Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Kinetics and Mechanism Effects of 2D Carbon Supports in Hydrogen Spillover Composites

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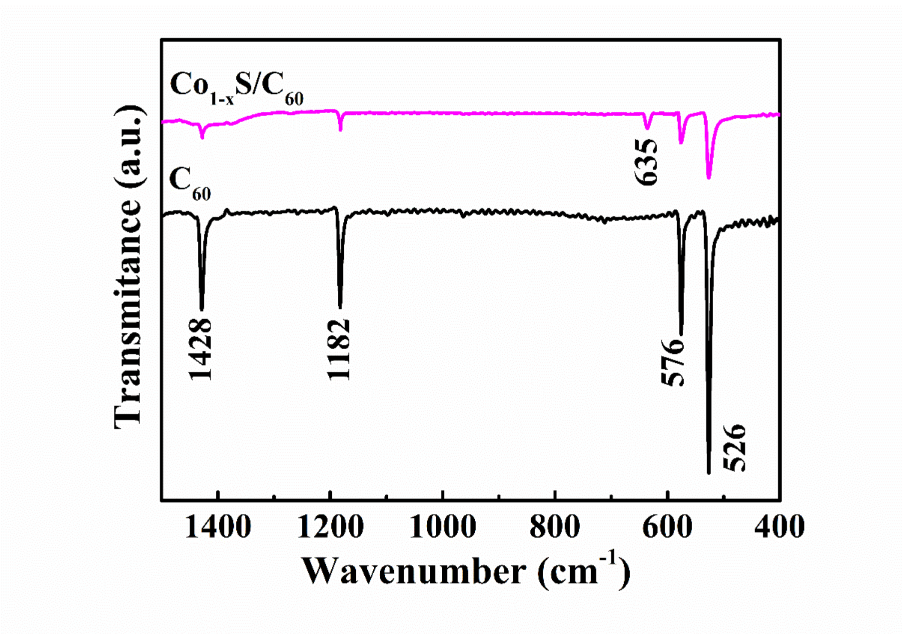

Fig. S1 Raman spectra of the raw C_{60} and $Co_{1-x}S/C_{60}$ composites.

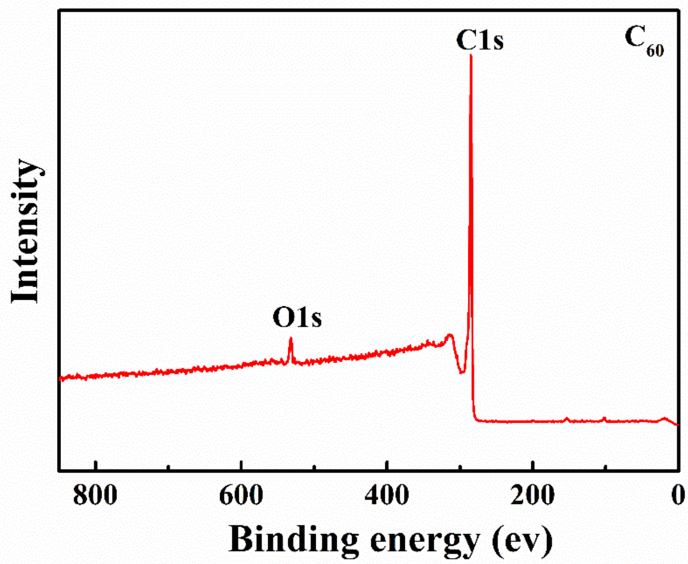

Fig. S2 XPS spectrum of the raw C_{60}.

