Supporting information for

Study of iron oxide nanoparticle phases in graphene aerogels for oxygen reduction reaction

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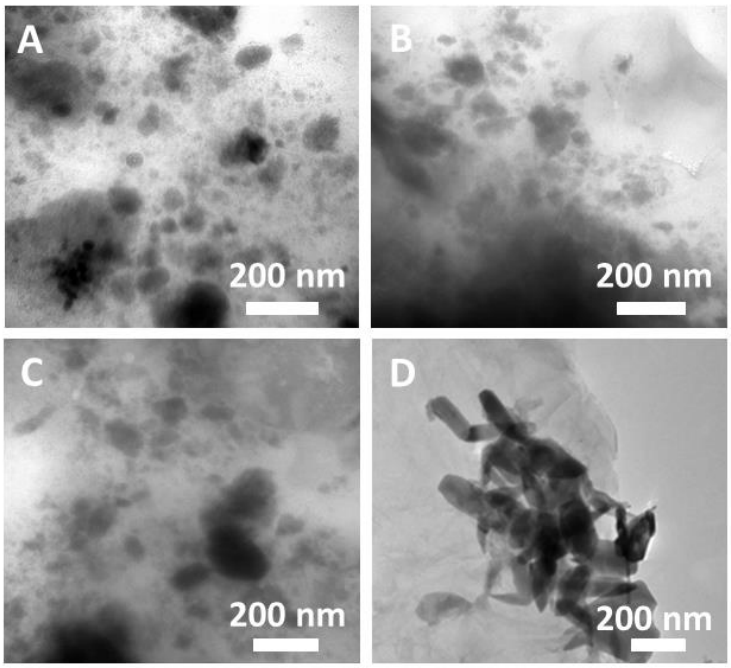


Fig. S1 TEM images of (A) rGO/Fe_3O_4, (B) rGO/γ-Fe_2O_3, (C) rGO/α-Fe_2O_3 and (D) rGO/α-FeOOH aerogel.

