

## Supplementary information:

### Facile fabrication of silver nanoparticle embedded $\text{CaCO}_3$ microspheres *via* microalgae-templated $\text{CO}_2$ biomineralization: application in antimicrobial paint development

Prakash Chandra Sahoo <sup>a</sup>, Farzana Kausar <sup>b</sup>, Jay Hyung Lee <sup>a\*</sup>, and Jong In Han <sup>b\*</sup>

<sup>a</sup>Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

<sup>b</sup>Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

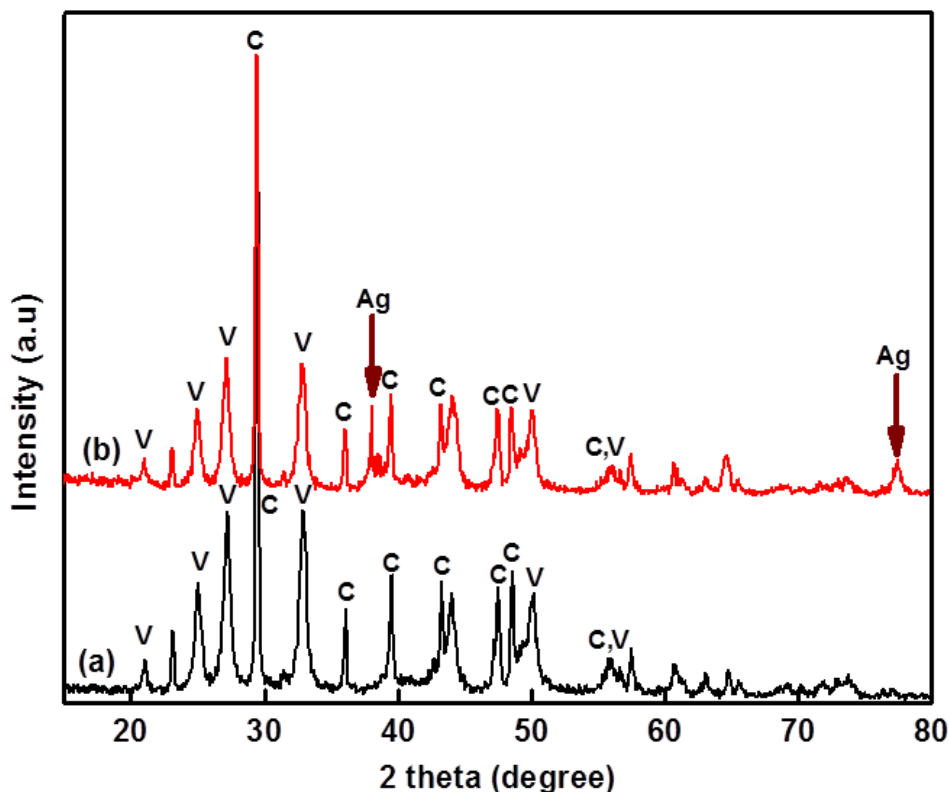


Fig. S1. XRD spectra (a)  $\text{CaCO}_3$  micro spheres precipitates in the presence of microalgae at room temperature (b)  $\text{nAg}/\text{CaCO}_3$  micro spheres.

