Supporting information

Importance of Doping Sequence in Multiple Heteroatom-Doped Reduced Graphene Oxide as Efficient Oxygen Reduction Reaction Electrocatalysts

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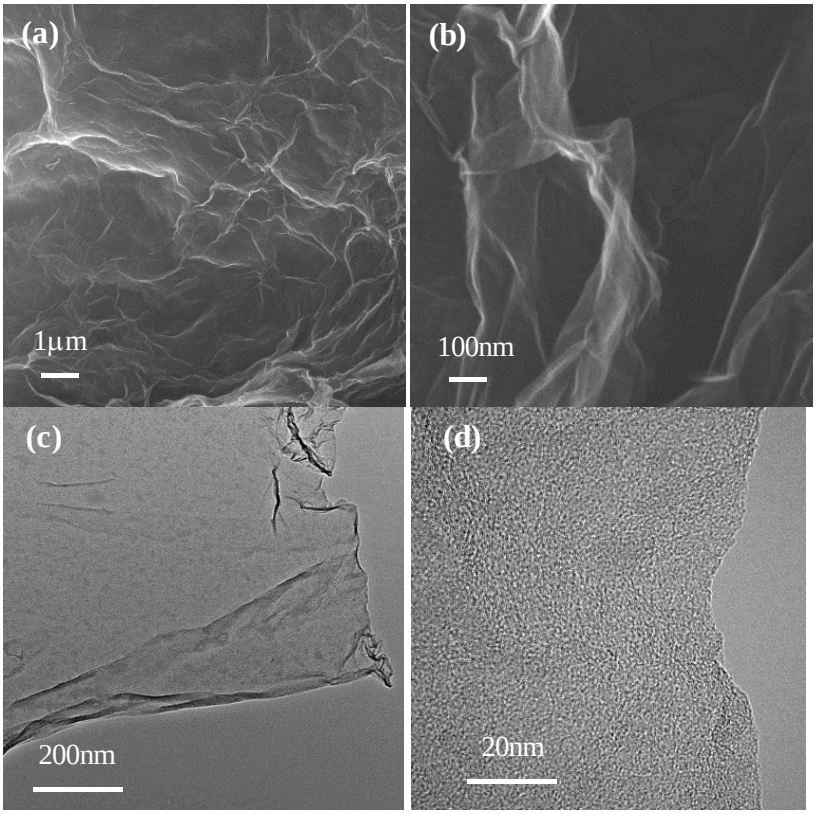

Figure S1. SEM (a, b) and TEM (c, d) images of N, P codoped reduced graphene oxide at different magnification. Note that sheet-like graphenes are corrugated and wrinkled. Note that dual doped reduced graphene oxide was obtained by thermally treating the GO and DNA mixture at 800^{o}C in argon.