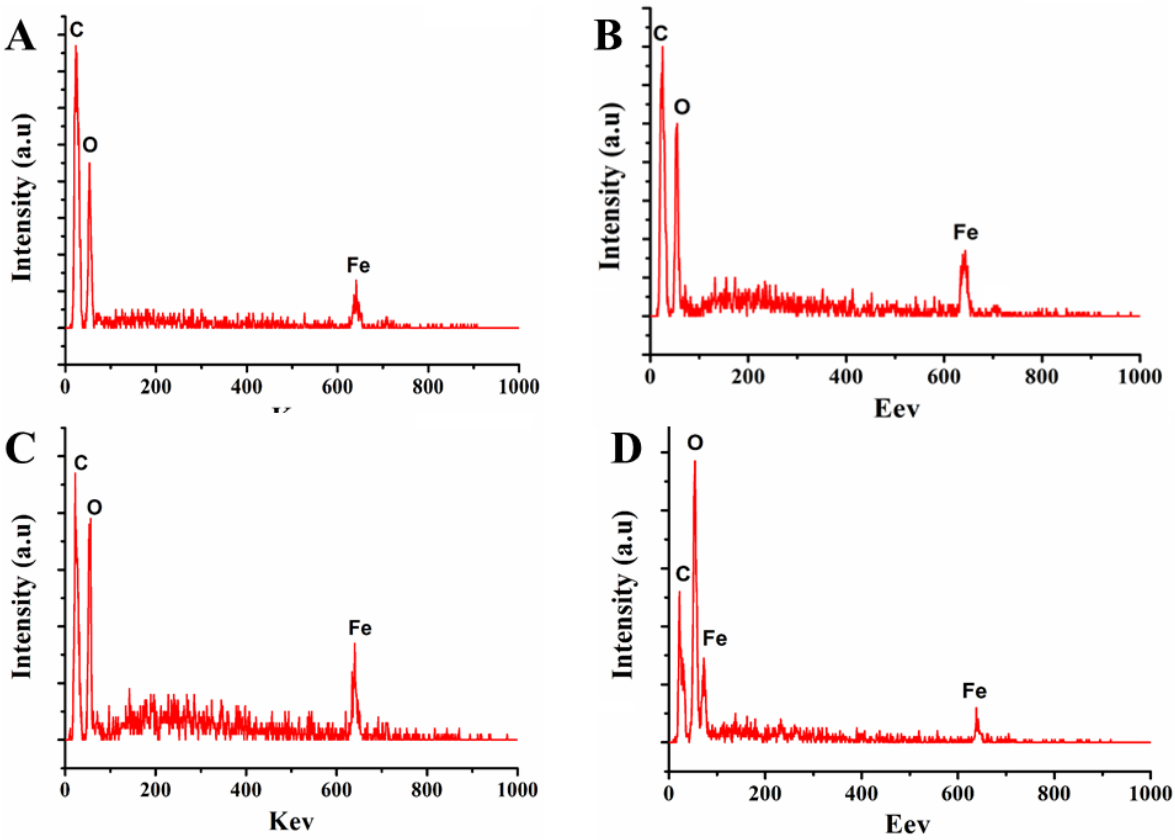


Fig. S2 EDX analysis of (A) rGO/Fe_3O_4, (B) rGO/γ-Fe_2O_3, (C) rGO/α-Fe_2O_3 and (D) rGO/α-FeOOH aerogel

Table S1 Atomic % of C, O and Fe present in (A) rGO/Fe_3O_4, (B) rGO/γ-Fe_2O_3, (C) rGO/α-Fe_2O_3 and (D) rGO/α-FeOOH aerogel determined by EDX analysis.

Catalyst	Atomic %		
	C	O	Fe
rGO/Fe_3O_4	18.87	56.36	24.77
rGO/γ-Fe_2O_3	17.60	52.96	29.44
rGO/α-Fe_2O_3	42.60	33.18	24.22
rGO/α-FeOOH	26.73	46.89	26.36

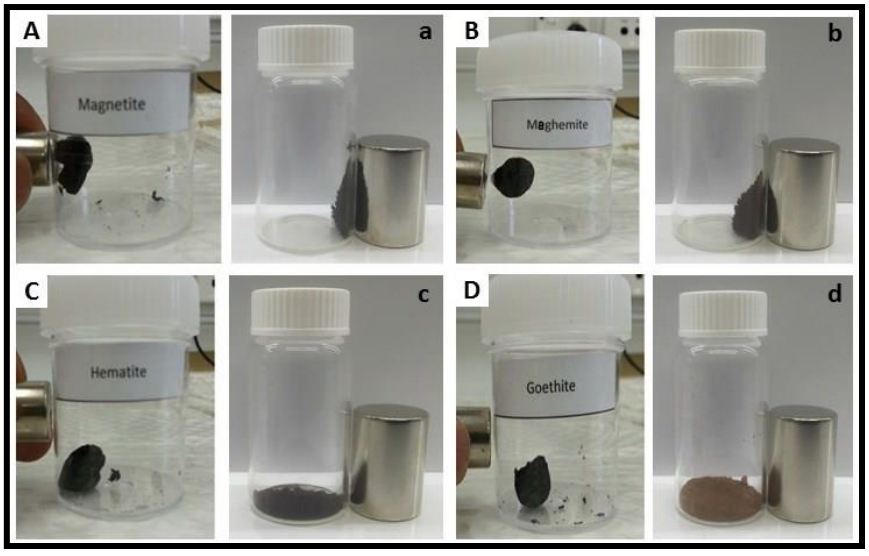


Fig. S3 Photographic image of (A) rGO/Fe_3O_4 and (a) Fe_3O_4 nanoparticle, (B) rGO/γ-Fe_2O_3 and (b) γ-Fe_2O_3 nanoparticle, (C) rGO/ α-Fe_2O_3 and (c) α-Fe_2O_3 nanoparticles and (D) rGO/ α-FeOOH and (d) α-FeOOH nanoparticle exposed to an external magnet.

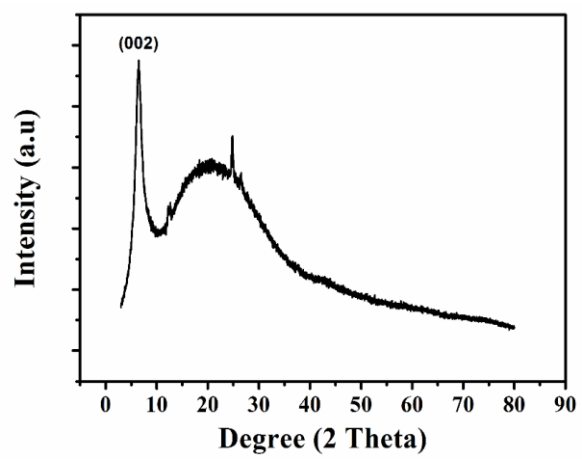


Fig. S4 XRD pattern of GO.

