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Facile synthesis of Ag/ZIF-8@ZIF-67 as electrochemical sensing platform for sensitive detection of halonitrophenols in drinking water

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Text S1 Process of the preparation and application of Ag/ZIF-8@ZIF-67/GCE

The process of synthesizing Ag/ZIF-8@ZIF-67 and the sensing methodology for 2,6-DCNP detection were depicted in Scheme 1. Because of the synergism and similar topology of ZIF-8 and ZIF-67, they were chosen as a raw material for the creation of core-shell materials. And ZIF-8@ZIF-67 was a suitable carrier for loaded AgNPs due to its stability and distinctive structure, large specific surface area and plentiful pores.

By using the two-solvent method, AgNPs were made to be loaded both on the carrier's surface and within the pores. 2-Meim was a precursor of both ZIF-8 and ZIF-67, and the abundant delocalized π bonds in its benzene ring structure can form π–π interaction with π-bonds in the material to be tested, which promotes the adsorption and the electrochemical reaction rate of 2,6-DCNP on the material. Moreover, the experimental finding showed that the approach of loading AgNPs on the surface of ZIF-8@ZIF-67 was straightforward, environmentally friendly, technically possible, and efficient for the synthesis of Ag/ZIF-8@ZIF-67, which only needs to be carried out in room temperature without complicated processes. 2,6-DCNP displayed a significant rising peak current by DPV test. Due to the catalytic activity of Ag/ZZIF-8@ZIF-67, the reduction current considerably increases as the concentration of 2,6-DCNP rises, and on this basis, the concentration of 2,6-DCNP can be detected by using the increase in current.

Text S2 Simulation of the XRD plot of ZIF-8@ZIF-67

The software "diamond" was commonly used to draw crystal structure diagrams. The crystal structure of ZIF-8@ZIF-67 was obtained by importing the interatomic distances and coordination numbers of ZIF-8 and ZIF-67 into the software. And the simulated XRD plot of ZIF-8@ZIF-67 was obtained by software simulation.

Text S3 Detailed information for crystal structure of ZIF-8 and ZIF-8@ZIF-67

ZIF-8@ZIF-67 was produced by ZIF-8 and ZIF-67 through epitaxial growth since their cell parameters and topological structure were quite similar (a = b = c = 16.9910 Å and 16.9589 Å, respectively).[1-3] According to Figure S1, the crystal structure diagram of ZIF-8 was displayed on the left side. The metal Co combined with the N of 2-Meim to form the MOFs structure. The yellow dummy atoms in the crystal structure diagram represent the pores of the MOFs material. The high specific surface area and strong adsorption property of the MOFs material were also caused by the abundance of pores in its structure. The crystal structure of ZIF-8@ZIF-67, which was generated by continuing grown on the exterior of ZIF-8, was shown on the right side.

Table S1 Raw data from the selective experiments.

