Probing capping mechanisms and polymer matrix loading of biogenic vaterite $CaCO_3$-Ag hybrid through X-ray photoelectron spectroscopy (XPS)

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Supplementary file

Atomic concentration determination

To determine the relative concentrations of constituents on the sample surface, the peak area and peak height sensitivity factors were utilized. For homogeneous sample, the number of photoelectrons per second in a specific spectra peak is given by:

$$I = nf\sigma\lambda\theta yAT$$

where n is the number of atoms of the element per cm^3 of the sample, f is the x-ray flux in photons/cm^2-sec, σ is the photoelectric cross-section for the atomic orbital of interest in cm^2, θ is an angular efficiency factor for the instrumental arrangement based on the angle between the photon path and detected electron, y js the efficiency in the photoelectric process for formation of photoelectrons of the normal photoelectron energy, λ is the mean free path of the

photoelectrons in the sample, A is the area of the sample from which photoelectrons are detected, and T is the detection efficiency for electrons emitted from the sample.

For our work, the atomic concentration of each element was calculated using the following equation.

$$Atomic\ Concentration = \frac{\frac{I_x}{S_x \times T_x}}{\sum_{i=1}^{n} \frac{I_i}{S_i \times T_i}} \times 100$$

where I is intensity or area pea, S is sensitivity factor (SF), and T is time per second. The relative sensitivity factor (RSF) and corrected values according to the machine of each sample are shown in the following table.

	C1s	**N1s**	**O1s**	**Na1s**	**Cl2p**	**Ca2p**	**Ag3d**
RSF	0.314	0.499	0.733	1.102	0.954	1.927	6.277
Corrected RSF	36.823	58.53	85.994	129.358	126.513	250.487	833.710

Table S1. The relative sensitivity factor (RSF) and corrected values

Scanning Electron Microscopy

The morphology and size of vaterite $CaCO_3$–Ag microspheres were observed through a field emission scanning electron microscope (FE-SEM) (JEOL JSM 7800F Tokyo, Japan) coupled with energy-dispersive X-ray spectroscopy (EDX). The samples were coated with gold before SEM measurements. The statistical image processing was performed in three stages: (1) the microsphere dimensions were measured through Digi Mizer software (Media Cybernetics, Rockville, MD), (2) size distribution (PSD) determination using software Minitab 17.2.0 (Minitab Ltd., Coventry, U.K.) to obtain the mean diameter (D_m) and their respective histograms, and (3) the elemental composition of the vaterite $CaCO_3$–Ag microspheres by ESX in the mapping mode.

ICP-OES

The release of AgNPs in both closed-like and open-like systems was investigated under slightly acidic pH (pH 6, acetate buffer). In the closed-like conditions, the samples were incubated in the corresponding buffer solutions at 37 °C with a concentration of 2 mg/mL. At various time intervals (1, 6, 12, 24, and 48 h), an aliquot equal to 5% of the volume was collected for silver quantification using ICP-OES. The collected aliquots were then replaced with an equal volume of fresh buffer to maintain the same final volume. In the open-like conditions, both films and powders were incubated in the respective buffer at 37 °C with a concentration of 2 mg/mL. Like the closed-like conditions, at various time intervals (1, 6, 12, 24, and 48 h), an aliquot equal to 75% of the total volume was collected for silver quantification using ICP-OES. The collected aliquots were replaced with an equivalent amount of fresh buffer to maintain the final volume. All experiments were carried out in triplicate.

BET Analysis

The Brunauer, Emmett, and Teller (BET) surface area measurements and porosity analysis were carried out by Micromeritics 3Flex BET analyser. All samples were degassed at 40 °C for 24 h in a vacuum before the examination.

