

## One-pot Green Synthesis of Palladium Doped Reduced Graphene Oxide Composite For Electrochemical Determination of Hydrogen Peroxide

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#### Abstract

In the present study, a modified electrosensor based on one-pot green synthesized palladium doped reduced graphene oxide composite (Pd@rGO) has been developed for the electrochemical determination of hydrogen peroxide. The electrochemical features of the electrosensor was appraised by cyclic voltammetry (CV) and differential puls voltammetry (DPV) techniques. The Pd@rGO modified glassy carbon electrode exhibited a superior electroactivity as against to unmodified glassy carbon electrode (GCE). It demonstrated a superior performance toward hydrogen peroxide in the concentration range of 10  $\mu$ M and 1.0 mM with a detection limit of 0.12  $\mu$ M. The selectivity of the sensor was investigated in the presence of various biological interferents like glucose, ascorbic acid, dopamine, paracetamol and uric acid. The results showed that the electrosensor had no considerable reponse to those of intererent substances.

Keywords: Reduced graphene oxide, Electrosensor, Hydrogen peroxide, Nanocomposite, Green synthesis.

# Hidrojen Peroksitin Elektrokimyasal Tayini İçin Paladyum Katkılı İndirgenmiş Grafen Oksit Kompozitinin Tek Basamaklı Yeşil Sentezi

### Öz

Bu çalışmada, hidrojen peroksitin elektrokimyasal tayini için bir basamakta yeşil yöntemle sentezlenmiş paladyum katkılı indirgenmiş grafen oksit kompozitine (Pd@rGO) dayalı modifiye bir elektrosensör geliştirilmiştir. Elektrosensörün elektrokimyasal özellikleri, döngüsel voltametri (CV) ve diferansiyel puls voltametri (DPV) teknikleriyle değerlendirilmiştir. Pd@rGO kompozit ile modifiye edilmiş camsı karbon elektrot, modifiye edilmemiş camsı karbon elektroduna (GCE) göre üstün bir elektroaktivite sergilemiştir. Elektrosensor 0.12 µM saptama limiti ile 10 µM ve 1.0 mM derişim aralığında hidrojen peroksite karşı iyi bir performans göstermiştir. Sensörün seçiciliği, glikoz, askorbik asit, dopamin, parasetamol ve ürik asit gibi girişim yapan çeşitli biyolojik moleküllerin varlığında araştırılmıştır. Sonuçlar, elektrosensörün girişim yapan maddelere karşı önemli bir cevap vermediği belirlenmiştir.

Anahtar Kelimeler: İndirgenmiş grafen oksit, Elektrosensör, Hidrojen peroksit, Nanokompozit, Yeşil sentez.

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## 1. Introduction

Graphene, due to its unrivaled atomic layered structure, unrivaled physical and electronic properties, has a very good electrical, electrochemical, optical, thermal and mechanical properties [Gan ve ark., 2019; Novoselov ve ark., 2004]. By virtue of its thermal and electrical conductivity, graphene finds application in various areas such as in strengthening nanocomposites, transparent conductive films, electronic circuits, chemical and biosensors, pharmaceutical and gene release agents, nanoelectronics and energy storage system [Geim ve ark., 2007; Geim, 2009]. Graphene oxide is layered and containing oxygenated species like epoxide, carboxyl, hydroxyl groups on their basal planes and edges, which is considered pioneer to largescale graphene synthesis [Chua ve ark., 2009]. These species not just extend the intermediate layer distance but also make the atomic-thick layers hydrophilic [Thakur ve ark., 2015; Ed ve ark., 2010]. And also these oxygen-containing functional groups can create a platform for attachment of nanoparticles, prevents nanoparticles from aggregating and enhance the stability [Hsu ve ark., 2014]. Furthermore, graphene-grafted with metallic nanoparticles have gained great importance because of their ability to exhibit synergistic effects that cause to enhance the electrocatalytic performance [Salazar ve ark., 2019]. Owing to comprising a great number of oxygen functional group on graphene oxide, it can be reduced by assorted processes like thermal annealing [Saleem ve ark., 2018], photochemical [dos Santos ve ark., 2018] and chemical [Gao ve ark, 2017]. Among these, the most applied approach is the chemical reduction method. The chemical route is based on use of hydroquinone, sodium borohydride and hydrazine as reductants [Das ve ark., 2018]. However, those chemical based reductants are extremely toxic and have noxious influence on environment and human wellness. Therefore, it is essential to evolve new eco-friendly routes for the productive reduction of graphene oxide into reduced graphene oxide [Gan ve ark., 2019]. In recent years, there have been а considerable interest to plants for nanomaterials/nanocomposites synthesis, which is eco-friendly, cost-effective and easy carry out [De Silva ve ark., 2017].