E	2,6-DCNP	Blank	Mg^{2+}	Cu^{2+}	Ca^{2+}	Phenol	NB	p-NP	4-Cl-2-NP	2,4-DC-5-NP	HA
V	µA	µA	µA	µA	µA	µA	µA	µA	µA	µA	µA
-0.404	-6.568	-4.797	-4.146	-3.623	-3.819	-2.455	-4.017	-4.230	-6.190	-5.765	-4.732
-0.408	-6.498	-4.644	-3.984	-3.615	-3.700	-2.424	-3.845	-4.019	-5.790	-5.550	-4.532
-0.412	-6.445	-4.513	-3.868	-3.619	-3.623	-2.385	-3.734	-3.869	-5.480	-5.390	-4.384
-0.416	-6.343	-4.394	-3.773	-3.620	-3.564	-2.336	-3.648	-3.753	-5.230	-5.265	-4.260
-0.420	-6.251	-4.287	-3.696	-3.625	-3.516	-2.282	-3.583	-3.659	-5.015	-5.160	-4.148
-0.424	-6.141	-4.189	-3.627	-3.631	-3.476	-2.219	-3.535	-3.583	-4.833	-5.070	-4.048
-0.428	-6.043	-4.095	-3.561	-3.637	-3.434	-2.156	-3.497	-3.521	-4.675	-4.987	-3.953
-0.432	-5.954	-4.006	-3.494	-3.641	-3.396	-2.092	-3.469	-3.471	-4.537	-4.911	-3.863
-0.436	-5.876	-3.919	-3.431	-3.646	-3.356	-2.028	-3.446	-3.430	-4.410	-4.838	-3.780
-0.440	-5.813	-3.829	-3.369	-3.647	-3.314	-1.967	-3.427	-3.400	-4.296	-4.765	-3.698
-0.444	-5.764	-3.740	-3.307	-3.643	-3.267	-1.910	-3.404	-3.378	-4.190	-4.691	-3.620
-0.448	-5.717	-3.649	-3.241	-3.642	-3.219	-1.855	-3.385	-3.364	-4.095	-4.619	-3.544
-0.452	-5.675	-3.557	-3.173	-3.634	-3.166	-1.804	-3.364	-3.354	-3.998	-4.547	-3.473
-0.456	-5.624	-3.464	-3.103	-3.623	-3.110	-1.756	-3.341	-3.353	-3.907	-4.472	-3.417
-0.460	-5.593	-3.372	-3.034	-3.608	-3.051	-1.713	-3.317	-3.356	-3.825	-4.394	-3.335
-0.464	-5.554	-3.280	-2.965	-3.588	-2.987	-1.671	-3.290	-3.364	-3.739	-4.315	-3.280
-0.468	-5.514	-3.190	-2.898	-3.566	-2.920	-1.633	-3.262	-3.374	-3.656	-4.237	-3.220
-0.472	-5.495	-3.100	-2.830	-3.539	-2.851	-1.597	-3.226	-3.387	-3.572	-4.156	-3.166
-0.476	-5.465	-3.014	-2.761	-3.505	-2.782	-1.563	-3.190	-3.402	-3.488	-4.073	-3.116
-0.480	-5.439	-2.931	-2.672	-3.470	-2.711	-1.533	-3.150	-3.416	-3.404	-3.988	-3.060
-0.484	-5.414	-2.850	-2.634	-3.429	-2.639	-1.504	-3.104	-3.428	-3.322	-3.904	-3.005
-0.488	-5.396	-2.774	-2.570	-3.386	-2.568	-1.478	-3.055	-3.441	-3.238	-3.819	-2.956
-0.492	-5.381	-2.702	-2.510	-3.336	-2.497	-1.453	-3.001	-3.450	-3.154	-3.737	-2.910
-0.496	-5.372	-2.635	-2.454	-3.287	-2.431	-1.430	-2.946	-3.456	-3.072	-3.654	-2.861
-0.500	-5.367	-2.571	-2.397	-3.235	-2.363	-1.409	-2.887	-3.458	-2.988	-3.571	-2.821
-0.504	-5.368	-2.510	-2.345	-3.180	-2.301	-1.389	-2.828	-3.456	-2.908	-3.485	-2.776
-0.508	-5.374	-2.452	-2.277	-3.125	-2.240	-1.371	-2.767	-3.449	-2.829	-3.403	-2.733
-0.512	-5.386	-2.399	-2.236	-3.067	-2.182	-1.354	-2.705	-3.436	-2.750	-3.322	-2.686
-0.516	-5.402	-2.348	-2.178	-3.010	-2.126	-1.338	-2.643	-3.417	-2.673	-3.241	-2.642
-0.520	-5.426	-2.299	-2.135	-2.952	-2.074	-1.321	-2.581	-3.392	-2.597	-3.161	-2.602
