

Supplementary data

Silver modified LDH/GCN heterostructures for visible-light degradation of estrogens

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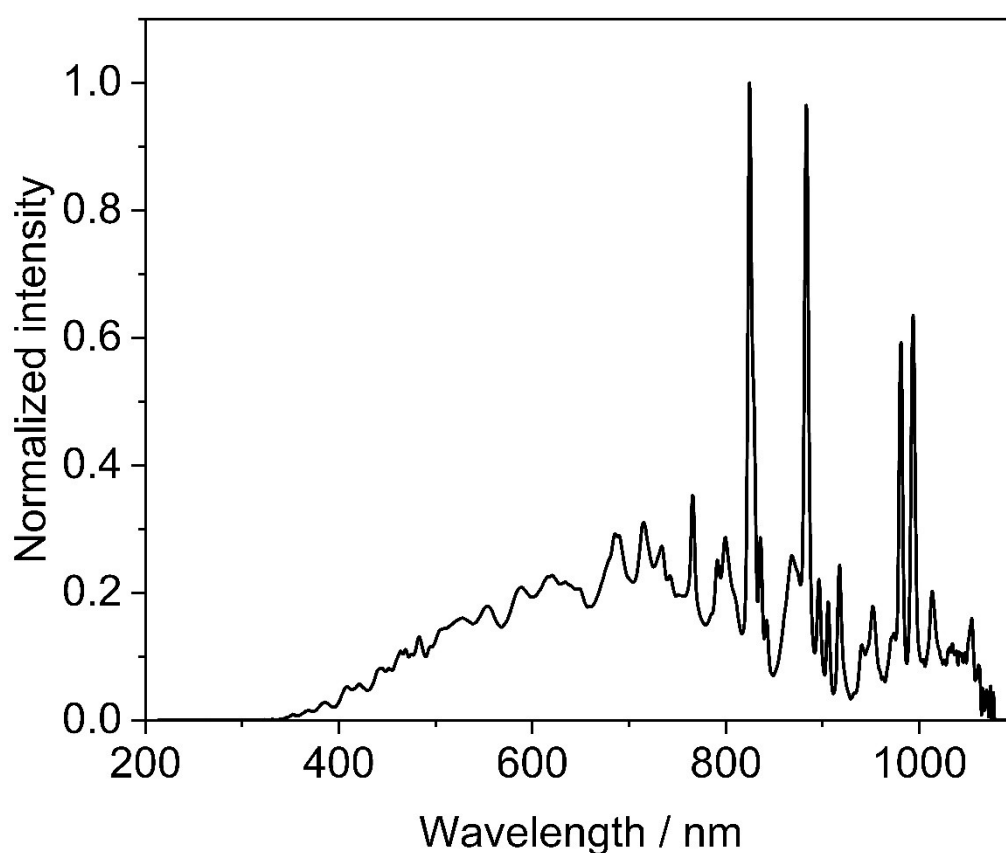


Figure S1. Spectrum of polychromatic light used for measurements of photocurrent response.