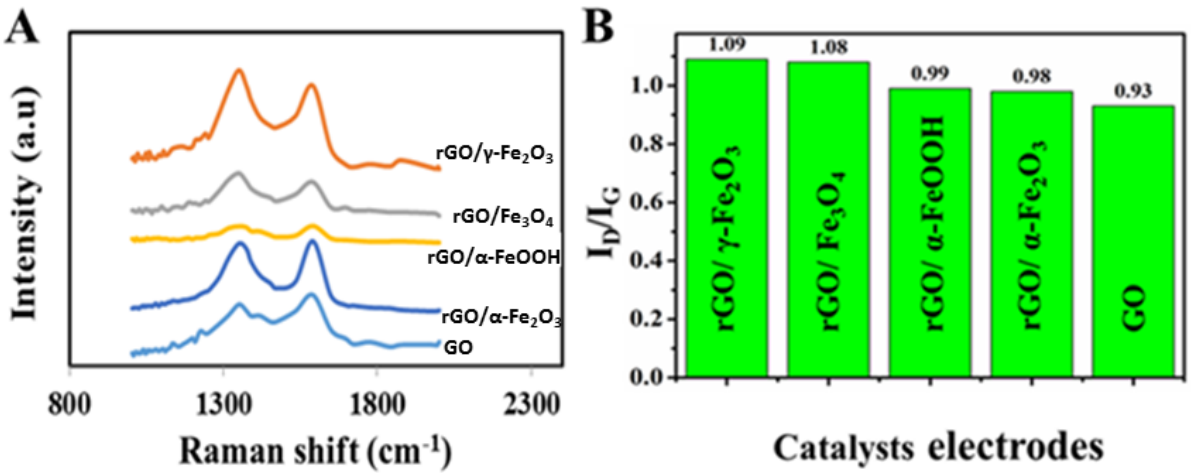


Fig. S5 (A) Raman spectrum and B) I_D/I_G ratio of all synthesized aerogels and GO