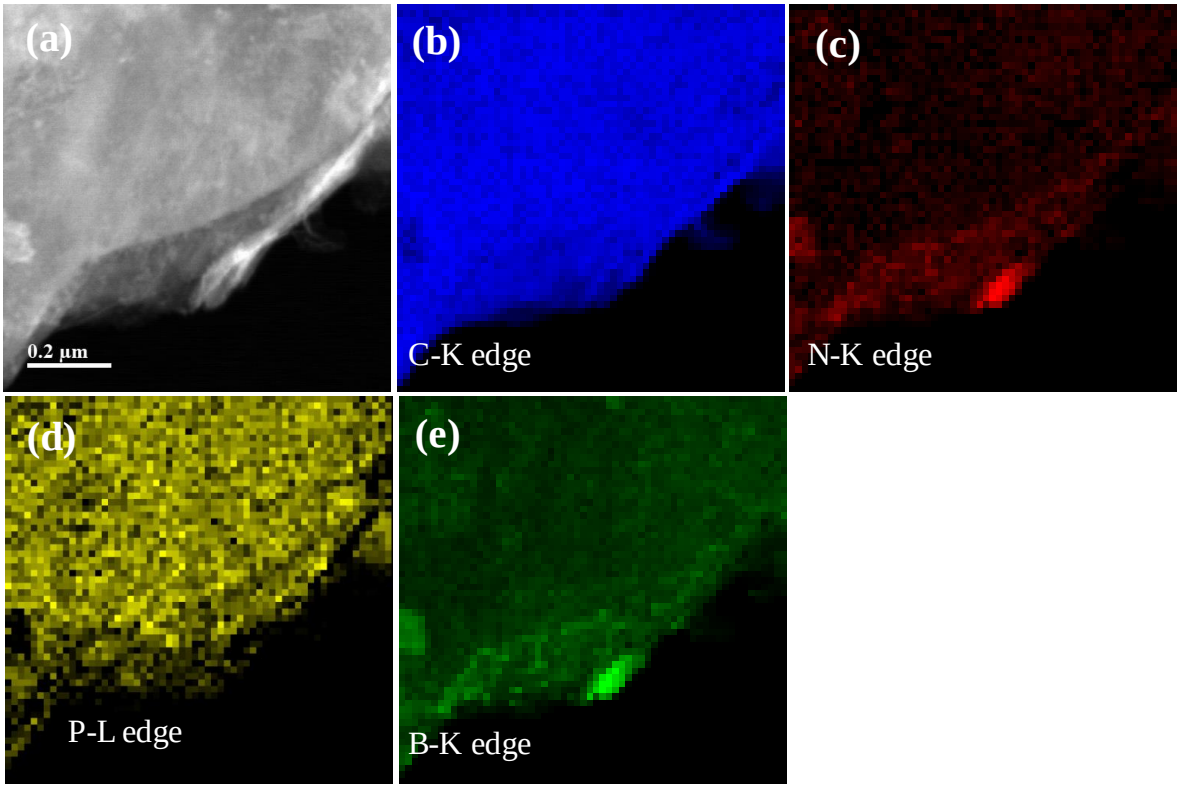

Figure S2. TEM image and EELS elemental mapping images of ternary doped reduced graphene oxide obtained using one-step method: (a) elastic TEM image and (b) carbon, (c) nitrogen, (d) phosphorus and (e) boron atoms. Note that the introduced heteroatoms are homogeneously distributed within graphene matrix.

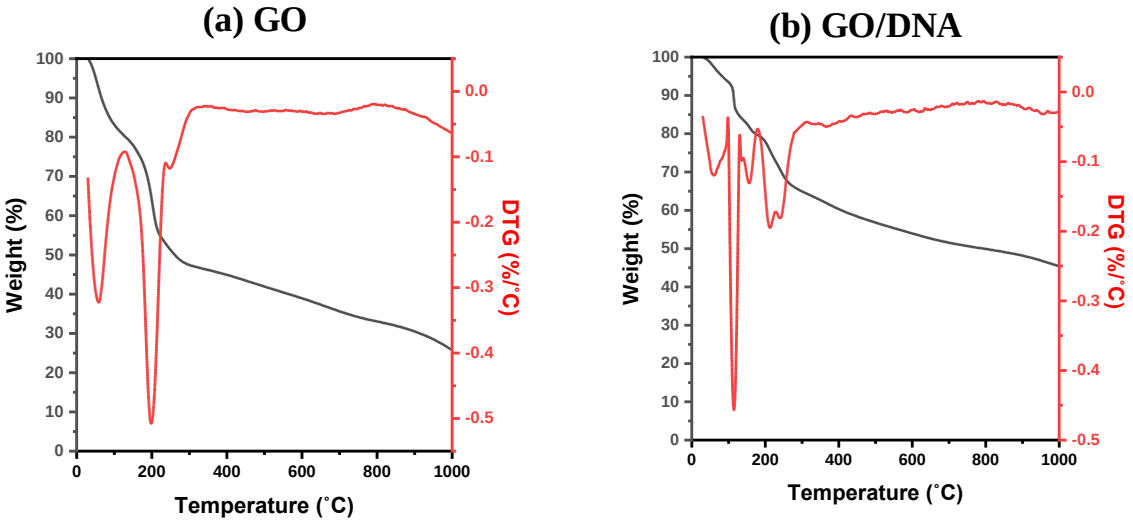

Figure S3. Thermogravimetric curves of (a) graphene oxide and (b) graphene oxide and DNA mixture in argon atmosphere and their derivatives.

