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The Ways for Bi on Pt to Enhance Formic Acid Oxidation

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Replacement of iodine with CO on plain Pt(poly)

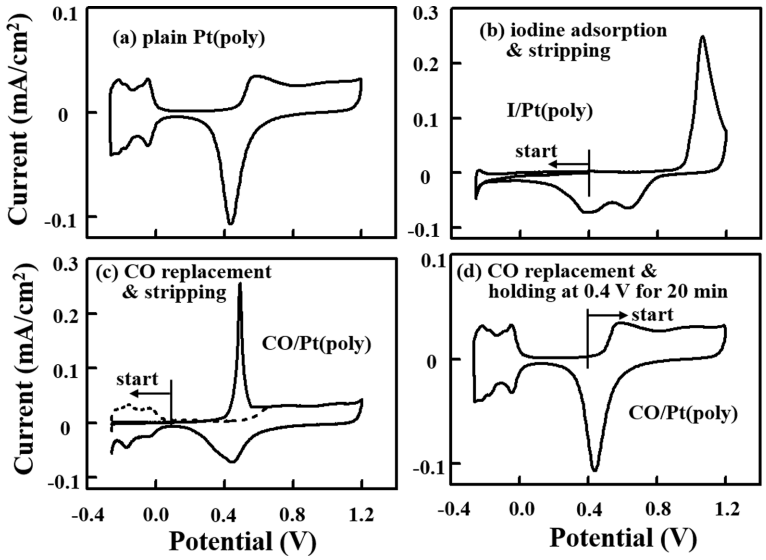

Fig. S1. Cyclic voltammograms of plain Pt(poly) during removal of adsorbed iodine using CO replacement: (a) plain Pt(poly), (b) iodine stripping of I/Pt(poly), (c) CO stripping of CO/Pt(poly) after immersion of I/Pt(poly) into a CO-saturated H_2SO_4 solution, and (d) CO/Pt(poly) after holding the potential at 0.4 V for 20 min. Solution: 0.10 M H_2SO_4. Scan rate: 50 $mV \cdot s^{-1}$.

Fig. S1 presents the cyclic voltammograms of plain Pt(poly) confirming removal of adsorbed iodine using CO replacement procedure. Fig. S1(a) is a cyclic voltammogram of plain Pt(poly) in 0.10 M H_2SO_4. After iodine adsorption in a solution of 0.10 M KI (> 99.0%, Aldrich) for 20 min, the initial negative-going scan from 0.4 V confirms the disappearance of hydrogen region, and the following positive-going scan reveals stripping of iodine, accompanied by Pt surface oxidation, above ~0.9 V as shown in Fig. S1(b). Fig. S1(c) is a voltammogram obtained after immersing the iodine-covered I/Pt(poly) with CO-saturated 0.10 M H_2SO_4 solution at 0.1 V for 15 min. There is no hydrogen adsorption charge, and the stripping process of CO stars at ~0.3 V without any trace of iodine oxidation. Thus, adsorbed iodine is verified to be replaced completely with CO in solution phase. Fig. S1(d) is a voltammogram of CO-covered plain Pt(poly), or CO/Pt(poly), held for 20 min at 0.4 V. There is no CO oxidation peak, confirming that complete removal of CO on plain Pt(poly) at 0.4 V for 20 min.

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Replacement of iodine with CO on Bi/Pt(poly)

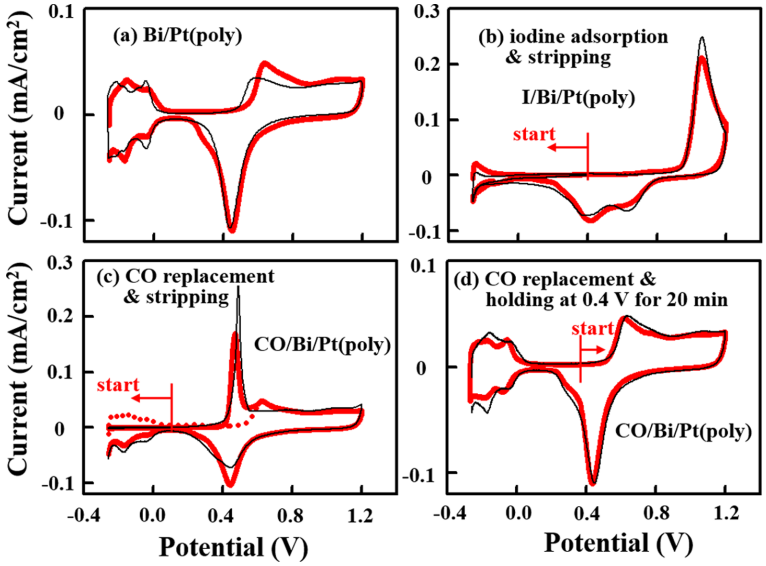

Fig. S2. Cyclic voltammograms of Bi/Pt(poly) during removal of adsorbed iodine using CO replacement: (a) Bi/Pt(poly), (b) iodine stripping of I/Bi/Pt(poly), (c) CO stripping of CO/Bi/Pt(poly) after immersion of I/Bi/Pt(poly) into a CO-saturated H_2SO_4 solution, and (d) CO/Bi/Pt(poly) after holding the potential at 0.4 V for 20 min. The thin line voltammograms are those of plain Pt(poly) for a purpose of comparison. Solution: 0.10 M H_2SO_4. Scan rate: 50 $mV \cdot s^{-1}$.

Fig. S2 displays the cyclic voltammograms of Bi/Pt(poly) during removal of adsorbed iodine using CO replacement procedure. It should be noted that the thin line voltammograms correspond to those of plain Pt(poly) to compare with the thick line voltammograms of Bi/Pt(poly). Fig. S2(a) is a cyclic voltammogram of Bi/Pt(poly) in 0.10 M H_2SO_4, clearly demonstrating oxidative removal of Bi peak at ~0.6 V. The voltammogram of I/Bi/Pt(poly), Fig. S2(b), demonstrates no hydrogen adsorption charge and the stripping peak of iodine whose charge is less than that of I/Pt(poly). The voltammogram of CO/Bi/Pt(poly), obtained after application of CO replacement procedure to I/Bi/Pt(poly), is similar to that of CO/Pt(poly) except a less stripping charge of CO. The less stripping charges of iodine on I/Bi/Pt(poly) and CO on CO/Pt(poly) are ascribable to no adsorption of iodine and CO on the Bi deposits. After holding CO/Bi/Pt(poly) at 0.4 V for 20 min, no CO is present on Bi/Pt(poly) as shown in Fig. S2(d). More important is that the stripping behavior of Bi does not alter significantly before and after iodine adsorption and subsequent CO replacement.

EC-STM images of Pt(111) modified with Bi of a high coverage (~0.25)

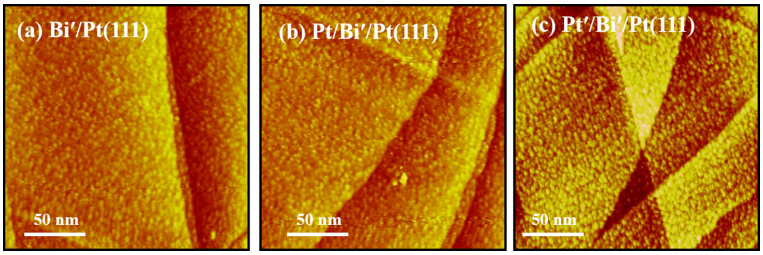

Fig. S3. EC-STM images of (a) plain Bi'/Pt(111), (b) Pt/Bi'/Pt(111), and (c) Pt'/Bi'/Pt(111).