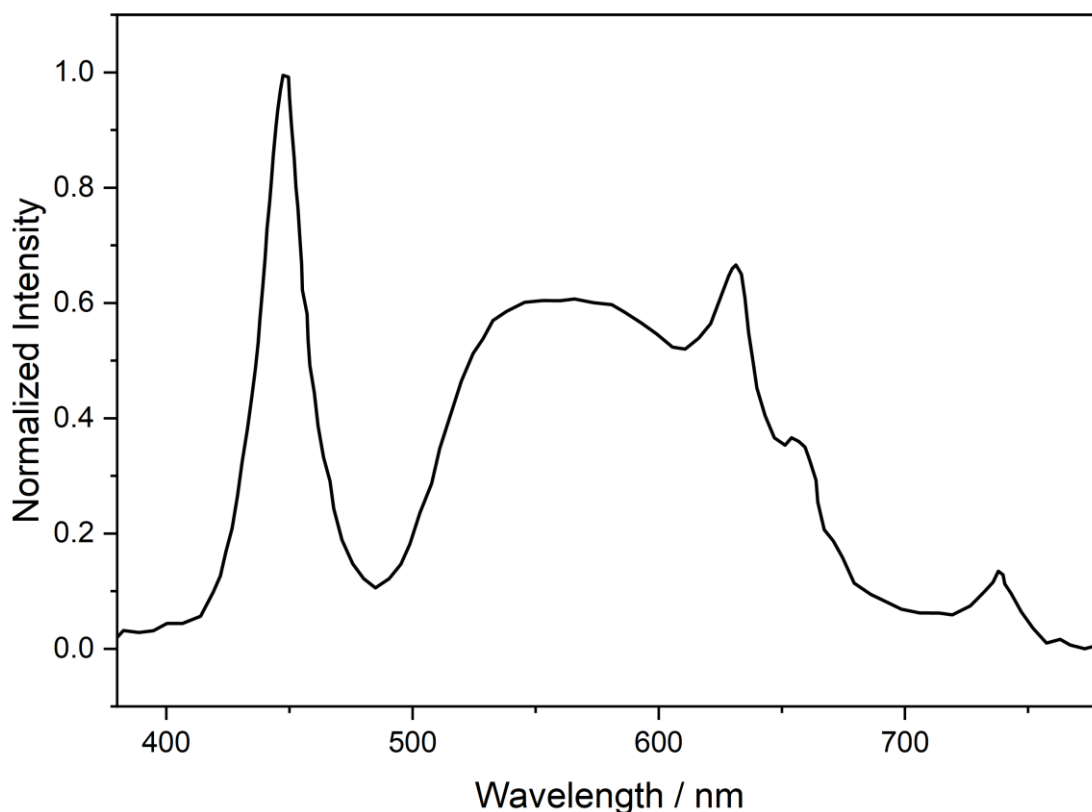


Figure S2. Spectrum of LED lamp used for photocatalytic experiments.

HPLC measurements conditions

Chromatographic separation was carried out on a Shim-pack Scepter C18-120 HPLC column (3.0 μm , 150 mm x 4.6 mm), protected by an ARION guard system (3.0 μm , 5 mm cartridges). The column temperature was set to 40°C. The mobile phase used was a mixture of acetonitrile and water in a 60:40 volume ratio.. The flow rate was equal to 1.0 mL/min, and the injection volume was 100 μL . The UV-Vis detector wavelength was set to 280 nm. The retention times for ethinylestradiol and estrone in these conditions were 4.25 and 4.7 min, respectively.

Table S1. Chemical data based on the XRF and CHN analyses for the studied materials.

Material	XRF							CHN			
	ZnO (wt. %)	Cr ₂ O ₃ (wt. %)	Ag ₂ O (wt. %)	Assumed Zn/Cr ratio	Measured Zn/Cr ratio	Assumed Ag/Zn ratio	Measured Ag/Zn ratio	C (wt. %)	N (wt. %)	Measured N/C ratio	GCN (wt. %)
0.5-Ag-LDH/GCN	53.70	25.95	0.24	2.00	2.43	0.005	0.005	15.59	26.89	1.72	42.65
1.0-Ag-LDH/GCN	55.66	26.21	0.43	2.00	2.49	0.010	0.009	16.41	28.45	1.73	45.16
5.0-Ag-LDH/GCN	53.96	25.61	2.01	2.00	2.47	0.053	0.043	16.29	28.21	1.73	44.78
10.0-Ag-LDH/GCN	51.74	25.21	4.25	2.00	2.41	0.111	0.095	17.05	29.67	1.74	47.14
1.0-Ag-LDH	45.69	33.14	0.30	2.00	1.62	0.010	0.008	2.06	0.77	0.38	0.00
GCN	-	-	-	-	-	-	-	34.74	62.13	1.79	100.00

