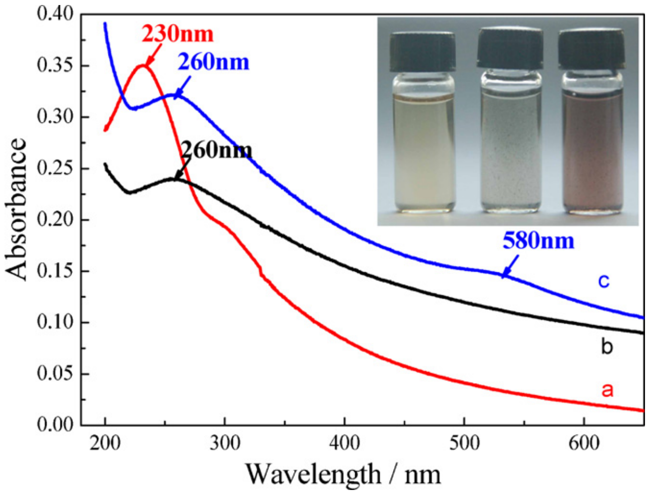

Fig. 1. UV–vis absorption spectra of graphene oxides,(a) PAA-protected graphene (b) and graphene/PAA–Au (c) in water. Inset: a photograph of GO (left), graphene (middle) and graphene/PAA–Au (right) nanocomposite solutions.

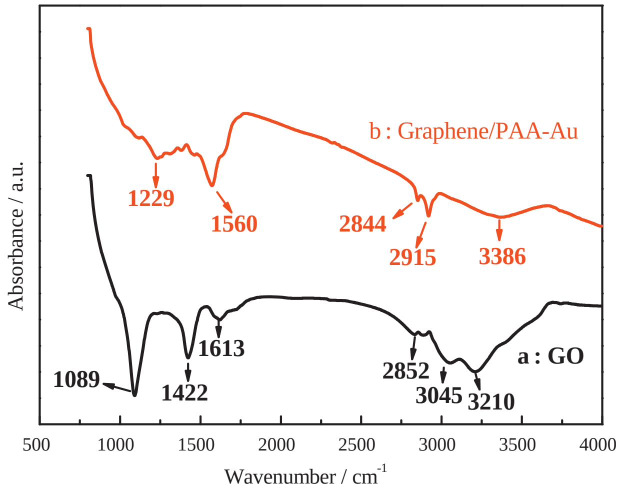

Fig. 3. FTIR spectra of GO (a) and graphene/PAA–Au (b).

an Ag/AgCl (saturated KCl) as reference in a DyneChem Electrochemical Workstation (DyneChem, China). The working electrodes were bare or modified GC electrode. The electrolyte solution for CV experiment was 0.05 M phosphate buffer solution (PBS, pH 7.4).

3. Results and discussion

Fig. 1 displays the UV–vis spectra of GO, (a) graphene/PAA (b) and graphene/PAA–Au. (c) The UV–vis spectrum of GO (curve a in Fig 1) shows an absorption peak at 230 nm, which is consistent with the previous report [14]. After formation of graphene through the PAA reduction, the peak of graphene/PAA (curve b) is observed at 260 nm. The redshifts from 230 to 260 nm suggests that the electronic conjugation within graphene sheets has been restored after the reduction [29]. When AuNPs has been decorated onto the graphene sheet, two absorption peaks of graphene/PAA–Au composites are observed at 260 and 528 nm (curve c), which are corresponding to the absorption of graphene and AuNPs, respectively. The reduction of GO is also confirmed by the color change of solution before and after reaction (from brown to dark, as shown in the inset in Fig. 1).

The morphology of graphene/PAA and graphene/PAA–Au were examined by TEM. Fig. 2A shows the TEM image of PAA/graphene nanosheets, which illustrates the flake-like shapes of graphene. Fig. 2B depicts a typical TEM image of the graphene sheets covered with AuNPs homogeneously. AuNPs appear as dark dots on a lighter shaded substrate in this image. These nanoparticles cover the graphene sheets with similar interparticle distance of several nanometers and occupy the whole surface of graphene sheets. A size-distribution histogram was obtained from measuring 220 randomly selected particles (inset of Fig. 2B). The diameter of Au nanoparticles ranges from 2.1 to 7.7 nm and the average diameter is ca. 4.2 nm. Moreover, there are nearly no isolated Au nanoparticles can be observed separated from the graphene nanosheets, which indicated that the interaction between the Au particles and graphene is strong.