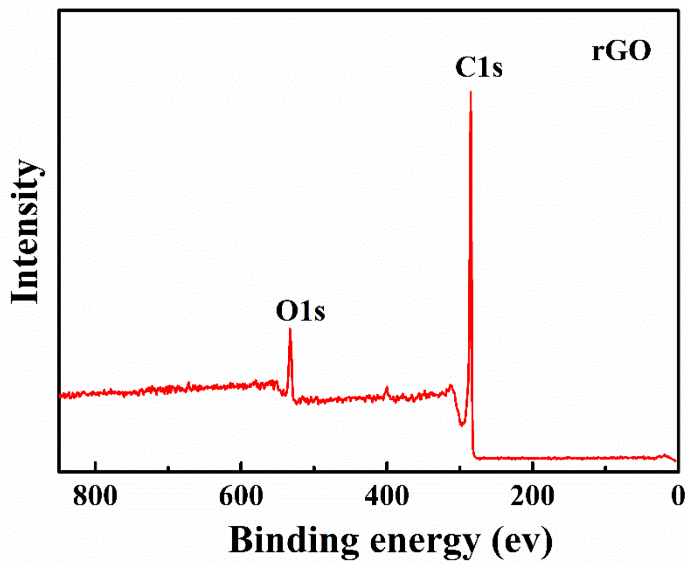

Fig. S3 XPS spectrum of the raw rGO.

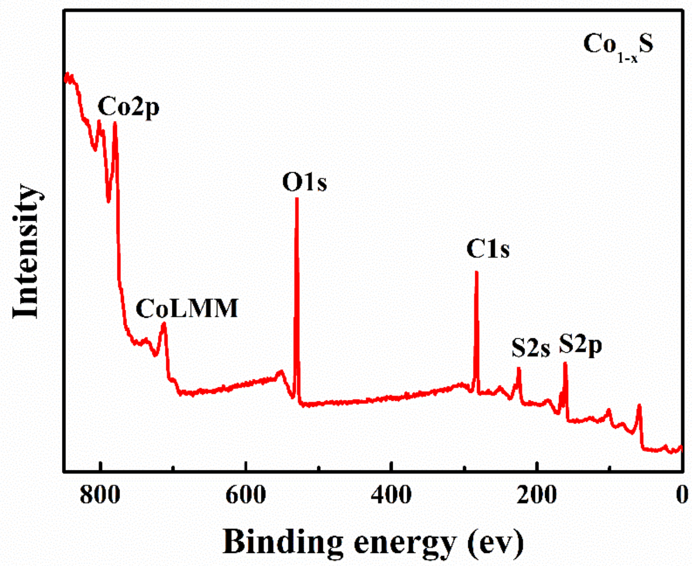

Fig. S4 XPS spectrum of the $Co_{1-x}S$.

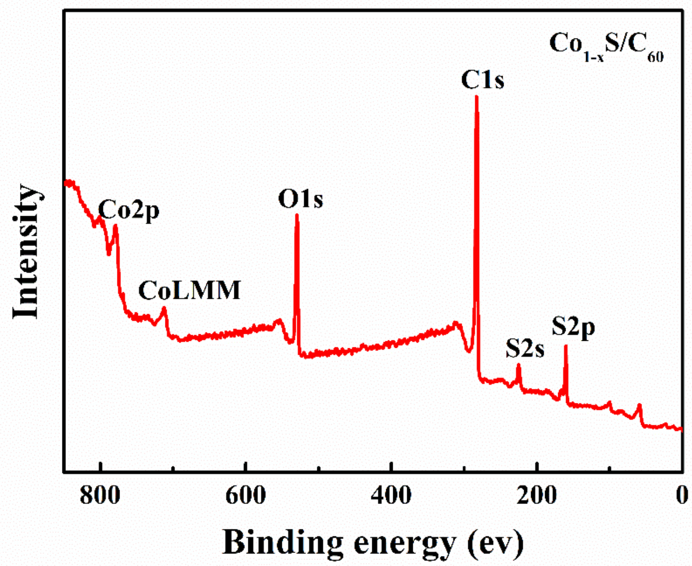

Fig. S5 XPS spectrum of the $Co_{1-x}S/C_{60}$ composites.