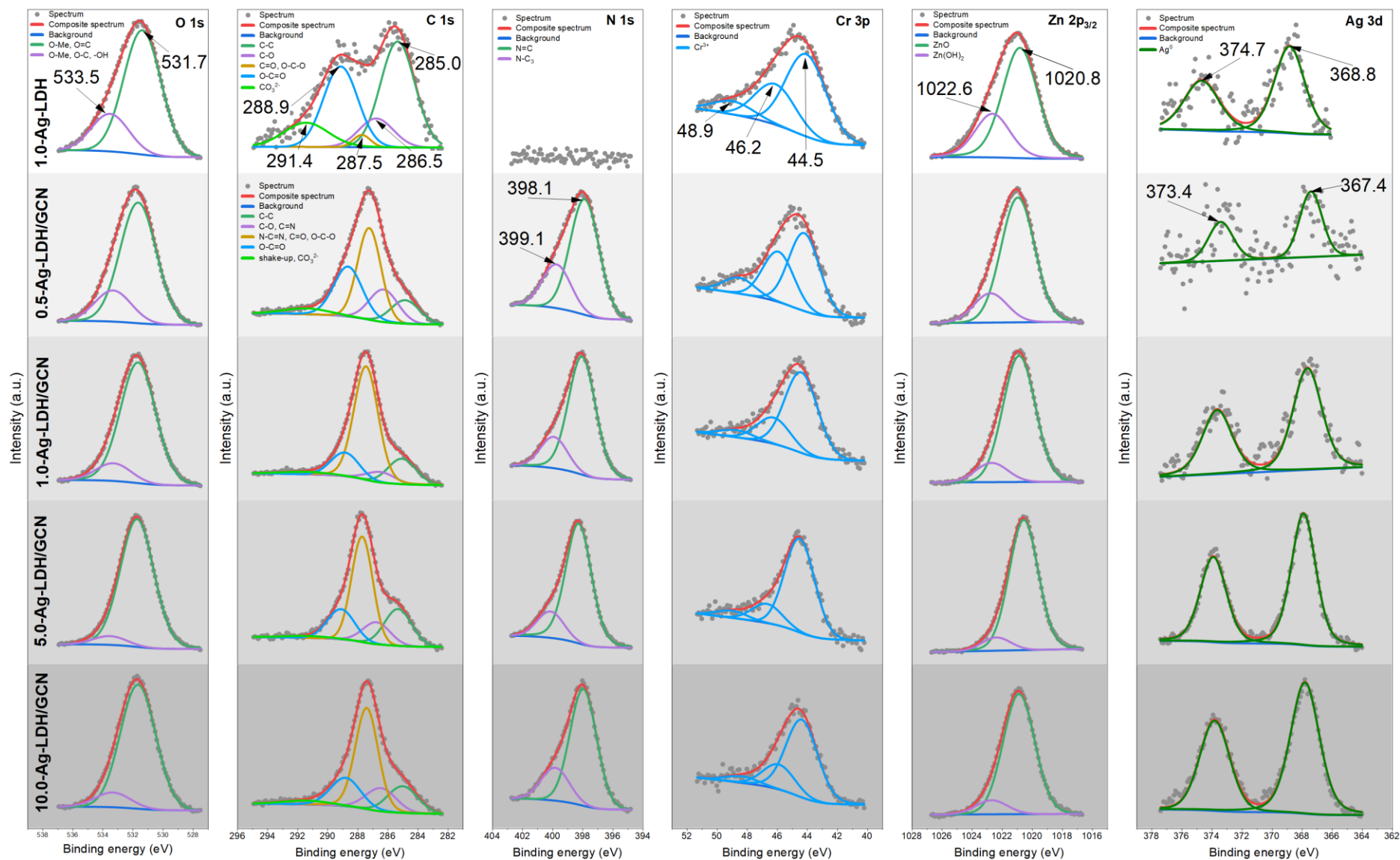


Figure S3. XPS spectra of O 1s, C 1s, N 1s, Cr 3p, Zn 2p_{3/2} and Ag 3d for the 1.0-Ag-LDH, 0.5-Ag-LDH/GCN, 1.0-Ag-LDH/GCN, 5.0-Ag-LDH/GCN and 10.0-Ag-LDH/GCN materials.

Table S2. Surface composition (atomic %) based on XPS analyses for all tested samples.

Sample	C (at. %)	N (at. %)	O (at. %)	Cr (at. %)	Zn (at. %)	Ag (at. %)	Zn/Cr ratio	Ag/Zn ratio	N/C ratio
1.0-Ag-LDH	11.5	0.0	53.6	12.1	14.1	0.1	1.17	0.01	0.00
0.5-Ag-LDH/GCN	24.3	21.0	34.6	5.2	9.4	0.0	1.81	0.00	0.86
1.0-Ag-LDH/GCN	25.8	25.6	30.6	4.2	8.4	0.1	2.00	0.01	0.99
5.0-Ag-LDH/GCN	21.3	20.0	36.2	4.8	9.5	0.5	1.98	0.05	0.94
10.0-Ag-LDH/GCN	23.9	20.7	34.0	4.9	9.7	0.6	1.98	0.06	0.87