-0.524	-5.453	-2.253	-2.092	-2.893	-2.026	-1.308	-2.521	-3.361	-2.523	-3.084	-2.560
-0.528	-5.487	-2.209	-2.052	-2.835	-1.978	-1.297	-2.466	-3.325	-2.449	-3.007	-2.516
-0.532	-5.524	-2.167	-2.014	-2.780	-1.934	-1.285	-2.409	-3.282	-2.380	-2.932	-2.475
-0.536	-5.567	-2.124	-1.977	-2.726	-1.892	-1.275	-2.354	-3.236	-2.311	-2.858	-2.435
-0.540	-5.614	-2.082	-1.943	-2.670	-1.853	-1.266	-2.302	-3.183	-2.246	-2.787	-2.392
-0.544	-5.666	-2.042	-1.910	-2.617	-1.814	-1.258	-2.255	-3.127	-2.184	-2.715	-2.352
-0.548	-5.719	-2.003	-1.875	-2.565	-1.778	-1.251	-2.208	-3.067	-2.125	-2.644	-2.315
-0.552	-5.778	-1.964	-1.844	-2.517	-1.744	-1.243	-2.164	-3.005	-2.068	-2.577	-2.274
-0.556	-5.839	-1.929	-1.811	-2.467	-1.710	-1.238	-2.124	-2.939	-2.016	-2.507	-2.236
-0.560	-5.901	-1.892	-1.781	-2.423	-1.678	-1.227	-2.081	-2.873	-1.962	-2.441	-2.194
-0.564	-5.963	-1.857	-1.753	-2.377	-1.646	-1.224	-2.043	-2.804	-1.910	-2.376	-2.156
-0.568	-6.025	-1.824	-1.724	-2.332	-1.615	-1.220	-2.012	-2.736	-1.864	-2.313	-2.117
-0.572	-6.087	-1.791	-1.696	-2.287	-1.586	-1.216	-1.978	-2.669	-1.822	-2.251	-2.076
-0.576	-6.147	-1.758	-1.668	-2.247	-1.557	-1.214	-1.950	-2.602	-1.781	-2.190	-2.039
-0.580	-6.202	-1.726	-1.642	-2.205	-1.529	-1.214	-1.919	-2.537	-1.740	-2.130	-2.003
-0.584	-6.256	-1.695	-1.614	-2.165	-1.501	-1.209	-1.893	-2.472	-1.704	-2.072	-1.968
-0.588	-6.301	-1.665	-1.588	-2.125	-1.486	-1.206	-1.866	-2.412	-1.673	-2.014	-1.931
-0.592	-6.340	-1.634	-1.563	-2.087	-1.448	-1.203	-1.842	-2.353	-1.638	-1.958	-1.896
-0.596	-6.370	-1.605	-1.537	-2.050	-1.423	-1.202	-1.818	-2.297	-1.609	-1.904	-1.864
-0.600	-6.391	-1.577	-1.512	-2.013	-1.398	-1.198	-1.795	-2.243	-1.582	-1.853	-1.830
-0.604	-6.400	-1.548	-1.487	-1.978	-1.373	-1.197	-1.775	-2.193	-1.556	-1.803	-1.800
-0.608	-6.397	-1.520	-1.463	-1.946	-1.349	-1.193	-1.753	-2.144	-1.534	-1.754	-1.770
-0.612	-6.381	-1.492	-1.439	-1.911	-1.325	-1.191	-1.732	-2.100	-1.512	-1.707	-1.737
-0.616	-6.352	-1.465	-1.416	-1.879	-1.302	-1.191	-1.715	-2.058	-1.492	-1.662	-1.711
-0.620	-6.309	-1.438	-1.392	-1.847	-1.279	-1.189	-1.694	-2.019	-1.474	-1.619	-1.681
-0.624	-6.251	-1.411	-1.370	-1.815	-1.257	-1.190	-1.676	-1.984	-1.457	-1.578	-1.654
-0.628	-6.177	-1.384	-1.347	-1.786	-1.235	-1.191	-1.658	-1.950	-1.441	-1.538	-1.631
-0.632	-6.091	-1.357	-1.326	-1.755	-1.214	-1.193	-1.640	-1.920	-1.429	-1.501	-1.609
-0.636	-5.990	-1.332	-1.304	-1.728	-1.193	-1.195	-1.625	-1.893	-1.416	-1.465	-1.583
-0.640	-5.879	-1.306	-1.283	-1.699	-1.173	-1.196	-1.608	-1.868	-1.402	-1.431	-1.561
-0.644	-5.755	-1.281	-1.262	-1.673	-1.153	-1.199	-1.592	-1.846	-1.391	-1.400	-1.540
-0.648	-5.622	-1.256	-1.242	-1.648	-1.134	-1.200	-1.576	-1.827	-1.381	-1.371	-1.516