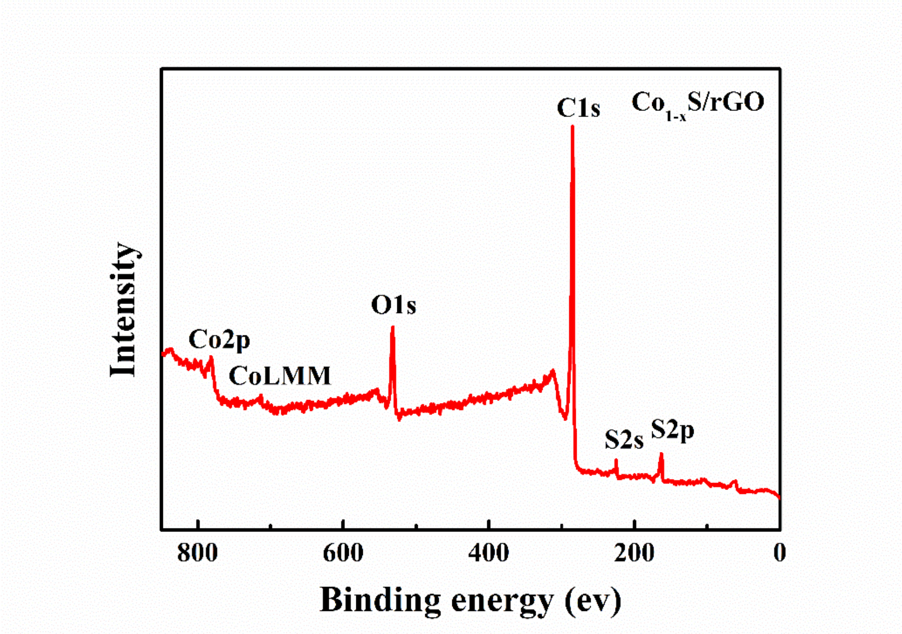

Fig. S6 XPS spectrum of the $Co_{1-x}S$/rGO composites.

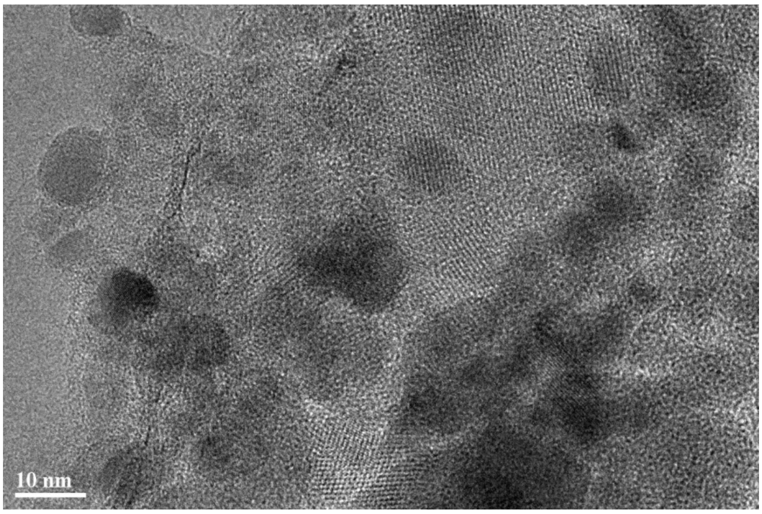

Fig. S7 HRTEM images of the $Co_{1-x}S/C_{60}$ composites.

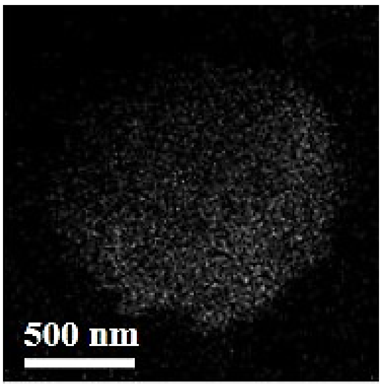

Fig. S8 EDS elemental mapping images of C in the $Co_{1-x}S/C_{60}$ composites.

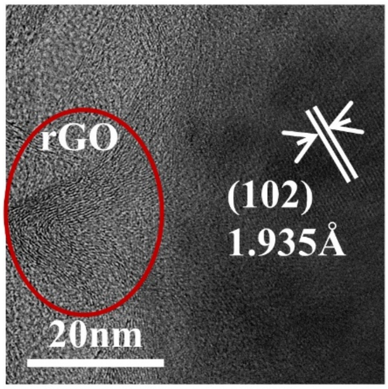

Fig. S9 HRTEM images of the $Co_{1-x}S$/rGO composites.