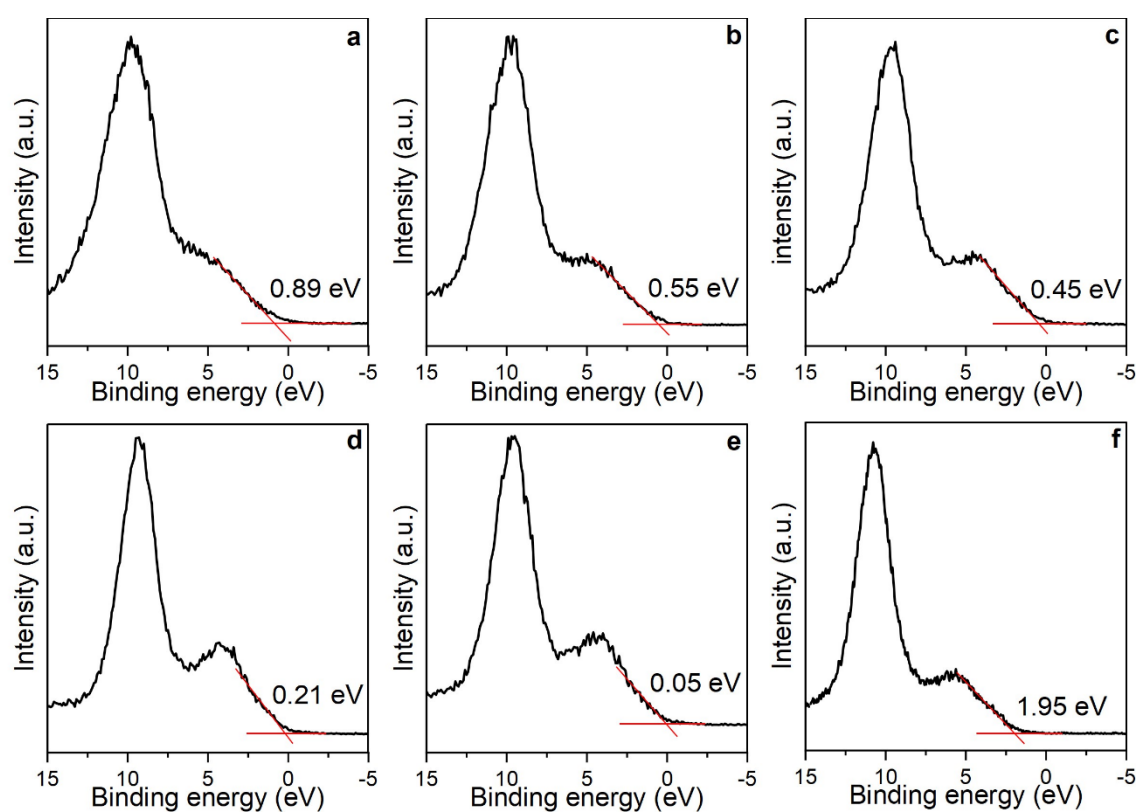


Figure S4. The VB-XPS of the (a) 1.0-Ag-LDH, (b) 0.5-Ag-LDH/GCN, (c) 1.0-Ag-LDH/GCN, (d) 5.0-Ag-LDH/GCN, (e) 10.0-Ag-LDH/GCN and (f) LDH/GCN.

Table S3. C/C₀ (-) values with standard deviations calculated in photocatalytic experiments for all tested materials.

E1 single pollutant tests																				
Material	Time (min)	-10	0	SD	5	SD	10	SD	15	SD	20	SD	25	SD	30	SD	35	SD	40	SD
0.5-Ag-LDH/GCN	1	0.9755	0.0028	0.7521	0.0013	0.5655	0.0024	0.4038	0.0013	0.3070	0.0022	0.2038	0.0039	0.1354	0.0010	0.0917	0.0054	0.0714	0.0037	
1.0-Ag-LDH/GCN	1	0.9582	0.0025	0.6934	0.0019	0.5023	0.0001	0.3340	0.0004	0.2098	0.0000	0.1175	0.0021	0.0499	0.0015	0.0315	0.0004	b.d.	-	
5.0-Ag-LDH/GCN	1	0.9673	0.0001	0.7256	0.0003	0.5459	0.0040	0.4194	0.0039	0.2922	0.0019	0.1987	0.0034	0.1264	0.0061	0.0785	0.0071	0.0517	0.0095	
10.0-Ag-LDH/GCN	1	0.9520	0.0011	0.7698	0.0006	0.6295	0.0005	0.4913	0.0013	0.3892	0.0008	0.2978	0.0014	0.2171	0.0058	0.1495	0.0070	0.0928	0.0072	
1.0-Ag-LDH	1	0.9969	0.0005	0.9963	0.0002	0.9911	0.0029	0.9902	0.0023	0.9896	0.0022	0.9882	0.0018	0.9869	0.0010	0.9819	0.0042	0.9797	0.0034	
LDH/GCN	1	0.9697	0.0006	0.8679	0.0019	0.8077	0.0003	0.7233	0.0011	0.6478	0.0024	0.5739	0.0009	0.5098	0.0024	0.4408	0.0017	0.3844	0.0012	
GCN	1	0.9530	0.0036	0.8938	0.0002	0.8345	0.0017	0.7858	0.0030	0.7255	0.0018	0.6845	0.0009	0.6229	0.0011	0.5763	0.0008	0.5237	0.0002	
EE2 single pollutant tests																				
Material	Time (min)	-10	0	SD	5	SD	10	SD	15	SD	20	SD	25	SD	30	SD	35	SD	40	SD
0.5-Ag-LDH/GCN	1	0.9705	0.0013	0.7563	0.0013	0.5762	0.0001	0.4378	0.0010	0.3090	0.0015	0.2053	0.0002	0.1210	0.0013	0.0606	0.0003	0.0219	0.0007	
1.0-Ag-LDH/GCN	1	0.9580	0.0007	0.7027	0.0022	0.5150	0.0024	0.3604	0.0006	0.2306	0.0002	0.1280	0.0004	0.0593	0.0001	0.0222	0.0002	0.0052	0.0005	
5.0-Ag-LDH/GCN	1	0.9935	0.0034	0.9567	0.0051	0.7422	0.0030	0.4358	0.0027	0.3095	0.0026	0.1954	0.0020	0.1183	0.0009	0.0564	0.0002	0.0185	0.0000	
10.0-Ag-LDH/GCN	1	0.9554	0.0019	0.7704	0.0025	0.6374	0.0003	0.5147	0.0004	0.4059	0.0012	0.3528	0.0230	0.2134	0.0012	0.1416	0.0013	0.0847	0.0003	
1.0-Ag-LDH	1	0.9835	0.0031	0.9826	0.0025	0.9796	0.0015	0.9766	0.0032	0.9750	0.0020	0.9745	0.0022	0.9741	0.0023	0.9729	0.0012	0.9707	0.0001	
LDH/GCN	1	0.9386	0.0001	0.8462	0.0008	0.7565	0.0013	0.6074	0.0010	0.4832	0.0001	0.4647	0.0012	0.4219	0.0003	0.3570	0.0005	0.2996	0.0004	