Hitherto, a large number of studies have been reported the eco-friendly one-pot synthesis of reduced graphene oxide grafted with metallic nanoparticles via plant extracts. Phyllanthus acidus, Salvadora persica L., Berberis vulgaris, Pulicaria glutinosa and Psidium guajava are to name of a few [Nayak ve ark., 2020; Al-Marri ve ark., 2016; Nasrollahzadeh ve ark., 2016; Khan ve ark., 2017; Chettri ve ark., 2017]. In our recent work, we have introduced one-step route for the synthesis of reduced GO/Pd nanocomposite using Onosma malatyana Binzet (OMB) root extract and tested on hydrogen evolution reaction [Kayan ve ark., 2021].

The genus Onosma L. is the most broad group in the Boraginaceae family and includes about 150 species that are spreaded out in Asia and Europe. It is depicted by 109 taxa (103 species) in Turkey with 50 % endemism rate among native species. Onosma malatyana Binzet is an endemic species that spreads in the Eastern Anatolia provinces of Malatya and Tunceli [Binzet *et al.*, 2016].

Hydrogen peroxide  $(H_2O_2)$  is greatly enforced in various industry as an essential mediator in food, biology, environment, pharmaceutical and clinical, but the most application area is as a bleaching item in the textile, pulp, and paper industries [Golsheikh ve ark., 2020]. In addition, the surveys in health area,  $H_2O_2$  suggested to be related to alzheimer's disease, myocardial infarction, atherosclerosis, Parkinson's disease and cancers [Guo ve ark., 2020]. Therefore, the determination of hydrogen peroxide is crucial for human and environmental health. Several analytical methods have been evolved for the determination of H<sub>2</sub>O<sub>2</sub> such as spectrophotometry [Apyari ve ark., 2019], colorimetry, fluorescence [Liu ve ark., 2020] and electroanalytical methods [Turunc ve ark., 2021]. Among these methods, electrochemical methods have been extensively utilized for determination of hydrogen peroxide owing to their cost-effectiveness, simplicity, sensitivity and selectivity.

In this study, palladium decorated reduced graphene oxide composite modified electrosensor has been developed and used in the determination of hydrogen peroxide.

## 2. Material and Method

### 2.1. Reagents

Deionezed water was used in all experiment. Hydrogen peroxide, sulphuric acid, phosphoric acid, potassium permanganat were purchased from Merck company. Graphite powder, potasyumtetrachloro palladate(II), sodium phosphate monobasic, sodium phosphate dibasic, dopamine hydrochloride, uric acid, ascorbic acid, paracetamol and glucose were supplied from Sigma-Aldrich. O. malatyana plant was provided from Mersin University Biology Herbarium.

### 2.1.1. Preparation of the extract

For the green synthesis of nanocomposite the roots of the O. malatyana were used. The root extract was obtained according to the procedure performed previously [Kayan ve ark., 2021]. Briefly, the roots were left to desiccate in shadow for about 10 days at room temperature. The desiccated roots were milled by crusher to get slender powder. The slender powder (5 g) was placed into 250 mL round bottom flask and boiled for 30 min in 100 mL of ultra pure water. After 30 min of exposure to boiling temperature, the solution was allowed to cool to room temperature, filtered and the supernatant was held in refrigerant at +4 °C until used.

