Sustainable utilization of natural sands for cleaner preparation of high-performance nanostructured cobalt blue composite pigments by dolomite-induced mechanochemistry

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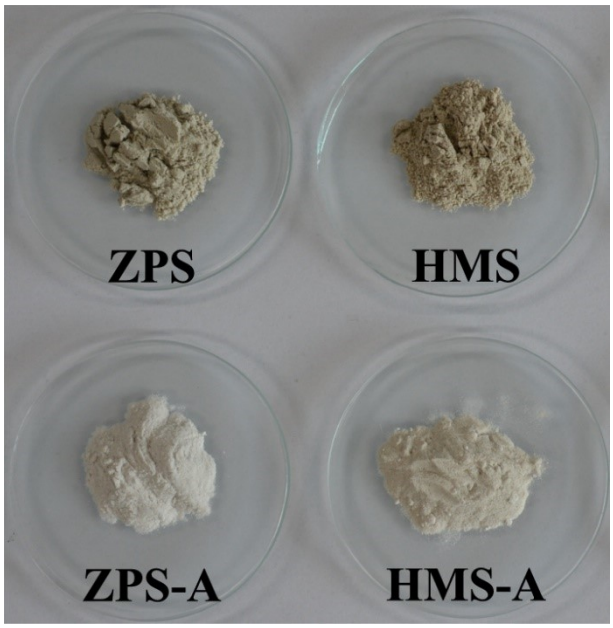

Figure S1 Digital images of ZPS, ZPS-A, HMS and HMS-A.