GCN	1	0.9469	0.0021	0.8911	0.0009	0.8359	0.0001	0.7684	0.0006	0.7000	0.0004	0.6573	0.0005	0.6102	0.0001	0.5560	0.0001	0.4991	0.0001	
E1 dual pollutant tests																				
Material	Time (min)	-10	0	SD	5	SD	10	SD	15	SD	20	SD	25	SD	30	SD	35	SD	40	SD
0.5-Ag-LDH/GCN	1	0.9692	0.0005	0.8402	0.0074	0.7135	0.0060	0.5993	0.0035	0.5407	0.0051	0.4635	0.0038	0.3938	0.0001	0.3251	0.0070	0.2676	0.0035	
1.0-Ag-LDH/GCN	1	0.9746	0.0004	0.8241	0.0014	0.7059	0.0027	0.5990	0.0013	0.5101	0.0003	0.4318	0.0028	0.3580	0.0041	0.3062	0.0057	0.2538	0.0080	
5.0-Ag-LDH/GCN	1	0.9717	0.0009	0.8138	0.0002	0.7032	0.0031	0.6120	0.0020	0.5301	0.0015	0.4536	0.0031	0.3984	0.0017	0.3438	0.0018	0.3056	0.0043	
10.0-Ag-LDH/GCN	1	0.9772	0.0026	0.8514	0.0063	0.7600	0.0063	0.6779	0.0069	0.5978	0.0076	0.5280	0.0069	0.4631	0.0089	0.3975	0.0077	0.3348	0.0095	
1.0-Ag-LDH	1	0.9982	0.0026	0.9927	0.0039	0.9878	0.0019	0.9912	0.0035	0.9909	0.0021	0.9923	0.0014	0.9908	0.0075	0.9884	0.0029	0.9933	0.0046	
LDH/GCN	1	0.9752	0.0005	0.8844	0.0028	0.8258	0.0023	0.7397	0.0024	0.6647	0.0005	0.6067	0.0029	0.5468	0.0047	0.4847	0.0017	0.4343	0.0066	
GCN	1	0.9730	0.0005	0.9138	0.0014	0.8696	0.0034	0.8328	0.0030	0.7910	0.0023	0.7554	0.0008	0.7101	0.0009	0.6862	0.0019	0.6474	0.0003	
EE2 dual pollutant tests																				
Material	Time (min)	-10	0	SD	5	SD	10	SD	15	SD	20	SD	25	SD	30	SD	35	SD	40	SD
0.5-Ag-LDH/GCN	1	0.9631	0.0008	0.8492	0.0023	0.7551	0.0212	0.6350	0.0115	0.5726	0.0003	0.4762	0.0120	0.4199	0.0023	0.3530	0.0128	0.2816	0.0105	
1.0-Ag-LDH/GCN	1	0.9683	0.0091	0.8537	0.0122	0.7564	0.0149	0.6354	0.0050	0.5412	0.0006	0.4575	0.0008	0.3809	0.0001	0.3308	0.0050	0.2656	0.0016	
5.0-Ag-LDH/GCN	1	0.9740	0.0088	0.8383	0.0011	0.7361	0.0061	0.6527	0.0010	0.5753	0.0071	0.4995	0.0016	0.4354	0.0032	0.3815	0.0083	0.3347	0.0045	
10.0-Ag-LDH/GCN	1	0.9718	0.0138	0.8756	0.0060	0.8131	0.0250	0.7231	0.0063	0.6445	0.0026	0.5719	0.0041	0.5059	0.0060	0.4350	0.0023	0.3645	0.0029	
1.0-Ag-LDH	1	0.9994	0.0001	0.9926	0.0005	0.9890	0.0015	0.9873	0.0024	0.9864	0.0023	0.9854	0.0022	0.9842	0.0026	0.9839	0.0028	0.9799	0.0005	
LDH/GCN	1	0.9699	0.0040	0.8889	0.0041	0.8409	0.0003	0.7595	0.0007	0.6901	0.0026	0.6318	0.0020	0.5731	0.0048	0.5129	0.0021	0.4567	0.0001	
GCN	1	0.9740	0.0037	0.9259	0.0012	0.8799	0.0059	0.8528	0.0070	0.8089	0.0036	0.7778	0.0007	0.7277	0.0003	0.7067	0.0026	0.6686	0.0012	