# 2.1.2. Synthesis of palladium decorated reduced graphene oxide (Pd@rGO)

Firstly, graphene oxide was synthesied by oxidation of graphite via modified Hummer's process [Tajiki ve ark., 2020]. Green synthesis of Pd@rGO nanocomposite was synthesized successfully according to the previous study and the structural characterization were given in Supplemantary files. Briefly, GO (25 mg) was poured into water (25 mL) and sonicated for 30 min. to acquire dispersed GO (1 mg/mL). 25 mL of K<sub>2</sub>PdCl<sub>4</sub> (1 mM) solutions was attached to GO suspension (1 mg/mL) and sonicated for another 30 min. Afterward, O. malatyana root extract were added into above concoction and refluxed at 80 °C for 10 h. The obtained mixture was left to cool to room temperature and separated. For comparison, rGO and pure PdNPs were synthesized by the same method as mentioned above.

### 2.1.2. Characterization

Structural morpholgy of the PdNPs, rGO and Pd@rGO nanocomposite were performed by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray spectrometer (EDX) (Zeiss) and Transmission Electron Microscopy (TEM) (JEOL JEM 1011 Megaview III Camera iTEM Software) techniques. Further analysis were carried out by UV-Vis spectrometer (Shimadzu 1800 spectrophotometer), X-ray

powder diffraction (XRD) (Rikagu diffractometer with CuKa,  $\lambda = 1.5406$  Å) and Dynamic light scattering (DLS) on account of determining the formation, crystallinity, the stability of the nanomaterials, respectively. Electrochemical investigations were performed CHI 660E electrochemical workstation at ambient temperatures. A conventional three-electrode system was used for electrochemical studies, where the Pt wire and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. A glassy carbon with diameter of ca. 3 mm was used as working electrode.

For the electrochemical determination of hydrogen peroxide, glassy carbon electrode (GCE) was modified with biosynthisized Pd@rGO composite. Prior to modification, the glassy carbon electrode (GCE) was polished utilizing 0.30 and 0.05  $\mu$ m alumina powder, and sonicated in 1:1 (v:v) nitric acid, acetone and deionized water for 5 min to get smooth surface, respectively. The polished GCE was modified by drop-casting of Pd@rGO nanocomposite suspension (5 mg/mL). A certain amount of Pd@rGO (8  $\mu$ L) suspension was casted on the shiny surface, covered with beaker and left to dry at ambient temperature. Finally, 5  $\mu$ L of Nafion® (5 % in alcohol) was encased by casting upon modified electrode surface. In order to the syllogism studies, rGO and PdNPs modified electrodes were prepared by subsequent the same procedure mentioned above.

### 3. Results and Discussion

#### 3.1. Electrochemical characterization

Cyclic voltammetry studies were performed utilizing 1.0 mM  $[Fe(CN)_6]^{4/3-}$  redox couple in 0.1 M KCl solution at scan rate of 100 mV/s. All of the electrodes showed a well-defined redox wave which corresponding to  $Fe^{2+} \leftrightarrow Fe^{3+}$  process. The anodic peak current acquired for bare GCE, rGO-GCE, PdNPs-GCE and Pd@rGO-GCE were 17.5, 22.5, 26.3 and 45.2  $\mu$ A respectively (Fig. 3.1). From, Pd@rGO-GCE showed highest current response and lower peak-to-peak separation, it evidenced that Pd@rGO composite modified electrode facilitate the electron transfer and displayed excellent electron transfer ability as per the other modified electrode. The superior electrocatalytic activity can be assigned to the synergistic effect of PdNPs along with rGO that enhances the rate of electron transfer at the electrode electrolyte boundary.



**Fig. 3.1.** Cyclic voltammograms of bare GCE, rGO-GCE, PdNPs-GCE and Pd@rGO-GCE in 0.1 M KCl comprasing 1.0 mM  $[Fe(CN)_6]^{4/3-}$  redox couple.

# **3.2.** Electrochemical performance of Pd@rGO-GCE toward hydrogen peroxide

For purpose of examining the electrochemical performance of the modified electrode toward  $H_2O_2$ , cyclic voltammograms were carried out to appraise the electrocatalytic efficiency of *e-ISSN: 2148-2683*  Pd@rGO-GCE. The electrocatalytic performance of the bare, rGO, PdNPs and Pd@rGO nanocomposite modified GCE in PBS (pH = 7.0) medium containing 1.0 mM H<sub>2</sub>O<sub>2</sub> in potential range between 0.0 to -0.8 V vs Ag/AgCl were given in Fig. 3.2a. As seen in Fig. 3.2a, no significant reduction response was obtained for bare GCE in presence of hydrogen peroxide. Meanwhile, rGO, PdNPs and Pd@rGO nanocomposite modified GCE exhibited well electrocatalytic reduction response for H<sub>2</sub>O<sub>2</sub> at same conditions. Moreover, Pd@rGO modified electrode exhibited excellent current response which was about 2 times higher than that of other modified electrodes.