-0.652	-5.481	-1.232	-1.223	-1.622	-1.115	-1.205	-1.563	-1.808	-1.371	-1.343	-1.497
-0.656	-5.334	-1.208	-1.203	-1.597	-1.097	-1.206	-1.547	-1.794	-1.362	-1.315	-1.476
-0.660	-5.182	-1.185	-1.186	-1.574	-1.079	-1.208	-1.533	-1.781	-1.352	-1.290	-1.458
-0.664	-5.026	-1.162	-1.165	-1.550	-1.062	-1.207	-1.520	-1.770	-1.345	-1.267	-1.442
-0.668	-4.870	-1.140	-1.147	-1.527	-1.044	-1.208	-1.507	-1.761	-1.335	-1.244	-1.424
-0.672	-4.713	-1.118	-1.130	-1.505	-1.029	-1.209	-1.495	-1.753	-1.328	-1.222	-1.407
-0.676	-4.558	-1.097	-1.113	-1.483	-1.012	-1.206	-1.482	-1.746	-1.321	-1.201	-1.390
-0.680	-4.406	-1.077	-1.096	-1.461	-0.997	-1.214	-1.468	-1.740	-1.314	-1.184	-1.376
-0.684	-4.258	-1.057	-1.079	-1.439	-0.982	-1.204	-1.457	-1.734	-1.306	-1.165	-1.367
-0.688	-4.113	-1.038	-1.063	-1.420	-0.968	-1.202	-1.447	-1.729	-1.299	-1.148	-1.351
-0.692	-3.972	-1.019	-1.047	-1.399	-0.953	-1.195	-1.437	-1.725	-1.292	-1.132	-1.336
-0.696	-3.836	-1.002	-1.032	-1.379	-0.940	-1.199	-1.423	-1.717	-1.286	-1.116	-1.325
-0.700	-3.706	-0.986	-1.016	-1.360	-0.925	-1.193	-1.412	-1.709	-1.278	-1.102	-1.314
-0.704	-3.582	-0.969	-1.001	-1.340	-0.913	-1.182	-1.402	-1.702	-1.271	-1.088	-1.304
-0.708	-3.464	-0.954	-0.986	-1.321	-0.900	-1.177	-1.392	-1.701	-1.266	-1.076	-1.295
-0.712	-3.349	-0.938	-0.972	-1.303	-0.888	-1.171	-1.382	-1.680	-1.259	-1.064	-1.286
-0.716	-3.241	-0.924	-0.958	-1.285	-0.875	-1.167	-1.373	-1.666	-1.252	-1.053	-1.275
-0.720	-3.137	-0.911	-0.944	-1.267	-0.863	-1.164	-1.364	-1.651	-1.247	-1.042	-1.264
-0.724	-3.038	-0.897	-0.930	-1.250	-0.851	-1.160	-1.354	-1.632	-1.239	-1.031	-1.256
-0.728	-2.942	-0.884	-0.916	-1.234	-0.840	-1.157	-1.350	-1.612	-1.232	-1.021	-1.248
-0.732	-2.853	-0.872	-0.904	-1.216	-0.831	-1.154	-1.341	-1.592	-1.225	-1.011	-1.240
-0.736	-2.768	-0.861	-0.891	-1.201	-0.818	-1.151	-1.333	-1.568	-1.219	-1.002	-1.231
-0.740	-2.685	-0.849	-0.879	-1.185	-0.808	-1.151	-1.325	-1.544	-1.215	-0.994	-1.226
-0.744	-2.607	-0.838	-0.867	-1.170	-0.797	-1.143	-1.317	-1.517	-1.206	-0.985	-1.216
-0.748	-2.533	-0.828	-0.855	-1.156	-0.789	-1.138	-1.310	-1.491	-1.200	-0.978	-1.208
-0.752	-2.462	-0.818	-0.844	-1.140	-0.778	-1.130	-1.304	-1.464	-1.194	-0.971	-1.202
-0.756	-2.392	-0.808	-0.832	-1.125	-0.769	-1.126	-1.299	-1.435	-1.188	-0.964	-1.195
-0.760	-2.325	-0.799	-0.821	-1.113	-0.761	-1.120	-1.293	-1.407	-1.183	-0.957	-1.189
-0.764	-2.263	-0.789	-0.810	-1.101	-0.752	-1.121	-1.287	-1.379	-1.177	-0.951	-1.186
-0.768	-2.200	-0.781	-0.801	-1.088	-0.744	-1.108	-1.282	-1.352	-1.172	-0.945	-1.179
-0.772	-2.143	-0.773	-0.791	-1.076	-0.737	-1.098	-1.276	-1.326	-1.165	-0.940	-1.174