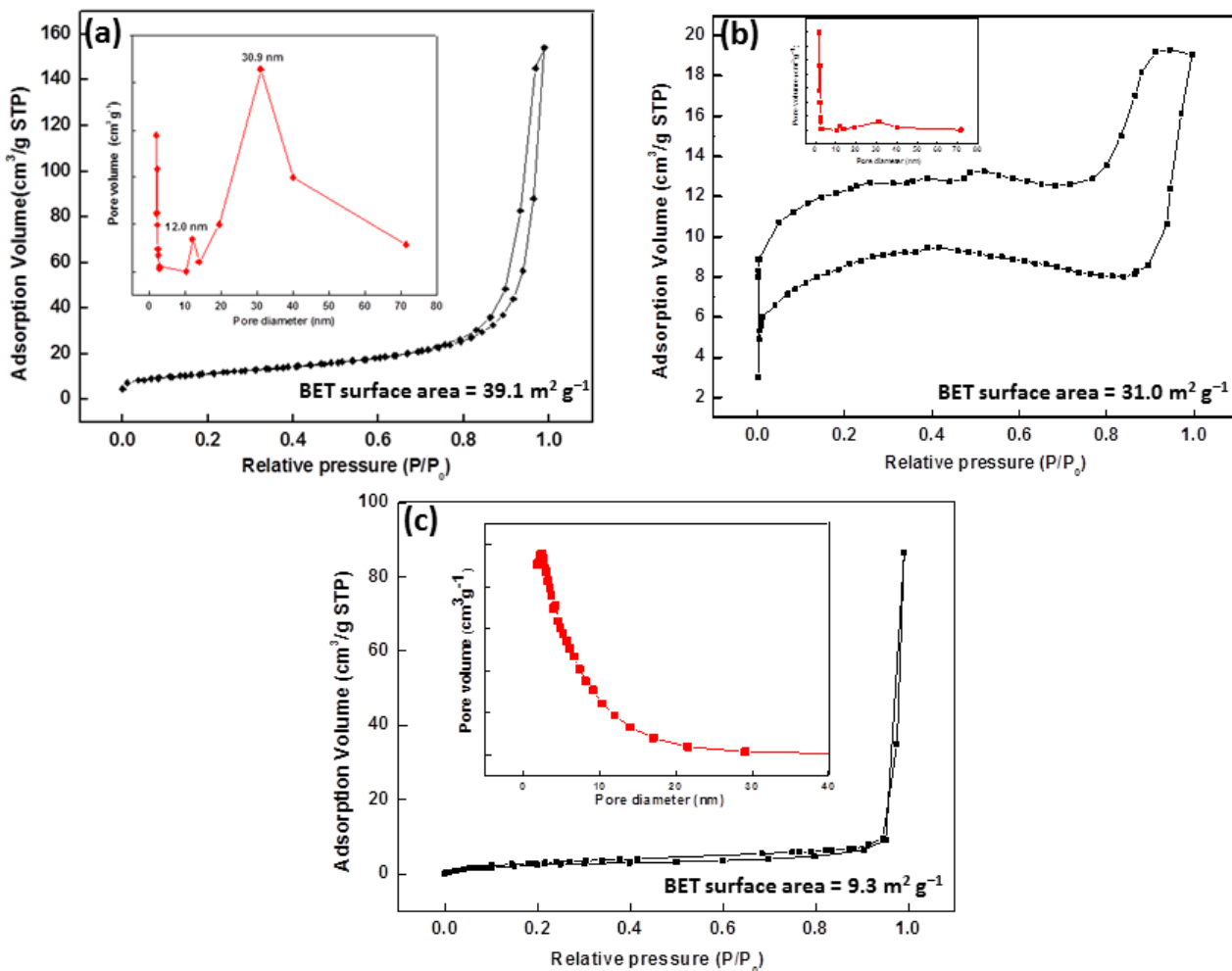


Fig. S2. Nitrogen adsorption–desorption isotherm loop of porous  $\text{CaCO}_3$  microsphere. The inset is the pore size distribution curve calculated from the adsorption branch by the BJH model. (a)  $\text{CaCO}_3$  microspheres obtained with  $[\text{Microalgae}]: 1.2 \text{ g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.3 \text{ M}$  (b)  $\text{CaCO}_3$  microspheres at  $[\text{Microalgae}]: 2.2 \text{ g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.3 \text{ M}$  (c)  $\text{CaCO}_3$  microspheres at  $[\text{Microalgae}]: 0.2 \text{ g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.3 \text{ M}$ . As shown in the figure the  $\text{CaCO}_3$  microsphere at  $0.3 \text{ M CaCl}_2$  showed different surface area and pore size at different microalgae concentration. At a microalgae concentration of  $1.2 \text{ g L}^{-1}$ , the  $\text{CaCO}_3$  spheres showed comparatively higher surface area ( $39.1 \text{ m}^2 \text{ g}^{-1}$ ) and distinct porosity compared to other samples.