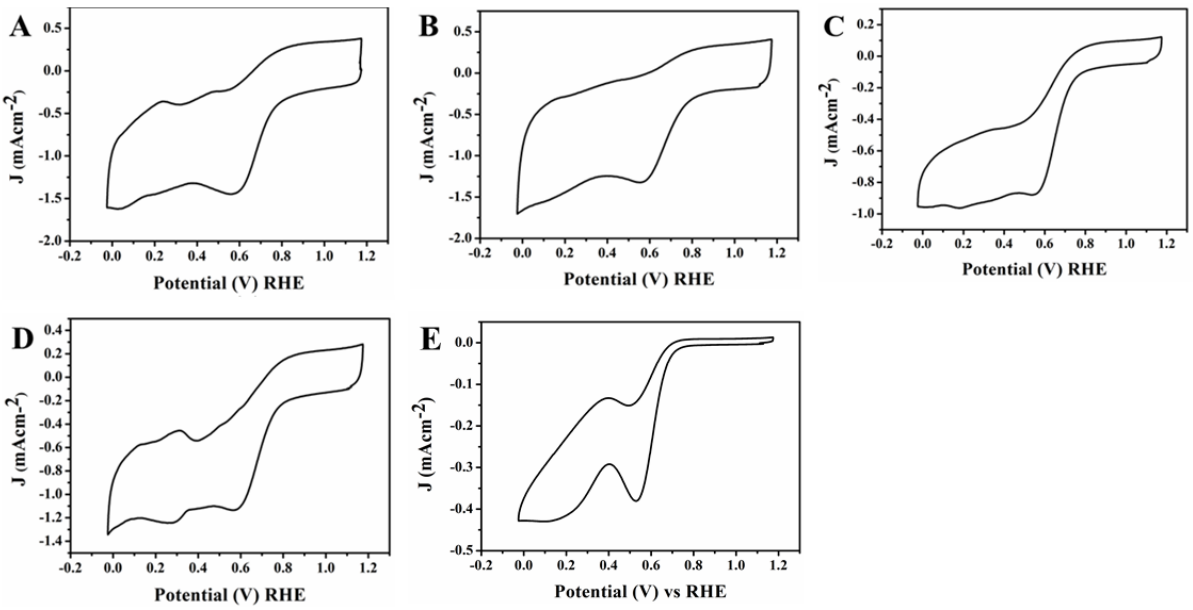


Fig. S6 CV curves of (A) rGO/Fe_3O_4 (B) rGO/γ-Fe_2O_3 (C) rGO/α-FeOOH, (D) rGO/α-FeOOH and (E) rGO at a scan rate of 100 mVS^{-1} in oxygen saturated 0.1 M KOH solution.

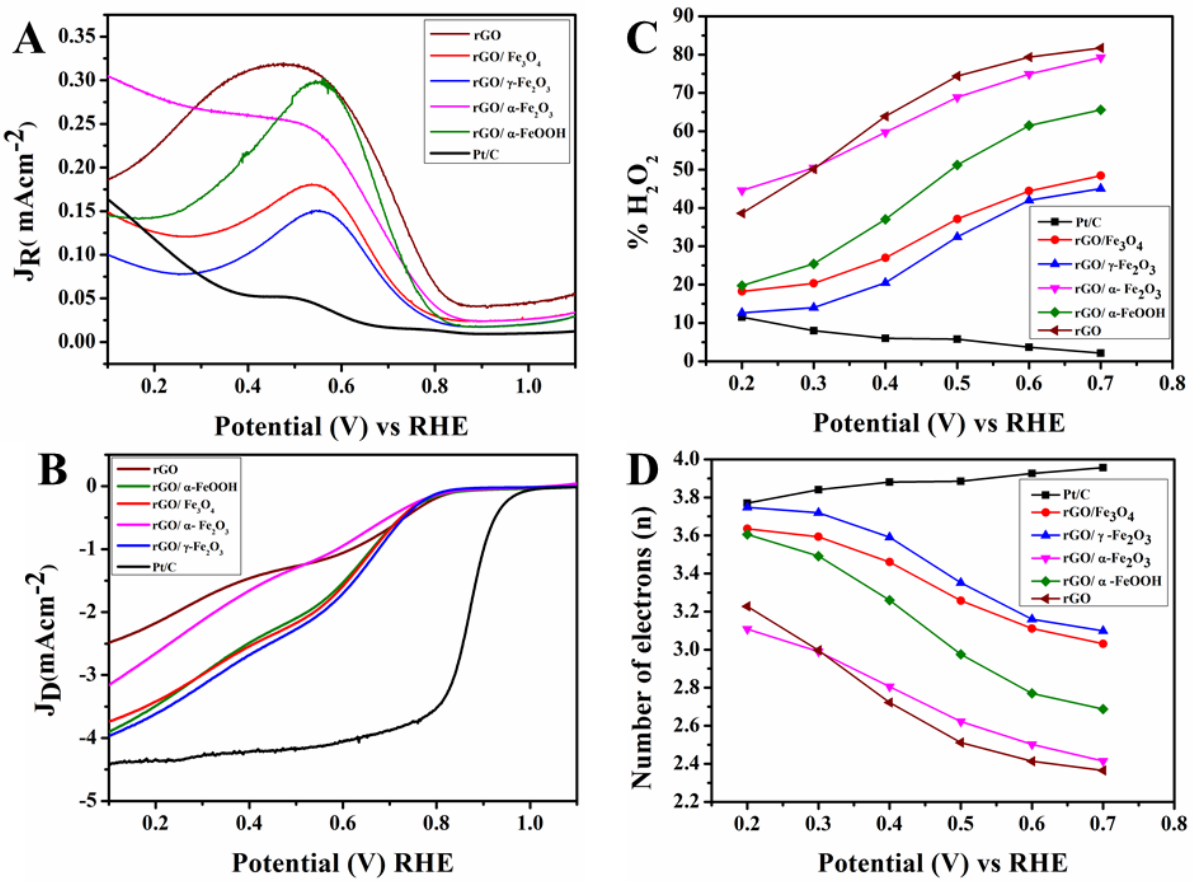


Fig. S7 RRDE voltammograms of (A) ring current, (B) disc current of rGO/Fe_3O_4, rGO/γ-Fe_2O_3, rGO/α-Fe_2O_3, rGO/α-FeOOH, rGO and Pt/C electrodes in oxygen saturated 0.1M KOH at 1600 rpm at a scan rate of 10 mV/s. (C) Percentage peroxide and (D) number of electrons of rGO/Fe_3O_4, rGO/γ-Fe_2O_3, rGO/α-Fe_2O_3,rGO/α-FeOOH, rGO and Pt/C electrodes at various potential calculated according to RRDE data.