-0.776	-2.088	-0.765	-0.782	-1.066	-0.729	-1.095	-1.274	-1.297	-1.159	-0.936	-1.169
-0.780	-2.032	-0.758	-0.773	-1.056	-0.722	-1.085	-1.267	-1.277	-1.153	-0.931	-1.163
-0.784	-1.981	-0.751	-0.765	-1.046	-0.716	-1.077	-1.262	-1.251	-1.147	-0.928	-1.159
-0.788	-1.932	-0.745	-0.757	-1.037	-0.709	-1.069	-1.257	-1.228	-1.142	-0.924	-1.156
-0.792	-1.884	-0.739	-0.750	-1.028	-0.703	-1.060	-1.251	-1.206	-1.138	-0.921	-1.153
-0.796	-1.839	-0.729	-0.741	-1.020	-0.698	-1.054	-1.247	-1.185	-1.133	-0.918	-1.148
-0.800	-1.795	-0.724	-0.735	-1.014	-0.692	-1.044	-1.244	-1.166	-1.127	-0.915	-1.145
-0.804	-1.752	-0.719	-0.729	-1.008	-0.688	-1.035	-1.241	-1.148	-1.123	-0.912	-1.143
-0.808	-1.713	-0.714	-0.723	-1.002	-0.684	-1.028	-1.236	-1.131	-1.119	-0.911	-1.140
-0.812	-1.674	-0.710	-0.718	-0.999	-0.680	-1.018	-1.245	-1.115	-1.115	-0.912	-1.137
-0.816	-1.639	-0.705	-0.713	-0.996	-0.678	-1.009	-1.235	-1.101	-1.111	-0.911	-1.137
-0.820	-1.604	-0.701	-0.710	-0.994	-0.675	-1.004	-1.233	-1.087	-1.107	-0.911	-1.136
-0.824	-1.571	-0.696	-0.705	-0.994	-0.673	-0.993	-1.235	-1.074	-1.103	-0.912	-1.136
-0.828	-1.542	-0.693	-0.704	-0.995	-0.671	-0.985	-1.235	-1.063	-1.101	-0.914	-1.134
-0.832	-1.513	-0.691	-0.702	-0.997	-0.671	-0.985	-1.234	-1.053	-1.099	-0.916	-1.137
-0.836	-1.487	-0.688	-0.701	-1.001	-0.671	-0.975	-1.234	-1.044	-1.098	-0.919	-1.138
-0.840	-1.462	-0.686	-0.701	-1.009	-0.672	-0.968	-1.233	-1.043	-1.098	-0.923	-1.140
-0.844	-1.439	-0.684	-0.704	-1.017	-0.672	-0.971	-1.234	-1.030	-1.097	-0.928	-1.141
-0.848	-1.419	-0.684	-0.704	-1.028	-0.679	-0.971	-1.237	-1.025	-1.097	-0.935	-1.145
-0.852	-1.399	-0.683	-0.708	-1.041	-0.683	-0.964	-1.241	-1.019	-1.097	-0.942	-1.150
-0.856	-1.382	-0.683	-0.712	-1.056	-0.688	-0.962	-1.243	-1.016	-1.099	-0.950	-1.155
-0.860	-1.366	-0.684	-0.719	-1.074	-0.694	-0.964	-1.247	-1.014	-1.104	-0.961	-1.164
-0.864	-1.352	-0.686	-0.725	-1.095	-0.702	-0.967	-1.254	-1.013	-1.106	-0.971	-1.172
-0.868	-1.338	-0.689	-0.734	-1.118	-0.711	-0.969	-1.259	-1.013	-1.110	-0.984	-1.181
-0.872	-1.327	-0.692	-0.744	-1.144	-0.720	-0.975	-1.267	-1.014	-1.115	-0.999	-1.194
-0.876	-1.318	-0.696	-0.755	-1.175	-0.733	-0.979	-1.276	-1.017	-1.121	-1.016	-1.203
-0.880	-1.310	-0.702	-0.769	-1.206	-0.746	-0.988	-1.290	-1.024	-1.128	-1.034	-1.216
-0.884	-1.302	-0.708	-0.784	-1.242	-0.759	-0.999	-1.302	-1.033	-1.136	-1.055	-1.232
-0.888	-1.296	-0.716	-0.802	-1.280	-0.776	-1.013	-1.318	-1.043	-1.148	-1.080	-1.250
-0.892	-1.292	-0.725	-0.822	-1.324	-0.795	-1.033	-1.339	-1.053	-1.158	-1.107	-1.269
-0.896	-1.289	-0.737	-0.846	-1.370	-0.820	-1.058	-1.364	-1.066	-1.173	-1.139	-1.293
-0.900	-1.287	-0.750	-0.873	-1.422	-0.840	-1.090	-1.397	-1.079	-1.190	-1.177	-1.318