Table S4. C/C_0 (-) values with standard deviations calculated in adsorption experiments for all tested materials.

E1 single pollutant tests											
Material \ Time (min)	0	10	SD	20	SD	30	SD	40	SD	50	SD
0.5-Ag-LDH/GCN	1	0.9656	0.0029	0.9697	0.0031	0.9623	0.0019	0.9691	0.0001	0.9722	0.0024
1.0-Ag-LDH/GCN	1	0.9690	0.0014	0.9673	0.0018	0.9638	0.0004	0.9662	0.0035	0.9591	0.0023
5.0-Ag-LDH/GCN	1	0.9621	0.0020	0.9612	0.0001	0.9680	0.0001	0.9640	0.0008	0.9545	0.0013
10.0-Ag-LDH/GCN	1	0.9637	0.0027	0.9639	0.0019	0.9581	0.0004	0.9666	0.0036	0.9551	0.0048
1.0-Ag-LDH	1	0.9970	0.0013	0.9987	0.0024	0.9926	0.0020	0.9947	0.0034	0.9856	0.0030
LDH/GCN	1	0.9569	0.0024	0.9793	0.0057	0.9707	0.0009	0.9798	0.0001	0.9753	0.0021
GCN	1	0.9679	0.0018	0.9710	0.0028	0.9694	0.0022	0.9665	0.0021	0.9776	0.0001
EE2 single pollutant tests											
Material \ Time (min)	0	10	SD	20	SD	30	SD	40	SD	50	SD
0.5-Ag-LDH/GCN	1	0.9762	0.0015	0.9647	0.0005	0.9699	0.0011	0.9661	0.0008	0.9542	0.0020
1.0-Ag-LDH/GCN	1	0.9640	0.0049	0.9596	0.0001	0.9570	0.0014	0.9509	0.0008	0.9629	0.0007
5.0-Ag-LDH/GCN	1	0.9601	0.0006	0.9552	0.0002	0.9533	0.0013	0.9560	0.0010	0.9620	0.0009
10.0-Ag-LDH/GCN	1	0.9684	0.0006	0.9630	0.0008	0.9594	0.0014	0.9445	0.0043	0.9526	0.0013
1.0-Ag-LDH	1	0.9577	0.0011	0.9574	0.0019	0.9395	0.0017	0.9597	0.0008	0.9456	0.0009
LDH/GCN	1	0.9412	0.0020	0.9456	0.0016	0.9577	0.0060	0.9569	0.0010	0.9579	0.0015
GCN	1	0.9471	0.0006	0.9436	0.0001	0.9469	0.0004	0.9434	0.0010	0.9433	0.0011
E1 dual pollutant tests											
Material \ Time (min)	0	10	SD	20	SD	30	SD	40	SD	50	SD
0.5-Ag-LDH/GCN	1	0.9613	0.0019	0.9776	0.0054	0.9594	0.0035	0.9680	0.0010	0.9618	0.0028
1.0-Ag-LDH/GCN	1	0.9668	0.0045	0.9739	0.0018	0.9724	0.0037	0.9693	0.0021	0.9676	0.0018
5.0-Ag-LDH/GCN	1	0.9590	0.0014	0.9703	0.0004	0.9668	0.0038	0.9666	0.0001	0.9612	0.0032
10.0-Ag-LDH/GCN	1	0.9990	0.0001	0.9978	0.0003	0.9974	0.0001	0.9944	0.0003	0.9936	0.0008
1.0-Ag-LDH	1	0.9909	0.0006	0.9860	0.0031	0.9882	0.0018	0.9870	0.0003	0.9836	0.0016
LDH/GCN	1	0.9721	0.0005	0.9744	0.0024	0.9736	0.0042	0.9719	0.0022	0.9743	0.0028
GCN	1	0.9551	0.0023	0.9518	0.0009	0.9546	0.0035	0.9584	0.0001	0.9659	0.0010
EE2 dual pollutant tests											
Material \ Time (min)	0	10	SD	20	SD	30	SD	40	SD	50	SD
0.5-Ag-LDH/GCN	1	0.9429	0.0071	0.9507	0.0034	0.9375	0.0060	0.9526	0.0046	0.9496	0.0016
1.0-Ag-LDH/GCN	1	0.9697	0.0040	0.9613	0.0090	0.9548	0.0082	0.9630	0.0024	0.9660	0.0021
5.0-Ag-LDH/GCN	1	0.9350	0.0009	0.9503	0.0007	0.9482	0.0002	0.9459	0.0022	0.9411	0.0013
10.0-Ag-LDH/GCN	1	0.9457	0.0054	0.9597	0.0106	0.9578	0.0106	0.9598	0.0080	0.9592	0.0043
1.0-Ag-LDH	1	0.9874	0.0033	0.9720	0.0009	0.9797	0.0010	0.9760	0.0016	0.9721	0.0026
LDH/GCN	1	0.9639	0.0039	0.9660	0.0048	0.9662	0.0025	0.9650	0.0010	0.9640	0.0041
GCN	1	0.9485	0.0009	0.9470	0.0042	0.9532	0.0001	0.9495	0.0017	0.9625	0.0017

Table S5. Values of the degradation rate calculated for E1 and EE2 for all tested materials.

Degradation rate k (1/min)		
Material	E1	EE2
0.5-Ag-LDH/GCN	0.0598	0.0583
1.0-Ag-LDH/GCN	0.0776	0.0736
5.0-Ag-LDH/GCN	0.0605	0.0578
10.0-Ag-LDH/GCN	0.0451	0.0410
1.0-Ag-LDH	0.0004	0.0004
LDH/GCN	0.0203	0.0291
GCN	0.0133	0.0144

Table S6. C/C₀ (-) values with standard deviations calculated in dual pollutant tests for 1.0-Ag-LDH/GCN at different pH_{in} values.