Morphology

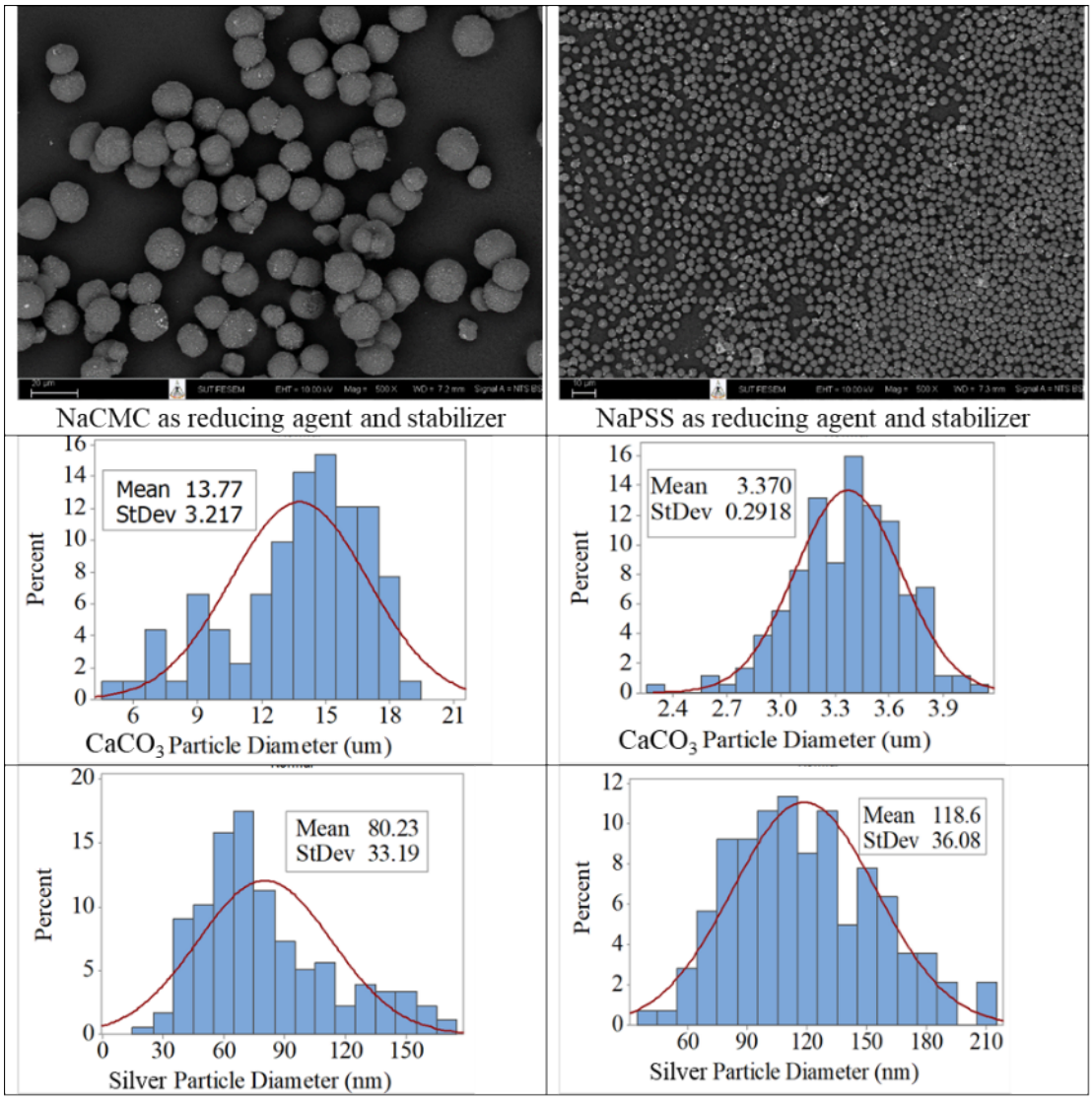

Figure S1. SEM images of $CaCO_3$-Ag-CMC and $CaCO_3$-Ag-PSS (500x magnification). Histogram of $CaCO_3$ microparticles, AgNPs and their size distribution.

Table S2. Table summarizing XPS data analysis results.