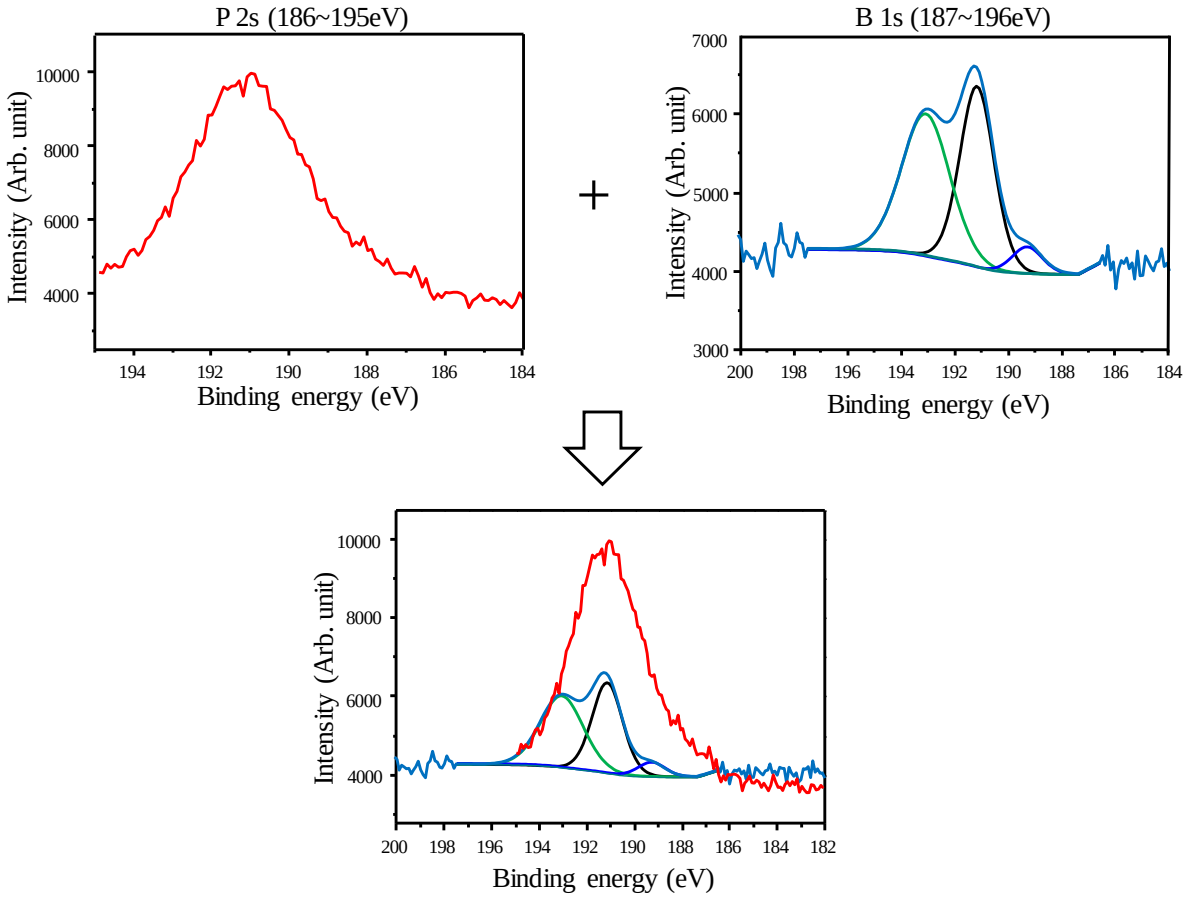

Figure S4. P 2s and B 1s spectra of ternary doped reduced graphene oxide using two-step.

