Formation of composite dimers consisting of Ag$_2$S and hollow structured Pd nanoparticles

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Financial support from the 100 Talents Program of the Chinese Academy of Sciences and National Natural Science Foundation of China (No.: 21173226, 21376247, 21476246) is gratefully acknowledged.
Fig. S1 TEM images (a,c) and HRTEM images (b,d) of the as-prepared Ag seed particles in oleylamine in the presence of ionic liquid (a,b) and in the absence of ionic liquid (c,d).

Fig. S2 X-ray diffraction (XRD) patterns of Ag seed particles synthesized in oleylamine in the presence of ionic liquid (a), core-shell Ag@Ag-Pd nanoparticles by galvanic replacement reaction between as-prepared Ag seeds and Pd^{2+} precursors (b), and dimeric Ag_{2}S-hPd nanocomposites derived from core-shell Ag@Ag-Pd nanoparticles (c), in which the reference for monoclinic Ag_{2}S (JCPDS Card File 140072, blue columns) is displayed.
Fig. S3 UV-Visible spectra of colloidal solution of Ag seeds synthesized in oleylamine in the presence of ionic liquid (a), core-shell Ag@Ag-Pd nanoparticles by galvanic replacement reaction between as-prepared Ag seeds and Pd$^{2+}$ precursors (b), and core-shell Ag@Ag-Pd nanoparticles after element S treatment at 50$^\circ$C for 8 h (c).

Fig. S4 TEM image (a) and HRTEM image (b) of the Ag@Ag-Pd nanoparticles by galvanic replacement reaction between Ag seeds synthesized in the absence of ionic liquid and Pd$^{2+}$ precursors.
Fig. S5 Cyclic voltammograms for CO stripping on the core-shell Ag@Ag-Pd nanoparticles aging with element S for 8 h (a), 16 h (b), 24 h (c), and on the original core-shell Ag@Ag-Pd templates (d), respectively, in 0.1 M HClO₄ at scan rate of 50 mV s⁻¹. Black line: 1st scan; red line: 2nd scan.

Fig. S6 The 3d XPS spectra of Pd in commercial Pd/C-JM catalyst (a) and dimeric Ag₂S-hPd nanocomposites (b).
**Fig. S7** Cyclic voltammograms for CO stripping on the commercial Pd/C-JM catalyst in 0.1 M HClO$_4$ at scan rate of 50 mV s$^{-1}$. Black line: 1$^{st}$ scan; red line: 2$^{nd}$ scan.

**Table S1** Electrochemical measurements of formic acid oxidation on dimeric Ag$_2$S-hPd nanocomposites and commercial Pd/C-JM catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>FPP (V)</th>
<th>EPCD (mA cm$^{-2}$)</th>
<th>BPP (V)</th>
<th>BPCD (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$S-hPd/C</td>
<td>0.31</td>
<td>1.54</td>
<td>0.48</td>
<td>1.73</td>
</tr>
<tr>
<td>Pd/C-JM</td>
<td>0.85</td>
<td>1.10</td>
<td>0.64</td>
<td>1.08</td>
</tr>
</tbody>
</table>

FPP: Forward peak potential; FPCD: Forward peak current density; BPP: Backward peak potential; BPCD: Backward peak current density. The data were obtained from Fig. 4a.