The influence of scan rate on the electrocatalytic reduction of  $H_2O_2$  on Pd@rGO-GCE was also examined in 0.1 PBS (pH = 7.0) media comprising 1.0 mM H<sub>2</sub>O<sub>2</sub> at different scan rates varying from 50 to 500 mV/s (Fig. 3.2b). As can be seen in Fig. 3.2b, the current response of reduction of hydrogen peroxide rises with increment scan rate. In addition, the increased scan rate caused the reduction potential to shift to a more negative direction. Fig. 3.2c demonstrates the addiction of reduction peak current with square root of scan rate with a correlation coefficient of 0.995. The outcome points out that the reduction of hydrogen peroxide is a characteristic diffusion-controlled electrochemical process. The relation of logarithmic peak current (log i) versus logarithmic scan rate (log v) can also give information about electrochemical process. As seen in Fig. 3.2d, the relationship between the log i and log v gives a straight line with linear equation log  $i = 0.429\log i$ v + 1.04 and correlation coefficient of 0.994. The slope value of 0.429, which is close to 0.5 [Turunc ve ark., 2020], indicates that the diffusion process control the electrochemical reduction of hydrogen peroxide. This result confirms that the electrochemical reduction of hydrogen peroxide is controlled by the diffusion phenomenon.





**Fig. 3.2.** CV diagrams of GCE, rGO-GCE, Pd-GCE and Pd@rGO-GCE in 0.1 M PBS (pH 7.0) comprising 1.0 mM  $H_2O_2$  with a scan rate of 50 mV/s (a), CV diagrams of Pd@rGO-GCE in 0.1 M PBS (pH = 7.0) comprasing 1.0 mM  $H_2O_2$  at different scan rate (b), the relation of cathodic peak current and square root of scan rate (c) and the variation of logarithmic peak current via logarithmic scan rate (d).

Further investigation was carried using amperometric technique. The amperometric *i* - t studies was performed at constant potential (-0.40  $V_{Ag/AgCl}$ ) in a continuously mixed solution of 0.1 M PBS. The amperometric response of Pd@rGO-GCE to sequential addition of H<sub>2</sub>O<sub>2</sub> was recorded for a period of time (Fig. 3.3). The reduction current was prominent raised with sequential addition of H<sub>2</sub>O<sub>2</sub> and the current response of the modified electrode was observed within ca 3s, representing that Pd@rGO-GCE displays fast response for electrochemical reduction of H<sub>2</sub>O<sub>2</sub>.



**Fig. 3.3.** Amperometric *i* - t response of Pd@rGO-GCE for the sequential addition of  $H_2O_2$  into well-mixed 0.1 M PBS at -0.40 V.

# **3.3.** Electrochemical determination of hydrogen peroxide

Further analysis was realized by using differential pulse voltammetry (DPV) technique to determine the performance of the Pd@rGO-GCE as a sensor (Fig. 3.4). Fig. 3.4 depicts the differential puls voltammograms and the linear plot of  $H_2O_2$  solutions with concentrations ranging from 10  $\mu$ M to 1.0 mM in 0.1 M PBS (pH = 7.0) utilizing Pd@rGO-GCE. It can be seen from the DPV that there is a commensurate increase in current

response with raising H2O2 concentration, with linear equation of  $I(\mu A) = 42.87[H_2O_2](mM) + 15.18$  (R<sup>2</sup>=0.995). The limit of detection (LOD) and the sensitivity were calculated to be 0.12  $\mu$ M and 42.87  $\mu$ A/mM, respectively. It can be inferred that the Pd@rGO-GCE exhibited a good electroactivity with low LOD. For the purpose of appraise the performance of the developed electrode, the Pd@rGO-GCE sensor was checked against previously reported H<sub>2</sub>O<sub>2</sub> sensors and listed in Table 1.



