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## **Supplementary Information**

Proposed reaction path of PATP coupling into DMAB under O<sub>2</sub>-free condition:

$$PATP \rightarrow PATP(NH) + H_2 \tag{1}$$

$$PATP(NH) \rightarrow PATP(N) + H_2$$
 (2)

$$PATP(N) + PATP(N) \rightarrow DMAB$$
 (3)

Proposed reaction path of PATP coupling into DMAB under O<sub>2</sub>-rich condition:

$$PATP + Ag_2O(AgOH) \rightarrow DMAB + H_2O + Ag$$





Fig. S1. Cyclic voltammogram of the graphite foil in the aqueous electrolyte of  $1.0 \text{ mM KNO}_3$  and  $0.1 \text{ mM AgNO}_3$ . Scan rate:  $10 \text{ mV s}^{-1}$ .



Fig. S2. Linear sweep voltammogram of DMAB adsorbed on the Ag-NPs/graphite in the aqueous electrolyte of  $1.0 \text{ mM KNO}_3$ . Scan rate:  $5 \text{ mV s}^{-1}$ .



Fig. S3. Linear sweep voltammogram of the Ag-NPs/graphite after the laser irradiation under  $O_2$ -free and  $O_2$ -rich conditions in the aqueous electrolyte of 1.0 mM KCl. Scan rate: 10 mV s<sup>-1</sup>.



Fig. S4. Calculated Raman spectra of PATP(N) and PATP(NH)



**Fig. S5**. The Raman intensity ratios of the 1253 cm<sup>-1</sup> and 1540 cm<sup>-1</sup> bands with respect to the 1080 cm<sup>-1</sup> band. Analysis is based on the data of figure 3a.



**Fig. S6**. Derivatives of the relative intensity of the 1143 cm<sup>-1</sup> band with respect to the 1080 cm<sup>-1</sup> band under  $O_2$ -rich and no ethanol conditions (black dot and line), and under  $O_2$ -rich plus ethanol conditions (red dot and line).



**Fig. S7**. Derivatives of the relative intensity of the 1143 cm<sup>-1</sup> band with respect to the 1080 cm<sup>-1</sup> band under  $O_2$ -free and neutral pH conditions (black dot and line), and under  $O_2$ -free and alkaline (pH 8.0) conditions (red dot and line).



**Fig. S8**. Derivatives of the relative intensity of the 1143 cm<sup>-1</sup> band with respect to the 1080 cm<sup>-1</sup> band under  $O_2$ -rich and neutral pH conditions (black dot and line), and under  $O_2$ -rich and alkaline (pH 8.0) conditions (red dot and line).



Fig. S9. Successive SERS measurements of DMAB adsorbed on the Ag-NPs/graphite under  $O_2$ -free and acidic (pH 3.0) conditions. The integration time of each spectrum was 10s. These spectra are normalized at the 1080 cm<sup>-1</sup> band.



Fig. S10. SERS measurement after PATP and ethanol were added under  $O_2$ -free condition onto Ag-NPs/graphite which was irradiated by the laser for 10 minutes under  $O_2$ -rich condition. The integration time was 20 s.