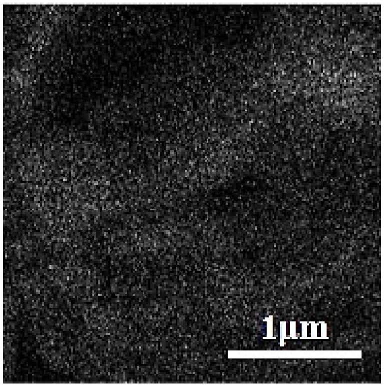

Fig. S10 EDS elemental mapping images of C in the $Co_{1-x}S$/rGO composites.

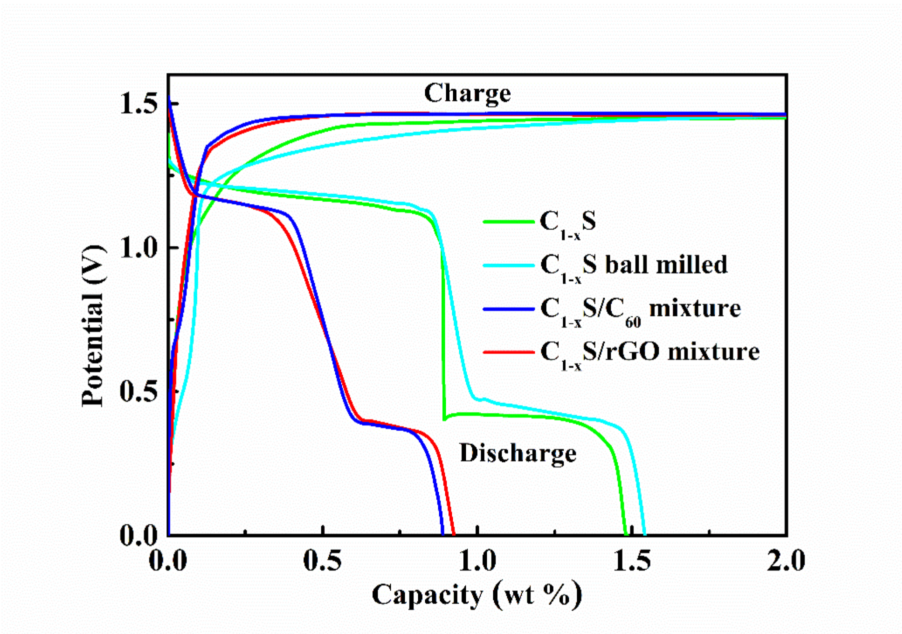

Fig. S11 Charge-discharge curves of the $Co_{1-x}S$ and $Co_{1-x}S$ ball milled for 10 h and $Co_{1-x}S/C_{60}$ and $Co_{1-x}S$/rGO mixtures.

Tab. S1 Hydrogen storage capacity retention ratios of the different samples.

Sample	Hydrogen storage capacity (wt %)	Capacity (wt %)/Ratio (%)		
		I voltage plateaus	II voltage plateaus	III voltage plateaus
C_{60}	0.50	——	——	——
rGO	0.31	——	——	——
$Co_{1-x}S$	1.49	0.89/59	——	0.60/41
$Co_{1-x}S$ ball milled	1.54	0.99/64	——	0.55/36
$Co_{1-x}S/C_{60}$ composites	4.36	0.78/18	2.57/59	1.00/23
$Co_{1-x}S/C_{60}$ mixture	0.94	0.59/63		0.35/37
$Co_{1-x}S$/rGO composites	5.02	0.50/10	2.71/54	1.81/36
$Co_{1-x}S$/rGO mixture	1.00	0.63/63		0.37/37

Tab. S2 Comparison of hydrogen storage capacity with other reported materials.

No	Materials	Hydrogen Storage Capacities (wt %)	Reference
1	Pd/B-rGO	0.33 wt %	[1]
2	$BaMoO_4$/ZnO-GO	0.79 wt %	[2]
3	Co_9S_8 + CoRGO	2.38 wt %	[3]
4	Ni-ZrO_2-rGO	1.54 wt %	[4]
5	C_{60}/Co	3.32 wt %	[5]
6	C_{60}/CoB	2.24 wt %	[6]
7	Pt-C_{60}	1.6 wt %	[7]
8	Na_6C_{60}	2.1 wt %	[8]
9	$Co_{1-x}S/C_{60}$ this work	4.36 wt %	----
10	$C_{1-x}S$/rGO this work	5.02 wt %	----

Tab. S3 Hydrogen storage capacities of the different samples.