Table S2 2,6-DCNP detection in real water sample (n = 3)

Sample	Added	Found	Recovery	RSD
	μmol/L	μmol/L	%	%,
Tap water	0	ND*	-	-
	4.8	4.72	98.41%	4.03%
	48	48.7	101.64%	1.45%
Swimming pool water	0	ND*	-	-
	4.8	4.72	98.24%	2.31%
	48	48.7	100.96%	0.92%

ND*: not detected

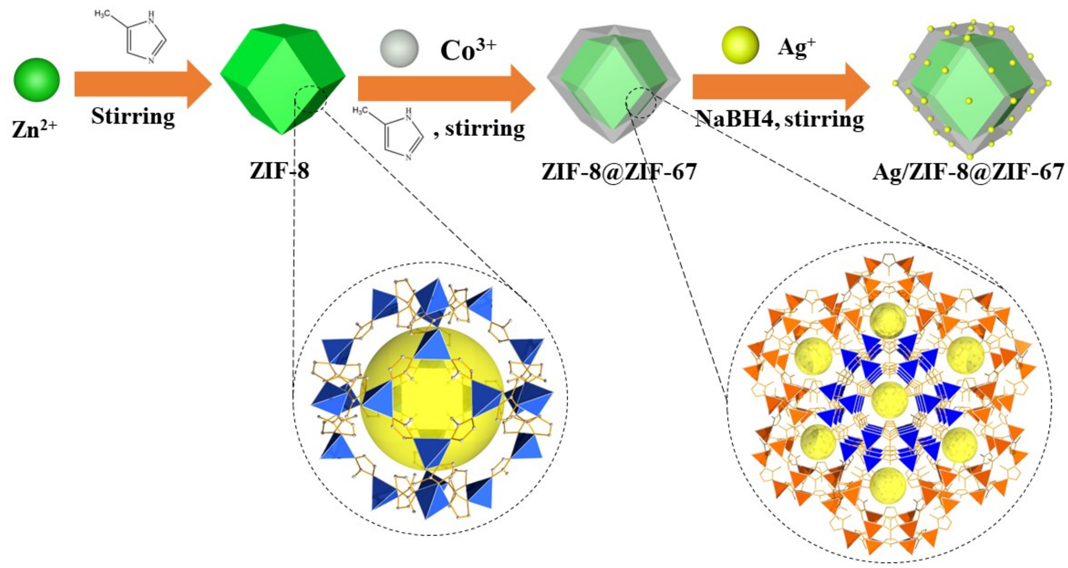

Figure S1 Schematic illustration of the preparation and structure of materials.