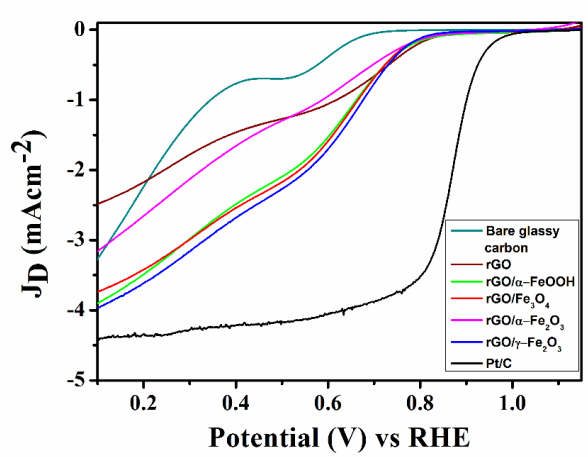


Fig. S8 Comparison of the LSV of the catalysts with the glassy carbon electrode in oxygen saturated 0.1M KOH at 1600 rpm at a scan rate of 10 mV/s.

S1 Conductivity measurements

The electrical conductivity of the rGo/iron oxide catalysts were conducted using the following equation S1[1].

$$\sigma = \frac{l}{RA} \qquad \text{(S1)}$$

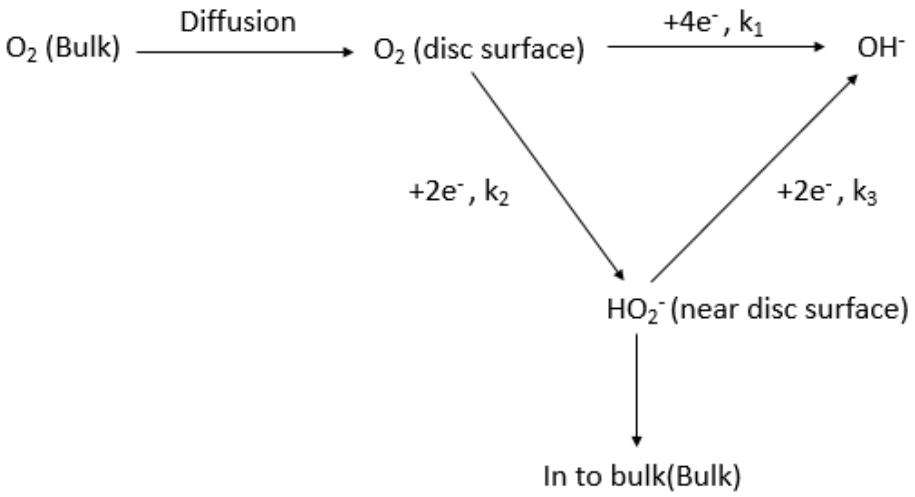
Where σ, *l*, *R* and *A* are the conductivity (S/m), length (m), electrical resistance (Ω) and cross sectional area (m^2) respectively. Samples for the measurement of conductivity was prepared by pressing (50 PSI) them in to a 10 mm diameter cylinder of 1mm thickness. To measure the conductivity, the as-prepared catalysts samples were placed in between two gold plated glass electrodes and connected to a two-probe digital multi meter (Fluke -87V) to measure the resistance. The conductivity was measured by using the resistance, length and area in to equation S1.

Table S2. Conductivity measurements of GN/Fe_3O_4, GN/γ-Fe_2O_3, GN/α-Fe_2O_3 and GN/α-FeOOH catalysts.