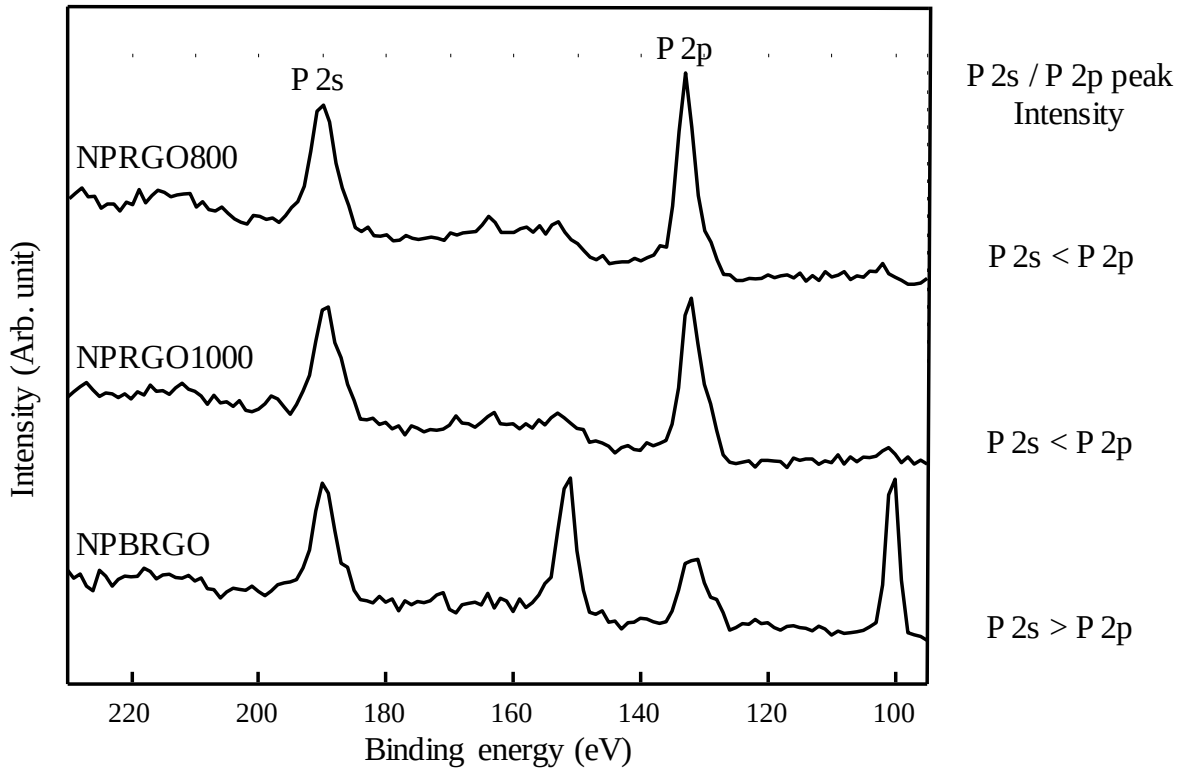

Figure S5. Comparative XPS spectra of N, P dual doped RGO that are prepared at different temperatures and ternary doped RGO. Note the relative intensity of P 2s and P 2p.