	Region	Binding energy (eV)	FWHM (eV)	Height	Area
ESP	C1s	281.20	2.00	157	367
		283.44	2.00	327	762
		284.80	2.00	535	1248
		287.48	2.00	229	533
		289.07	1.66	521	1006
	O1s	529.21	1.80	1000	2099
		530.97	1.80	3642	7642
		532.58	1.80	177	3.67
	Ca2p	346.34	2.18	2106	5444
		349.94	2.25	1040	2722
	N1s	399.28	2.01	78	182
$CaCO_3$-Ag-CMC	C1s	282.34	2.00	492	1148
		284.00	1.90	665	1474
		286.33	1.56	407	742
		287.62	1.93	235	530
		289.54	1.79	457	957
	O1s	529.87	1.80	70	1485
		531.7	1.82	3157	6607
		533.08	1.80	943	1998
	Ca2p	347.06	2.18	1692	4268
		350.66	2.24	817	2134
	Ag3d	367.80	2.09	169	410
		368.84	2.03	128	303
		373.80	2.07	119	287
		374.84	1.90	96	212
$CaCO_3$-Ag-PSS	C1s	282.78	2.00	657	1531
		284.80	2.00	1038	2419
		286.6	2.00	312	727
		189.86	2.10	273	667
	O1s	529.80	1.80	623	1307
		531.54	1.80	2545	5340
		532.58	1.91	1067	2379
	Ca2p	347.29	1.96	1423	3275
		350.89	2.16	649	1637
	Ag3d	367.80	1.90	145	321
		368.99	1.80	204	427
		373.80	2.00	96	225
		374.99	1.76	146	299
Neat CMC	C1s	284.80	1.14	548	730
		286.29	1.34	4388	6879
		287.73	1.23	697	1002
		530.93	1.38	987	1587

	O1s	532.72	1.52	5782	10215
		535.52	1.60	129	241
	Na1s	1071	1.65	571	1094
CMC/$CaCO_3$-Ag-CMC	C1s	284.80	1.40	1607	2624
		286.33	1.40	2097	3432
		287.91	1.87	300	652
	O1s	530.96	1.53	439	788
		532.69	1.70	2710	5371
	Ca2p	346.84	1.37	192	306
		347.71	1.58	126	236
		350.44	1.37	96	153
		351.31	1.94	52	118
	Ag3d	367.57	1.52	157	278
		373.57	2.00	84	195
	Na1s	1071.73	1.80	106	222
		1073.63	1.75	104	211
	Cl2p	198.24	1.70	78	154
		199.83	1.36	49	77
		200.56	1.58	142	262
		202.15	1.53	73	131
CMC/$CaCO_3$-Ag-PSS	C1s	284.80	1.29	3323	5007
		286.42	1.19	1883	2610
		288.25	1.57	269	493
	O1s	531.28	1.39	644	1041
		532.74	1.59	2245	4115
	Ca2p	346.84	1.39	147	237
		347.68	1.30	164	248
		350.44	1.11	92	119
		351.28	0.88	121	124
	Ag3d	367.95	1.50	144	252
		373.95	1.51	101	177
	Cl2p	198.73	2.58	58	176
		200.32	2.26	33	88
Neat PVA	C1s	284.80	1.70	1449	2807
		286.33	1.80	1412	2963
	O1s	532.46	1.82	3328	7063
PVA/$CaCO_3$-Ag-CMC	C1s	284.80	1.77	3373	6814
		288.49	1.42	143	238
	O1s	531.31	1.80	516	1110
		532.09	1.80	446	936
	Ca2p	347.23	1.83	298	637
		350.83	2.01	136	318
	Ag3d	367.82	1.55	388	705
		373.82	1.51	279	493
PVA/$CaCO_3$-Ag-PSS	C1s	284.80	1.81	2995	6319
		288.04	20.1	111	2.94
	O1s	531.18	1.75	597	1217
		532.22	1.82	468	1004
	Ca2p	347.28	1.91	331	736
		350.88	2.05	154	368

	Ag3d	367.80	1.86	243	527
		373.80	1.74	182	369