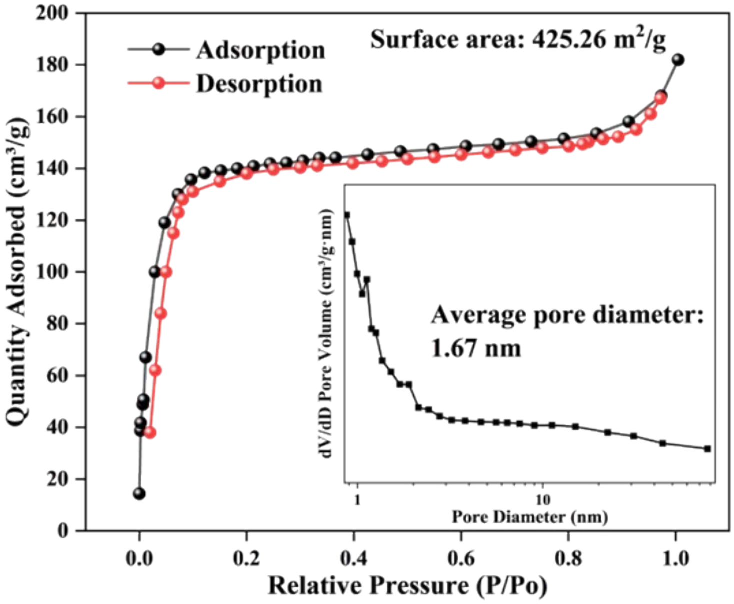

Figure S2 N_2 adsorption-desorption isotherms of Ag/ZIF-8@ZIF-67.

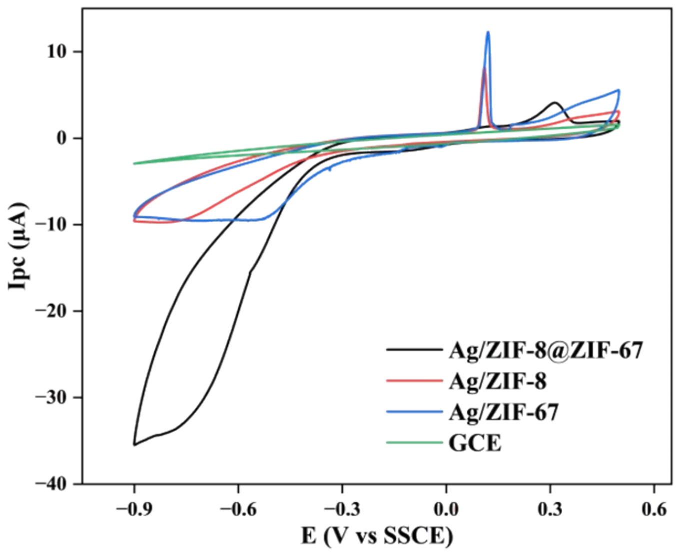

Figure S3 CV responses of different electrodes in a solution without 2,6-DCNP.

As shown in Figure S3, in the absence of 2,6-DCNP in the solution, the CV curves of the four electrodes exhibit no reduction peak near -0.75 V. This result confirmed that the distinct reduction peak observed around -0.75 V in Figure 3a was attributed by 2,6-DCNP rather than an effect originating from the modification materials themselves.