**Fig. 3.4.** Differential puls voltammetric responses of Pd@rGO-GCE against to different concentrations of  $H_2O_2$  in 0.1 M PBS (pH = 7.0). Inset diagram is the magnification of voltammograms of the lower concentration region, and (b) the linear plot of the DPV current response versus  $H_2O_2$  concentration.

# **3.4.** Interference, reproducibility and stability studies

Alongside the LOD and sensitivity, interference property and reproducibility are also significant parameters for electrochemical sensors. Fig. 3.5a demonstrates the amperometric current response of the Pd@rGO-GCE toward  $H_2O_2$  in presence of interfering species such as ascorbic acid, glucose, paracetamol, dopamine and uric acid. As represented in Fig. 5a, no current response was pursued with addition of interfering species, shows that the Pd@rGO sensor exhibits good selectivity against  $H_2O_2$  at -0.40 V.

The reproducibility of the Pd@rGO modified electrode was examined by four electrodes for 1.0 mM  $H_2O_2$ , with relative standart deviation of 2.60 % (Fig. 3.5b).





Fig. 3.5. Amperometric response of Pd@rGO-GCE to consecutive addition of  $H_2O_2$  and interfering species (a) and CV diagram of four indepent Pd@rGO-GCE in 0.1 M PBS (pH = 7.0) comprising 1.0 mM  $H_2O_2$ . Scan rate is 50 mV.s<sup>-1</sup>.

Electrode	<b>Concentration range</b>	LOD (µM)	Sensitivity	Reference
CuS/GR	5 μM - 1.5 mM	0.27	-	[Bai ve ark., 2013]
GO-Cu <sup>2+</sup> composite	5 μΜ - 85 μΜ	0.50	72 μA.mM <sup>-1</sup>	[Muralikrishna ve ark., 2016
AuNPS/ZnO/Gr	6 μM - 1.13 mM	0.80	-	[Xie ve ark., 2013]
3D RGO-MoS <sub>2</sub> QDs	10 μM - 5.57 mM	1.9	-	[Lin ve ark., 2018]
rGO/FeNPs	0.1 μM - 2.15 mM	0.056	98 μA.mM <sup>-1</sup>	[Amanullan ve ark., 2017]
Au/rGO	20 μM - 10 mM	0.10	$1238 \ \mu A.mM^{-1}.cm^{-2}$	[Dhara ve ark., 2016]
Cat-Fe <sub>3</sub> O <sub>4</sub> /rGO	3.3 μM - 55.6 mM	0.11	1840 µA.mM <sup>-1</sup> .cm <sup>-2</sup>	[Kıranşan ve ark., 2018]
RGO-PtNPs	0.05 μM - 0.75 mM	0.016	2550 μA.mM <sup>-1</sup> .cm <sup>-2</sup>	[Palansimay ve ark., 2015]
RGO@CeO2/Ag	0.5 μM - 12 mM	0.21	-	[Yao ve ark., 2016]
Ag/Co <sub>3</sub> O <sub>4</sub> /RGO	0.5 μM - 7.5 mM	0.30	146.5 µA.mM <sup>-1</sup> .cm <sup>-2</sup>	[Wu ve ark., 2016]
Pd@rGO	10 μM - 1 mM	0.12	42.87 μA.mM <sup>-1</sup>	This study

Table 1. The electroanalytical performance of the various  $H_2O_2$  sensors

## 4. Conclusions

In the present study, green synthesized Pd@rGO, which was previously utilized on hydrogen evaluation reaction, based electrosensor was prepared and investigated its usability in the electrochemical determination of hydrogen peroxide. For comparison, PdNPs and rGO based electrosensor were also constructed and tested on electrorduction of H2O2 using CV in PBS media. The results showed that Pd@rGO-GCE exhibited superior electrocatalytic performance due to synergitic effect of the composite modified electrode. The DPV studies were performed in wide range of concentration between 10 µM and 1 mM and the LOD was found to be 0.12 µM. Amperometric investigations showed that the interfering substances had no considerable effect on electrochemical determination of H2O2 at -0.40 V. This indicates that Pd@rGO-GCE is highly sensitive to H<sub>2</sub>O<sub>2</sub>. Based on performance characteristics such as fast response, wide linear concentration range, low LOD and high sensitivity, it can be recommended that the Pd@rGO can be used as an  $H_2O_2$ sensor.