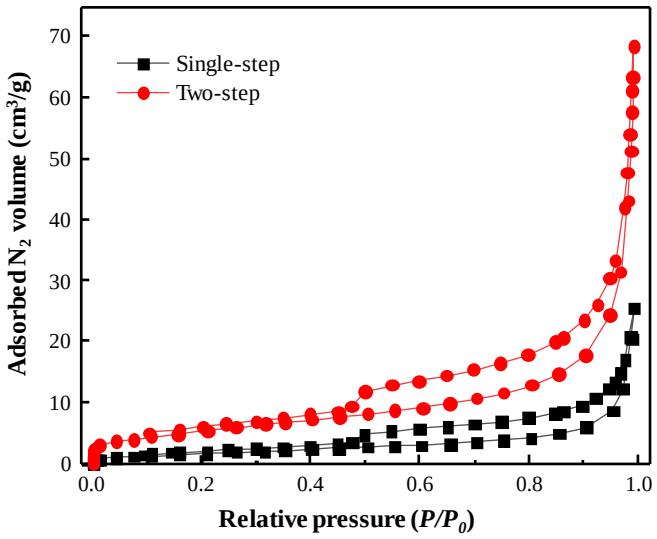

Figure S6. Nitrogen adsorption/desorption isotherms of ternary doped RGOs obtained using single-step and two-step methods.

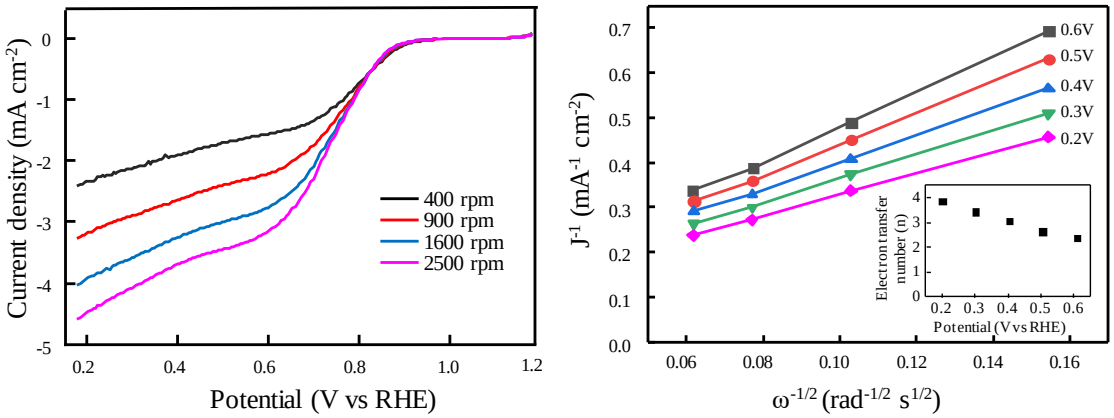

Figure S7. Linear sweep voltammograms of boron doped RGO obtained in 0.1 M O_2-saturated KOH electrolyte using different rotation speeds and their K-L plots in the range from 0.2 to 0.6 V (inset is the electron transfer number at different potential).