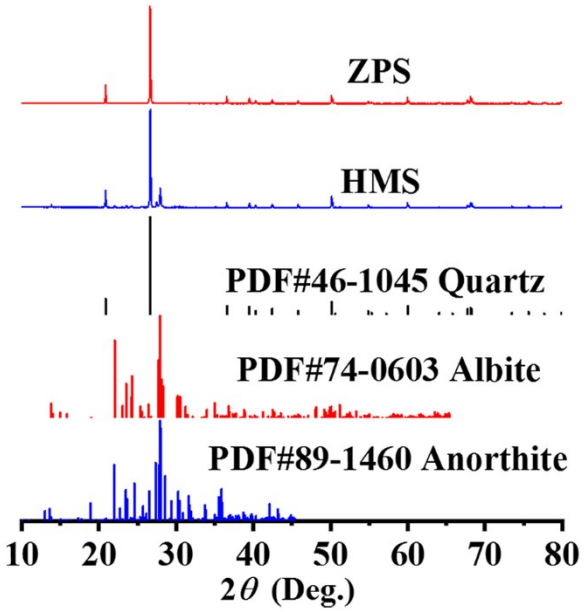

Figure S2 XRD patterns of ZPS and HMS as well as corresponding PDF card

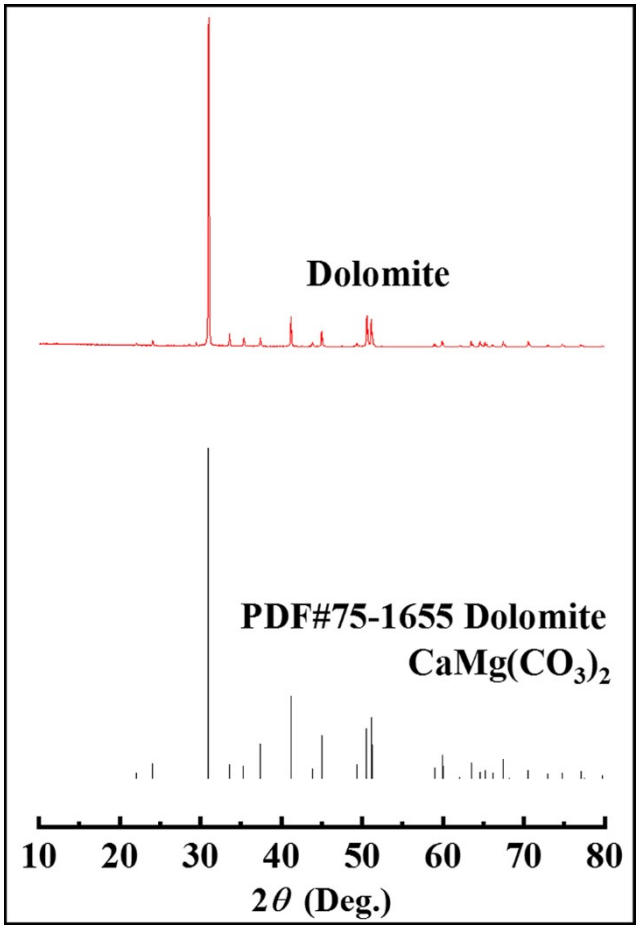

Figure S3 XRD pattern of dolomite and corresponding PDF card

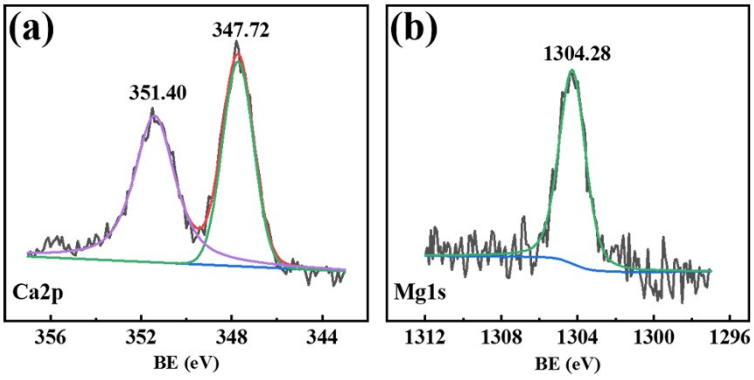

Figure S4 High-resolution XPS spectra of (a) Ca2p and (b) Mg1s of dolomite.

Table S1 XRF chemical compositions (wt%) of the involved dolomite

Composition	CaO	MgO	SiO_2	Fe_2O_3	CO_2
Wt%	58.19	30.143	1.303	0.298	10

Table S2 XRF chemical compositions (wt%) of ZPS and HMs before and after acid treatment

Samples	Acid treatment	SiO_2	Al_2O_3	Na_2O	K_2O	MgO	CaO	Fe_2O_3	CO_2
ZPS	Before	88.354	-	0.105	0.731	-	-	0.561	10
	After	87.249	1.938	-	0.569	-	-	-	10
HMS	Before	73.282	9.162	2.500	1.916	0.482	1.143	1.307	10
	After	74.979	8.796	2.503	1.948	0.183	0.959	0.507	10

Table S3 The chroma parameters of $CoAl_2O_4$ pigments compared between this study and other reports

Samples	Synthetic methods	Calcination temperature	Chroma parameters				Reference
			L^*	a^*	b^*	C^*	
CP-D/CB/ZPS	Mechanochemistry	1100°C	46.39	1.45	-48.12	48.15	This study
CP-D/CB/ZPS-A	Mechanochemistry	1100°C	42.97	4.56	-50.30	50.50	This study
CP-D/CB/HMS	Mechanochemistry	1100°C	44.55	0.19	-45.69	45.69	This study
CP-D/CB/HMS-A	Mechanochemistry	1100°C	42.59	3.38	-49.60	49.72	This study
Pure $CoAl_2O_4$	Mechanochemistry	1100°C	29.36	-8.28	-28.22	28.02	House-made
$CoAl_2O_4$	-	-	39.70	-1.22	-44.63	44.65	Commercial
Hibonite Blue	Solid phase	1350-1500°C	44.94	3.95	-42.24	42.24	[14]
$CoAl_2O_4/Al_2O_3$	Co-precipitation	1100°C	34.28	-2.87	-49.79	49.87	[16]
$CoAl_2O_4/TiO_2$	Co-precipitation	1100°C	54.32	-3.79	-44.16	44.32-	[34]
$CoAl_2O_4$	Electrospinning	1000°C	50.59	-12.30	-40.98	42.78	[35]
$CoAl_2O_4$	Combustion synthesis	1000°C	57.19	-1.99	-34.03	34.09	[36]
$CoAl_2O_4$	Hhydrothermal process	1100°C	47.31	-18.32	-37.60	41.83	[37]

Table S4 The binding energy of the fine spectra as well as corresponding assignment

Samples	Fine spectra	Binding energy (eV) and assignment
ZPS-A	Si2p	103.39 (Si-O), 102.14 ($Si-O_2$)
Dolomite	Ca2p	351.40, 347.72 (dolomite)
	Mg1s	1304.28 (dolomite)
Pure $CoAl_2O_4$	Co2p	781.53, 786.14, 797.07, 803.13 ($CoAl_2O_4$)
	Al2p	74.26 (Al_{VI}), 73.71 (Al_{IV})
Pre-D/CB/ZPS-A	Co2p	779.81, 787.07, 797.17, 803.27 (Co_3O_4)
	Al2p	75.06 (Al_2O_3)
	Ca2p	348.42, 352.13 ($Ca(NO_3)_2$)
	Mg1s	1304.11 ($Mg(NO_3)_2$)
	Si2p	102.07 ($SiO_2 \cdot Al_2O_3$), 103.07 (quartz)
	N1s	407.83 (NO_3^-), 400.13 (N-O-M)
D/CB/ZPS-A	Co2p	781.77, 786.86, 797.34, 803.13 ($CoAl_2O_4$)
	Al2p	75.07 ($CaAl_2O_4$), 74.44 (Al_{VI}), 73.78 (Al_{VI})
	Ca2p	347.69, 348.60, 351.51, 352.03 ($CaAl_2O_4$)
	Mg1s	1304.00 ($MgAl_2O_4$)
	Si2p	102.12 (Si-O-Al), 102.84 (quartz)