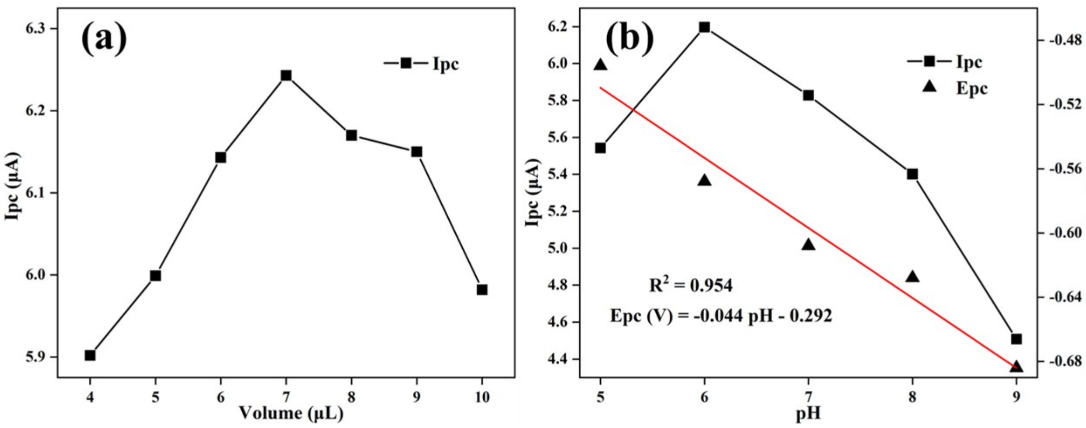

Figure S4 (a) The optimization tests of the amount of Ag/ZIF-8@ZIF-67 on GCE; (b) the pH value of the detection solution. The concentration of 2,6-DCNP is 20 mg/L in (a) and (b).

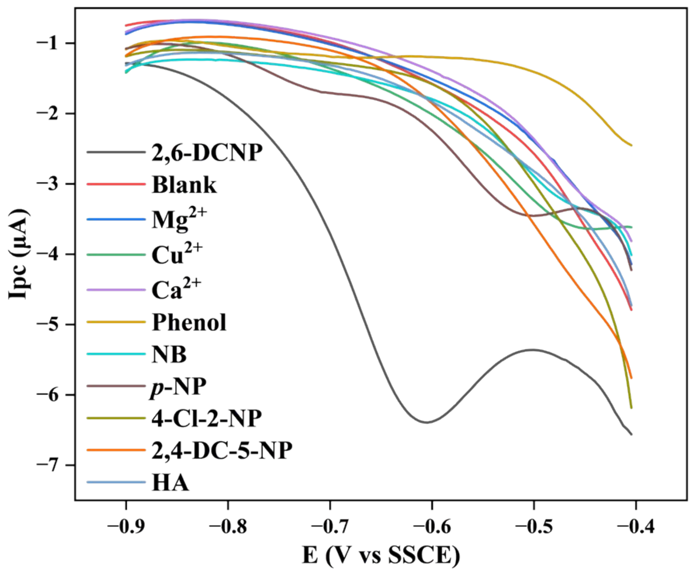

Figure S5 The impact of different interfering substances in the solution on the CV plots of the Ag/ZIF-8@ZIF-67 electrode.

As shown in Figure S4, CV tests were conducted by adding various interfering substances (Mg^{2+}, Cu^{2+}, Ca^{2+}, phenol, NB, P-NP, 4-Cl-2-NP, 2,4-DC-5-NP, HA) to the solution. These interferents did not generate reduction peaks or exhibited low reduction peak responses near -0.75V. This indicated that the electrode possesses strong interference resistance.

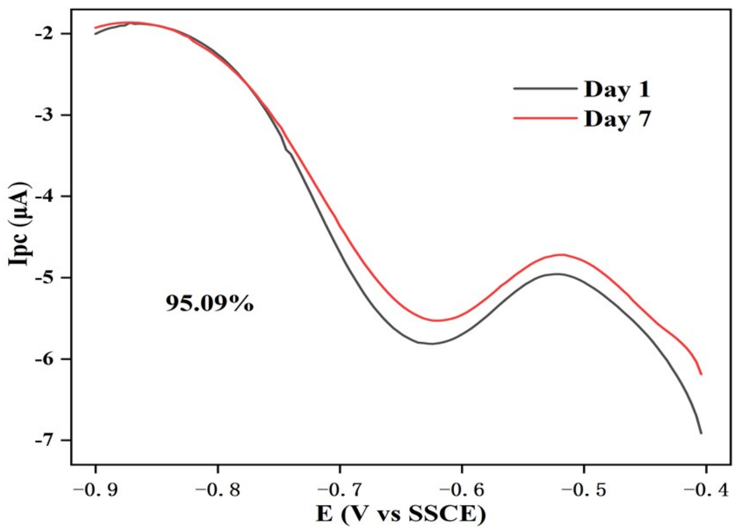

Figure S6 The stability results of Ag/ZIF-8@ZIF-67 electrode after storage in environmental conditions for 7 days.

Reference

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