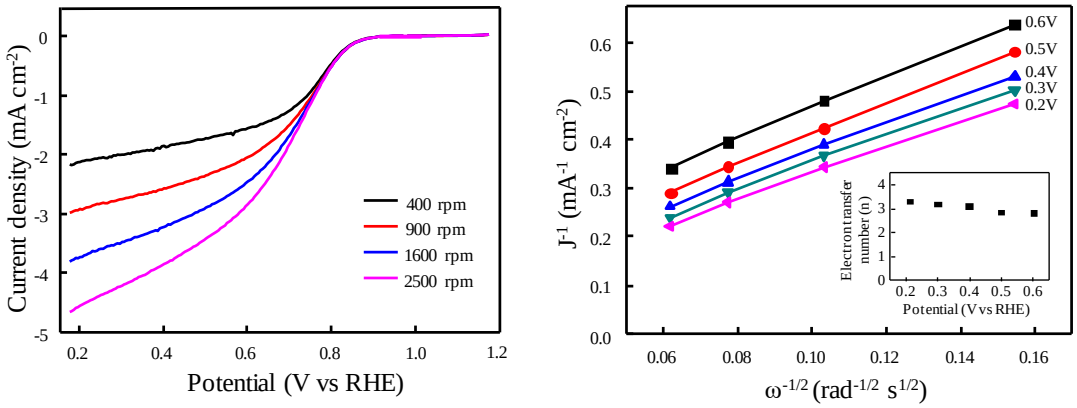

Figure S8. Linear sweep voltammograms of N, P codoped RGO obtained in 0.1 M O_2-saturated KOH electrolyte using different rotation speeds and their K-L plots in the range from 0.2 to 0.6 V (inset is the electron transfer number at different potential).

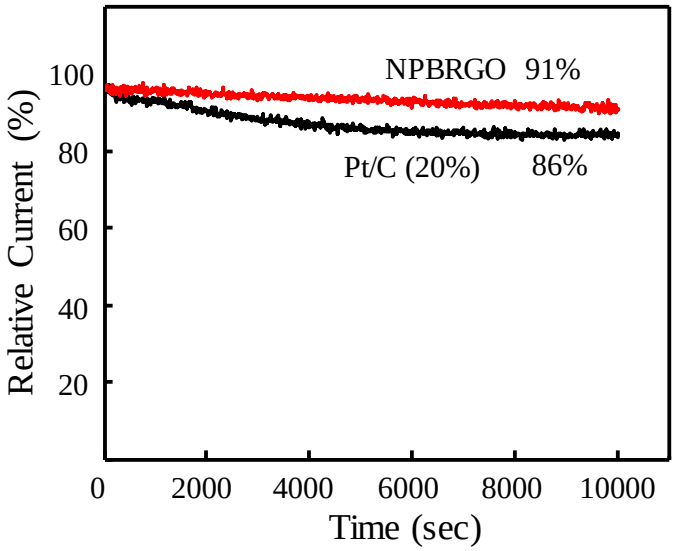

Figure S9. Chronoamperometic responses in O_2-saturated 0.1M KOH solution for two-step synthesized ternary RGOs and 20% Pt/C electrocatalysts at 0.7V vs. RHE with a rotation rate of 1600rpm.

Table S1 Relative amount of bonding configurations of three heteroatoms for ternary doped reduced graphene oxides obtained using single-step and two-step methods.

I.D.	Total B (atomic %)	Boron configuration (atomic %)		
		B_2O_3	BC_2O	BCO_2
Single-step	8.44	1.69	6.10	0.65
Two-step	3.90	1.27	1.90	0.74

I.D.	Total N (atomic %)	Nitrogen configuration (atomic %)			
		Pyridinic	Pyrrolic	Quaternary	N-Ox
Single-step	6.85	4.68	1.79	0.38	-
Two-step	3.02	0.94	1.02	0.90	0.14

I.D.	Total P (atomic %)	Phosphorus configuration (atomic %)		
		P-O	P-N	P-C
Single-step	1.01	0.27	0.42	0.32

Two-step	2.36	0.10	0.70	1.56

Table S2 Raman parameter of ternary doped reduced graphene oxides obtained using one-step and two-step methods.

I.D.	W_D (cm^{-1}) [a]	W_G (cm^{-1}) [b]	I_D/I_G [c]	$I_D/(I_D + I_G)$
One-step	88.4	73.2	0.95	0.49
Two-step	76.3	68.9	1.36	0.58

a) W_D is the full width at half maxim of the D band, b) W_G is the full width at half maxim of the G band, and c) I_D/I_G is the integrated intensity of the D band divided by the integrated intensity of the G band.

Table S3 Atomic composition of dual- and ternary-doped reduced graphene oxides.

I.D.	Atomic %				
	C	O	N	P	B
NPRGO	79.69	11.34	5.11	3.86	-
NPBRGO	77.50	13.23	3.02	2.36	3.90