Sample	Hydrogen storage Capacity (wt %)	Capacity after 50 Cycles (wt %)	Capacity retention Ratio (%)
$Co_{1-x}S$/rGO composites	5.02	4.41	88
$Co_{1-x}S/C_{60}$ composites	4.36	3.48	80
$Co_{1-x}S$ composites	1.49	0.90	64
rGO	0.30	——	——
C_{60}	0.50	——	——

Tab. S4 Comparison of CoS/C_{60} and CoS/rGO hydrogen absorption systems.

Items	CoS/C_{60}	CoS/rGO
H-H bond length for CoS-H_2	0.78 Å	
Adsorption energy for CoS-H_2	-6.9 kcal mol^{-1}	
H-H bond length for one H_2 adsorption	0.79 Å	0.78 Å
C-Co bond length for one H_2 adsorption	1.82 Å	1.70 Å
Adsorption energy when one H_2 is adsorbed	-29.4 kcal mol^{-1}	-15.5 kcal mol^{-1}
H-H bond length when spillover occurs	0.79 Å	0.79 Å
C-Co bond length for one H_2 adsorption	1.70 Å	1.69 Å
Adsorption energy when spillover occurs	-30.7 kcal mol^{-1}	-16.2 kcal mol^{-1}
Specific surface area	C_{60}: 33.6 m^2 g^{-1}	rGO: 269.8 m^2 g^{-1}

Quantum chemical computational details

All calculations in this work were performed using Gaussian 09 program package[9]. Full geometry optimizations were performed to locate all the stationary points, using the B3LYP method[10] with the 6-31++G**[11,12] basis for S, C, H, and LANL2DZ for Co, namely B3LYP/6-31++G**//LANL2DZ. Dispersion corrections were computed with Grimme's D3(BJ) method in optimization[13]. Harmonic vibrational frequency was performed at the same level to guarantee no imaginary frequency in the molecules, i.e., they locate on the minima of the potential energy surface. Convergence parameters of the default threshold were retained (maximum force within 4.5×10^{-4} Hartrees/Bohr and root mean square (RMS) force within 3.0×10^{-4} Hartrees/Radian) to obtain the optimized structure. The optimal structure was identified, given that all calculations for structural optimization were successfully converged within the convergence threshold of no imaginary frequency during the process of vibration analysis.

Tab. S5 High rate discharge performances of the different electrodes.

Sample	*HRD200*	*HRD400*	*HRD600*	*HRD800*	*HRD1000*
$Co_{1-x}S$/rGO Composites	93.2	89.3	84.7	82.1	80.4
$Co_{1-x}S/C_{60}$ Composites	88.1	82.4	77.6	73.7	70.5

Tab. S6 Electrochemical kinetic parameters of different electrodes.

Sample	R_p (mΩ)	i_0 (mA g^{-1})	D/r_0^2 (10^{-5} cm^2 s^{-1})
$Co_{1-x}S$/rGO Composites	363	70.69	6.92
$Co_{1-x}S/C_{60}$ Composites	498	51.55	5.38

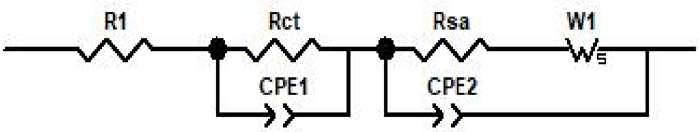

Fig. S12 Equivalent circuit of EIS of hydrogen storage electrodes.

Tab. S7 Component parameters of the equivalent circuit of EIS.

Sample	R_1 (Ω)	R_{ct} (Ω)	R_{sa} (Ω)
$Co_{1-x}S$/rGO Composites	0.253	0.031	0.526
$Co_{1-x}S/C_{60}$ Composites	0.294	0.052	0.740

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