E1 dual pollutant tests																			
pH \ Time (min)	-10	0	SD	5	SD	10	SD	15	SD	20	SD	25	SD	30	SD	35	SD	40	SD
4	1	0.9812	0.0070	0.8519	0.0189	0.7553	0.0175	0.6719	0.0181	0.5913	0.0185	0.5004	0.0170	0.4630	0.0170	0.4035	0.0129	0.3178	0.0062
6	1	0.9933	0.0044	0.8582	0.0008	0.7405	0.0001	0.6269	0.0008	0.5365	0.0012	0.4220	0.0022	0.2992	0.0031	0.2393	0.0024	0.1743	0.0014
8	1	0.9797	0.0010	0.7469	0.0004	0.5475	0.0009	0.4048	0.0015	0.2825	0.0004	0.1822	0.0005	0.1099	0.0004	0.0561	0.0038	0.0284	0.0000
10	1	0.9488	0.0019	0.6446	0.0014	0.4342	0.0001	0.2978	0.0016	0.1808	0.0005	0.0611	0.0007	0.0217	0.0018	0.0022	0.0008	0.0000	0.0000
EE2 dual pollutant tests																			
pH \ Time (min)	-10	0	SD	5	SD	10	SD	15	SD	20	SD	25	SD	30	SD	35	SD	40	SD
4	1	0.9663	0.0122	0.8724	0.0180	0.7805	0.0113	0.7081	0.0055	0.6252	0.0055	0.5352	0.0030	0.4955	0.0015	0.4360	0.0039	0.4148	0.0119
6	1	0.9937	0.0111	0.8797	0.0034	0.7806	0.0075	0.6648	0.0104	0.5731	0.0035	0.4712	0.0003	0.3419	0.0016	0.2787	0.0009	0.2128	0.0012
8	1	0.9768	0.0245	0.7793	0.0190	0.5929	0.0185	0.4599	0.0215	0.3409	0.0233	0.2371	0.0207	0.1656	0.0276	0.1034	0.0269	0.0769	0.0250
10	1	0.9503	0.0026	0.6716	0.0036	0.4742	0.0048	0.3397	0.0037	0.2209	0.0068	0.0926	0.0118	0.0377	0.0068	0.0129	0.0065	0.0084	0.0023

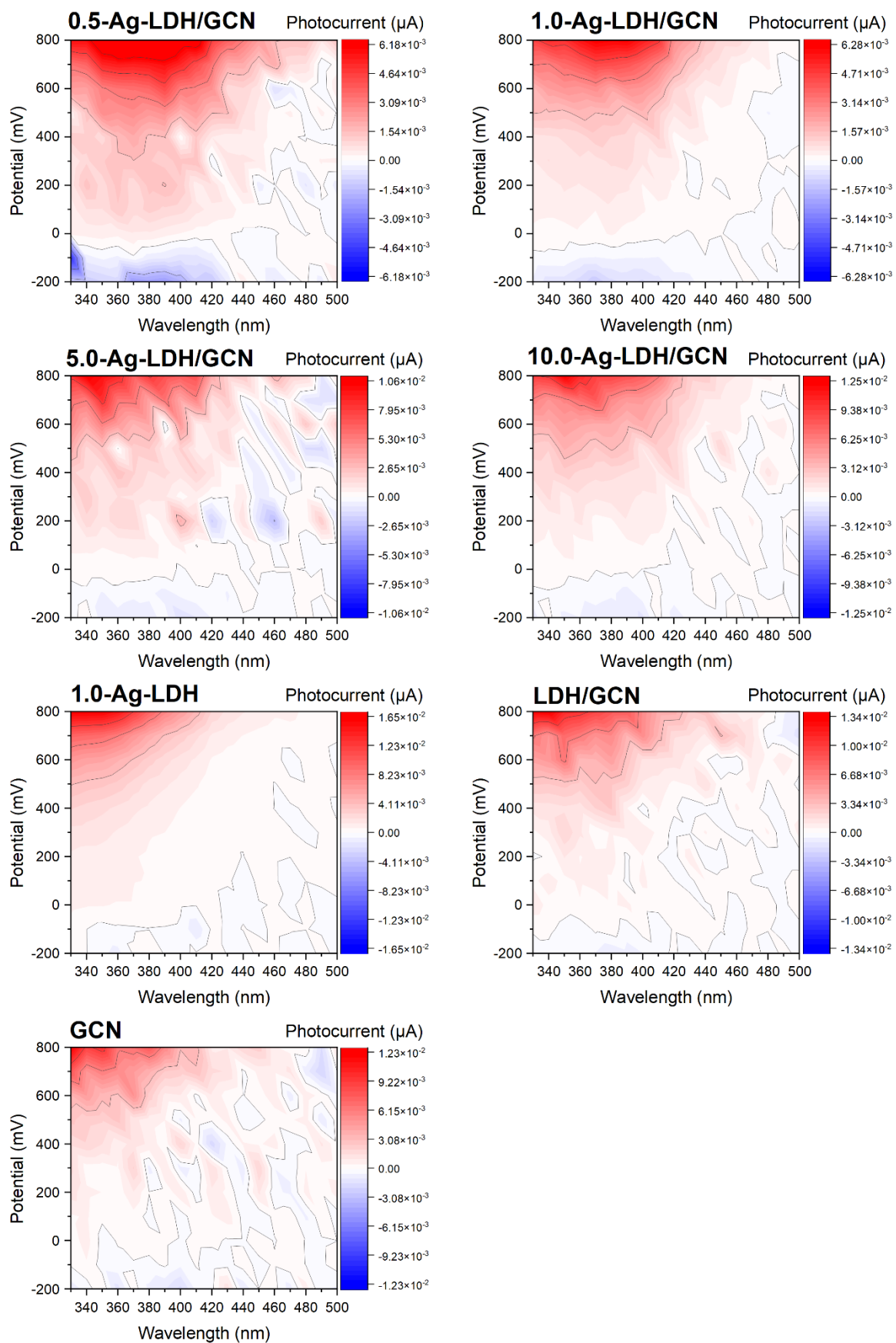


Figure S5. The maps showing the dependence of materials' photocurrent density on the applied potential and wavelength.