Graphene–AuNPs which were grafted covalently by PAA can be confirmed from FTIR measurements (Fig. 3). The presence of O—H ($\nu_{\text{O–H}}$ at 3210 cm^{-1}), aromatic C=C ($\nu_{\text{C=C}}$ at 1613 cm^{-1}), carboxy C—O ($\nu_{\text{C=O}}$ at 1422 cm^{-1}), alkoxy C—O ($\nu_{\text{C=O}}$ at 1089 cm^{-1}) can be found in GO (curve a in Fig. 3). After reduction, the disappearance of these characteristic peaks of oxide groups in graphene/PAA–Au indicates that GO has been reduced to graphene. In addition, the FTIR spectrum of graphene/PAA–Au exhibits PAA absorption features, such as N—H ($\nu_{\text{N–H}}$ at 3386 cm^{-1}) and C—N ($\nu_{\text{C–N}}$ at 1560 cm^{-1}). The result confirms that the PAA not only played its role as reductant to reduce GO and $HAuCl_4$, but also has been covalently grafted to the graphene sheet successfully.Fig. 4(A) shows the XPS spectra of graphene/PAA–Au nanocomposites. The peaks of Au4f can be clearly observed, which are expected from Au atom; the peak of N1s comes from PAA; and the peak of C1s is attributed to

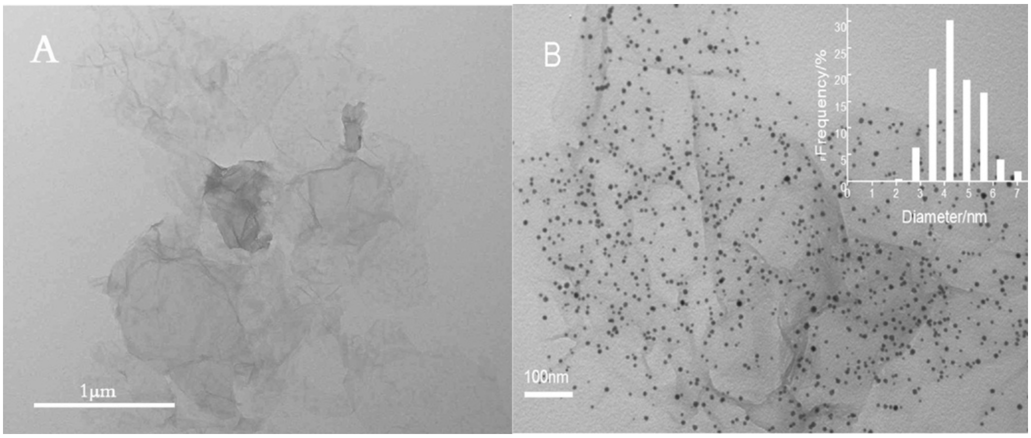

Fig. 2. TEM images of graphene (A) and graphene/PAA–Au (B) nanocomposite and the corresponding particle size analysis histogram of Au nanoparticles.

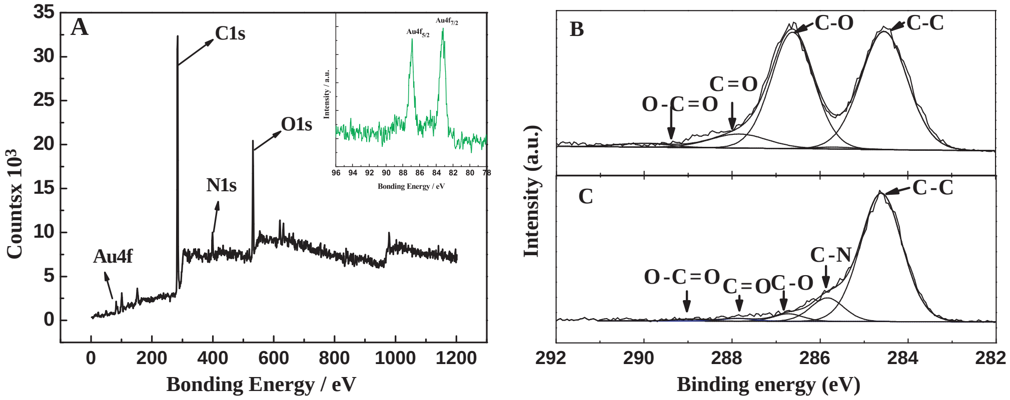

Fig. 4. XPS spectra of the graphene/PAA–Au nanocomposites (A); insets: the Au4f doublet; the C1s XPS spectra of the GO (B) and graphene/PAA–Au (C) composite films.

graphene sheets. As shown in the inset, the $Au4f_{7/2}$ peak appears at a binding energy of 83.4 eV and the $Au4f_{5/2}$ peak appeared at 87.0 eV (peak-to-peak distance is 3.6 eV), which confirms the formation of metallic gold [30]. While the experiment was conducted in the same way just without addition of PAA, AuNPs could not be observed. It indicated that PAA can act as a reductant for the formation of AuNPs.

The C1s XPS spectra of GO and graphene/PAA–Au nanocomposite films are shown in Fig. 4(B) and (C), respectively. Although the C1s feature of graphene–AuNPs showed the same oxygen functionalities as GO, the absorbance peaks of graphene at 286.2 eV (carbon in C—O), 287.7 eV (carbonyl carbon) and 289.0 eV (carboxylate carbon) were sharply decreased, which indicates a deoxygenation process. In addition, a new peak at 285.7 eV appeared and it is corresponding to the existence of C—N bonds. It also confirmed the presence of PAA in the graphene/PAA–Au composites.