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# **Supplemantary Information**

# One-pot Green Synthesis of Palladium Doped Reduced Graphene Oxide Composite For Electrochemical Determination of Hydrogen Peroxide

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The structural features of rGO, PdNPs and Pd@rGO nanocomposite were realized utilizing SEM and TEM analyses. EDX analysis was performed to identify the chemical composition of the Pd@rGO nanocomposite. The SEM images elicited that rGO had a layered structure (Figure 1.1a). As depicted in Figure 1.1b, PdNPs were in worm-like form. SEM image of Pd@rGO nanocomposite showed that the spherical Pd nanoparticles were homogeneously distributed on the surface of rGO layers (Figure 1.1c and d). The structual property of Pd@rGO nanocomposite was also ratified by TEM analysis (Figure 1.1e and f). As can be seen in Figure 1.1e and f, spherical palladium is homogeneous dispensed on the surface of GO stratum. EDX analysis was also performed to specify the composition of the nanocomposite (Figure 1.1g). EDX spectra showed that Pd@rGO nanocomposite comprise of Pd elements confirming the presence of PdNPs on the rGO sheets.





**Fig. 1.1.** SEM images of (a) rGO, (b) PdNPs, (c) and (d) Pd@rGO and its magnification view, (e) and (f) TEM image of Pd@rGO nanocomposite and its magnification view and (g) EDX spectra of Pd@rGO nanocomposite.

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The zeta potential of rGO, Pd-rGO nanocomposite in aqueous solution is measured in a Dynamic Light Scattering (DLS) instrument to observe the amount of stability (Fig. 1.2). The rGO shows an average zeta potential value of -16.6 mV explaining the existence of a sufficient amount of negative charge density arising from the carboxylic groups present in the rGO. Compared to rGO the synthesized Pd@rGO nanocomposite exhibits a zeta potential

of -25.3 mV. The presence of PdNPs in GO contributed to the increase of repulsion forces and to the facilitation of the stability of the nanocomposite.



Fig. 1.2. Zeta potential of rGO and Pd@rGO aqueous dispersion.

To identify the crystalline structure and monitor the chemical alteration of the graphite during bio-reduction proces, XRD analyses were carried out.

The purity and crystallinity nature of the synthesized rGO and Pd@rGO nanocomposite were characterized by X-ray diffraction analysis. As seen in Fig. 1.3a, a sharp peak at 11.25° correspond to (001) planes represents the successful oxidation of graphite to GO. After bio-reduction process, the diffraction peak of GO shifted to around  $2\theta$  of 24.0° which correspond to (002) planes of rGO (Fig. 1.3b). In case of Pd@rGO, owing to the inclusion of PdNPs in rGO, the broad diffraction peak of rGO was faded away and three diffraction peaks were observed. The diffraction peaks settled at 39.98°, 46.47° and 67.88° which can be indexed the PdNPs (ICDD: 00-005-0681) planes distrubuted on rGO as (111), (200) and (220), respectively. In the light of XRD patterns, it was concluded that Pd@rGO nanocomposite was successfully synthesized through one-step.





Fig. 1.3. XRD spectra of GO,rGO and Pd@rGO nanocomposite.

To approve the bio-genesis of the rGO and Pd@rGO nanocomposite, UV-Vis analyses was also performed (Fig. 1.4) The UV-Vis spectra of GO showed two absorption wavelenghts at around of 230 and 305 nm which were chiefly owing to  $\pi \to \pi^*$  of C = C and n  $\to \pi^*$  of C = O, respectively. In UV-Vis spectra of rGO, the maximum peak at 230 nm was shifted 260 nm and the broad absorption peak at around 305 nm was vanished due to reduction C = O functional group of GO. In case of Pd@rGO nanocomposite, the attendance of Pd nanoparticles to rGO was caused to red shifting in absorption peak to 280 nm.



Fig. 1.4. UV-Vis absorption spectra of GO, rGO and Pd@rGO nanocomposite.

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