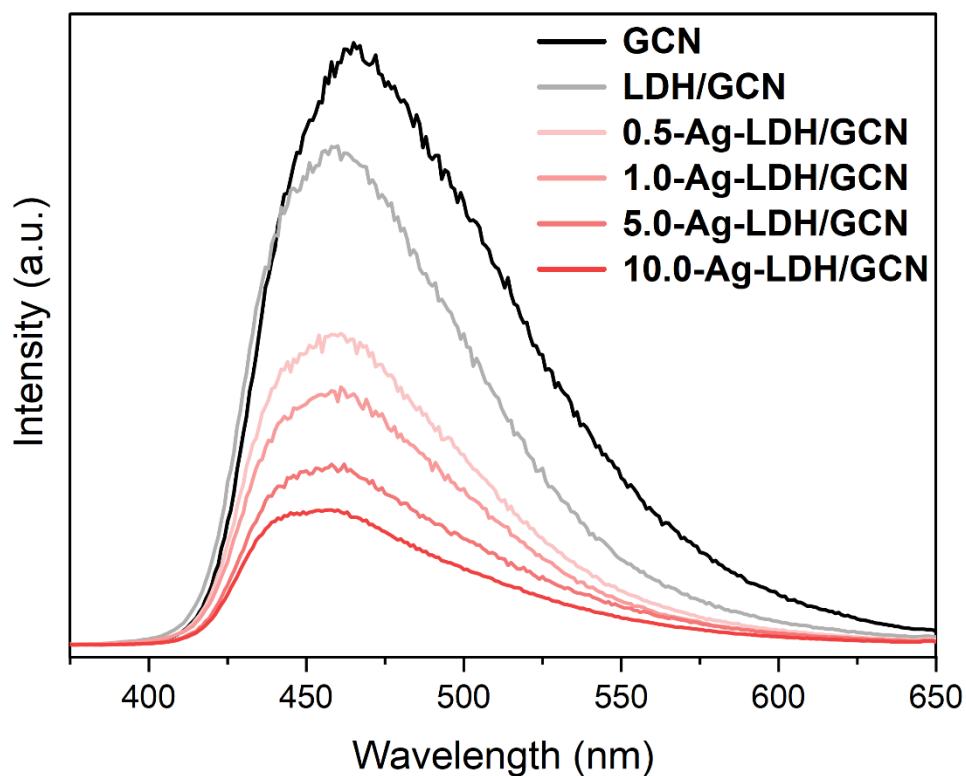


Figure S6. PL spectra of the obtained materials.

Table S7. Emission Decay Components from the time-resolved fluorescence measurements.

0.5-Ag-LDH/GCN	1.0-Ag-LDH/GCN	5.0-Ag-LDH/GCN	10.0-Ag-LDH/GCN	1.0-Ag-LDH	GCN	LDH/GCN
τ_1 1.91 ns τ_1	1.86 ns τ_1	1.71 ns τ_1	1.89 ns τ_1	2.35 ns τ_1	1.97 ns τ_1	1.91 ns
A_1 4.49E-02 A_1	8.68E-02 A_1	6.06E-02 A_1	3.60E-02 A_1	5.53E-02 A_1	4.14E-02 A_1	4.41E-02
τ_2 7.16 ns τ_2	7.80 ns τ_2	6.79 ns τ_2	6.85 ns τ_2	9.16 ns τ_2	6.60 ns τ_2	6.95 ns
A_2 7.29E-03 A_2	4.22E-03 A_2	8.36E-03 A_2	6.74E-03 A_2	7.06E-03 A_2	8.43E-03 A_2	7.62E-03
τ_3 47.04 ns τ_3	55.12 ns τ_3	42.52 ns τ_3	39.66 ns τ_3	57.90 ns τ_3	35.69 ns τ_3	40.57 ns
A_3 9.21E-04 A_3	7.92E-04 A_3	1.37E-03 A_3	1.33E-03 A_3	1.56E-03 A_3	1.08E-03 A_3	8.64E-04
χ^2 1.07421 χ^2	1.07495 χ^2	1.09107 χ^2	1.04114 χ^2	1.04326 χ^2	1.11638 χ^2	1.02687 χ^2

The decay curves for all of the materials were fitted with the use of a three-exponential kinetic function (eq. 1), where τ_1 , τ_2 , and τ_3 are the charge carrier lifetimes, and A_1 , A_2 , and A_3 are the relative amplitudes of the decay species.

$$I(t) = A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2} + A_3 e^{-x/\tau_3} \quad (1)$$