Graphene/iron oxide aerogel	Conductivity (S/m)
GN/ Fe_3O_4	3.54×10^{-4}
GN/ γ-Fe_2O_3	2.75×10^{-4}
GN/ α-Fe_2O_3	2.58×10^{-5}
GN/ α-FeOOH	2.97×10^{-4}

S2 Electron transfer kinetics

The reaction pathway sugested by Damjanovic *et al* [2] for oxygen reduction is shown in Scheme S1.



Scheme S1. Schematic representation of electrochemical reduction of oxygen in basic medium [2, 3].

Here, K_1 represents the direct reduction of oxygen to OH- ion without the formation of any intermidiate, which is desorbed and detected by the ring of the rortating ring disc electrode and K_2 is the overall formation of the adsorbed peroxide and K_3 is the rate constant for the

reduction of peroxides. It can be assumed that the HO_2^- ion maintains an adsorbtion desorption equillibrium depending on the applied potential [4].

Hsueh *et al*.[3] used a series of equations to calculate the rate constants K_1, K_2 *and* K_3 using the values of the intersept and the slope of plots of I_d / I_r vs $\omega^{-1/2}$ and $I_{dL} / (I_{dL}-I_d)$ vs $\omega^{-1/2}$, where Id, Ir, IdL and ω are the disc current, ring current, limiting disc current and the rotation speed respectively. The limiting disc current for these calculated was derived as the current at 0.0 V potential at 2400 rpm.The following equations (S2, S3 and S4) were used to calcutate the rate constants [3, 5].

$$K_1 = S_1 Z_1 \frac{I_1 N - 1}{I_1 N + 1} \qquad \text{(S2)}$$

$$K_2 = \frac{2 S_2 Z_1}{I_1 N + 1} \qquad \text{(S3)}$$

$$K_3 = \frac{N S_1 Z_2}{I_1 N + 1} \qquad \text{(S4)}$$

Where S_1 and I_1 are the slope and intercept correspond to the I_d / I_r vs $\omega^{-1/2}$ plots and S_2 is the slope of $I_{dL} / I_{dL} - I_d$ vs $\omega^{-1/2}$ plot. $Z_1 = 0.62 D_{O2}^{2/3} V^{-1/6}$, $Z_2 = 0.62 D_{H2O2}^{2/3} V^{-1/6}$, D_{H2O2} is 6.8 x 10^{-6} cm^2 s^{-1} and N is the collection efficiency [5].

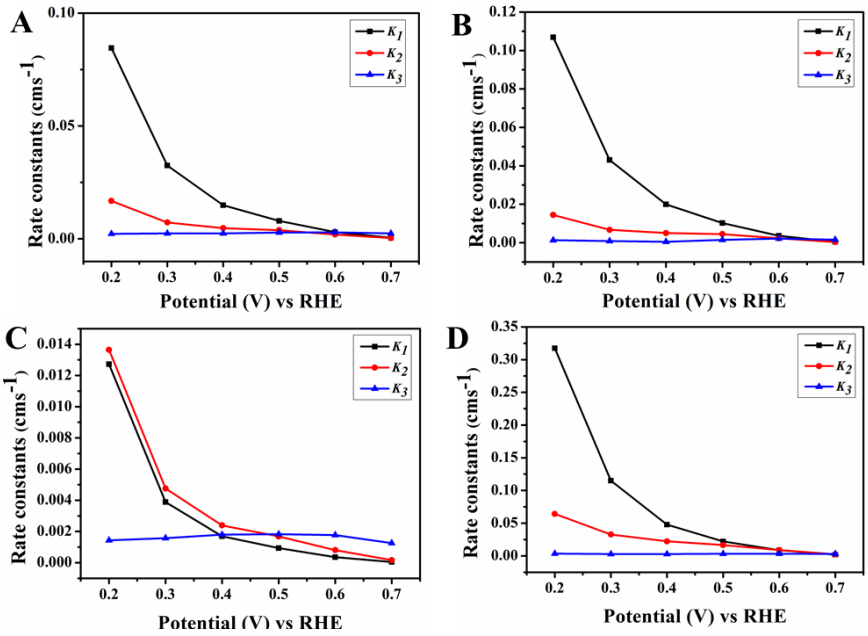


Fig. S9 Comparison of individual rate constants (K_1K_2, K_3) of (A) rGO/Fe_3O_4 (B) rGO/γ-Fe_2O_3 (C) rGO/α-Fe_2O_3 and (D) rGO/α-FeOOH.

References

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