Graphene/PAA–Au-GC exhibited obvious electrocatalytical activity toward reduction of H_2O_2. Fig. 5 shows the electrocatalytical reduction responses of H_2O_2 at graphene (A), AuNPs (B), and graphene/PAA–Au (C) modified electrode, respectively. An increased reduction current at GC/graphene/PAA–Au for H_2O_2 is observed. This demonstrated that graphene–AuNPs film had much better electrocatalytical activity towards reduction of H_2O_2 than pristine Au or graphene. In comparison to the reduction of H_2O_2 at AuNPs or graphene modified electrode, the peak current increases by ca. 4 times, which should be ascribed to the increase of active area of Au nanoparticles anchored onto the graphene sheets.

Similarly, graphene/PAA–Au also showed an excellent reduction activity towards O_2. As shown in Fig. 5(D), an obviously increased reduction signal of O_2 could be observed (solid line) in PBS solution. The above results clearly showed that graphene/PAA–Au nanocomposites is one of the electroactive materials towards reduction of

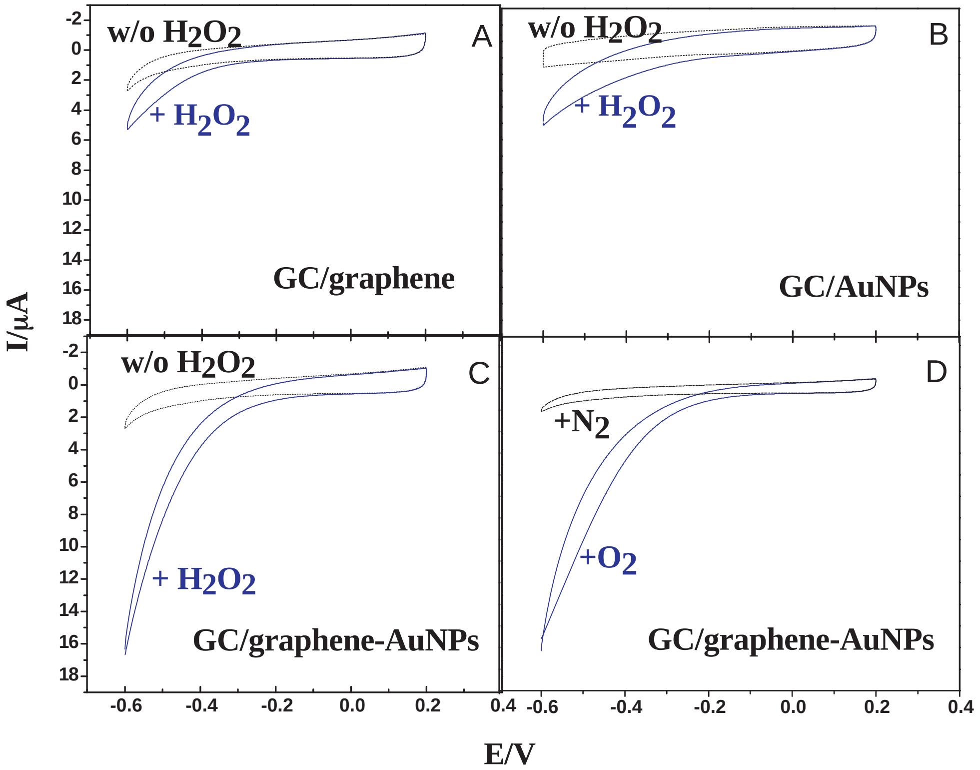

Fig. 5. Cyclic voltammograms at graphene-GC (A), AuNPs-GC (B), graphene/PAA–Au -GC (C) electrode in 0.05 M N_2-saturated PBS solution (pH 7.4) in the absence (dotted line) and presence of 0.05 M H_2O_2 (solid line) at scan rate of 0.1 V s^{-1}. Cyclic voltammograms at graphene/PAA–Au modified electrodes in 0.05 M PBS solution (pH 7.4) saturated with O_2 (solid line) and degassed with pure N_2 (dotted line) at a scan rate of 0.1 V s^{-1} (D).

H_2O_2 and O_2 and can be expected to served as candidate for further utilization of electrochemical sensing.

4. Conclusions

In summary, graphene/PAA–Au nanocomposites has been successfully prepared via a simple and “green” chemical reduction route. The amino groups in PAA can reduce GO and $HAuCl_4$ solutions simultaneously to the graphene/PAA–Au nanocomposites. Au nanoparticles distributed well on the graphene nanosheets and the resulting graphene/PAA–Au-GC electrode showed high electrocatalytical activity towards H_2O_2 and O_2. The electrocatalytic activity of graphene/PAA–Au may propose a possibility of constructing a practical biosensor in the future.

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