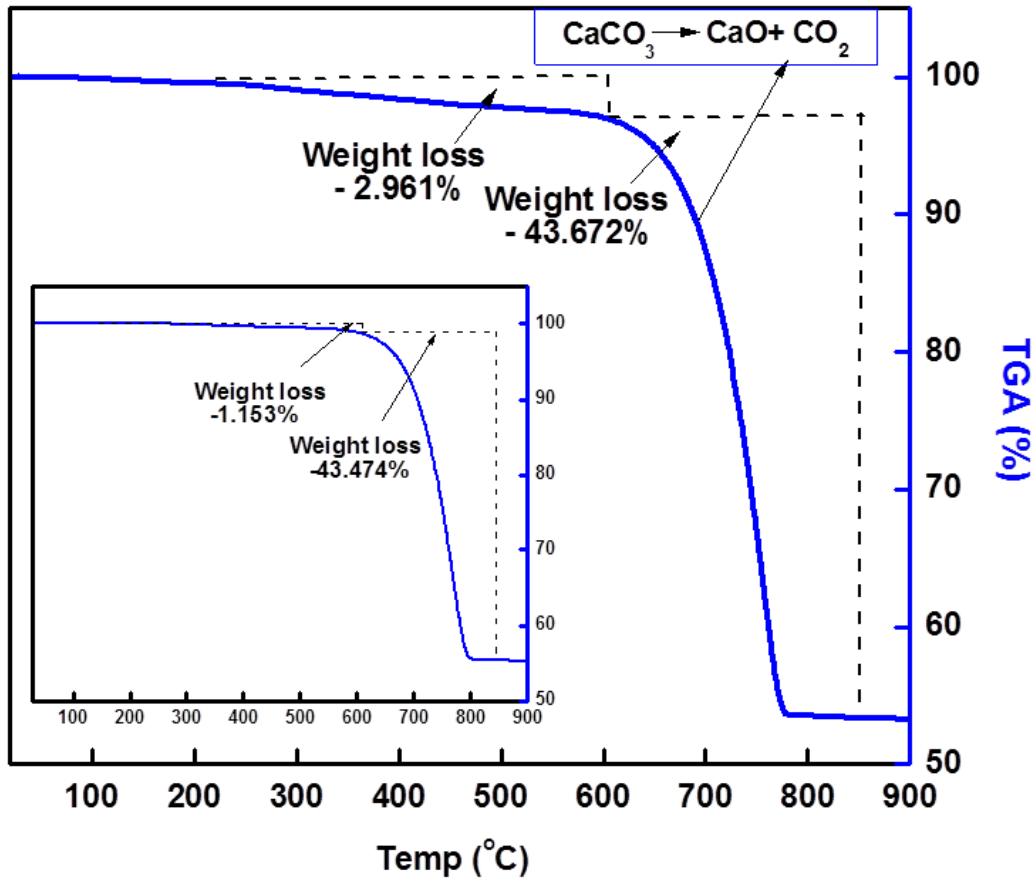
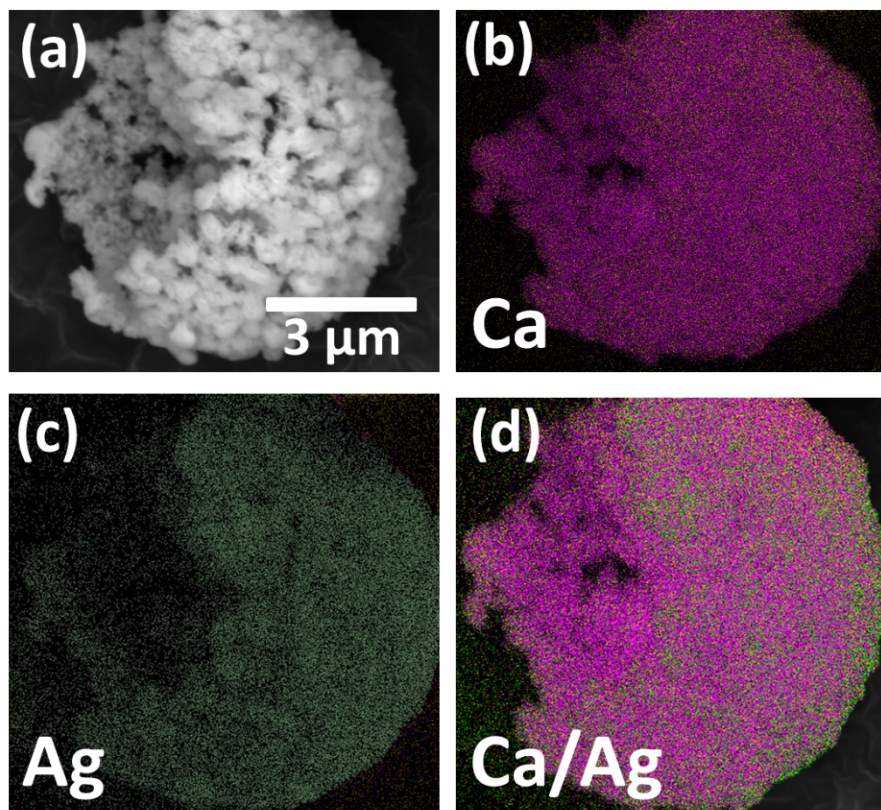
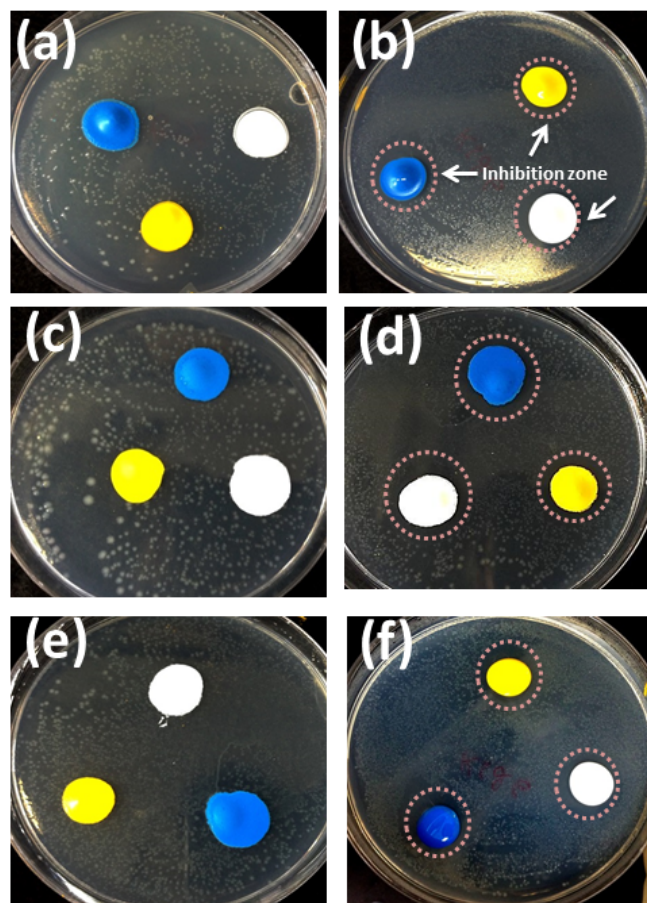


Fig. S3. TGA curves of porous  $\text{CaCO}_3$  microspheres prepared using microalgae as template. The inset represents the TGA curve for  $\text{CaCO}_3$  particle without algae template.



**Fig. S4.** SEM mapping photograph of Ca and Ag within a single particle of nAg/CaCO<sub>3</sub> microspheres (a) SEM image of the particle considered for mapping and (b) elemental mapping of Ca (c) elemental mapping of Ag (d) superimposed mapping image of both Ca and Ag together, the Ag-rich particle on the surface are clearly seen from the SEM mapping images.

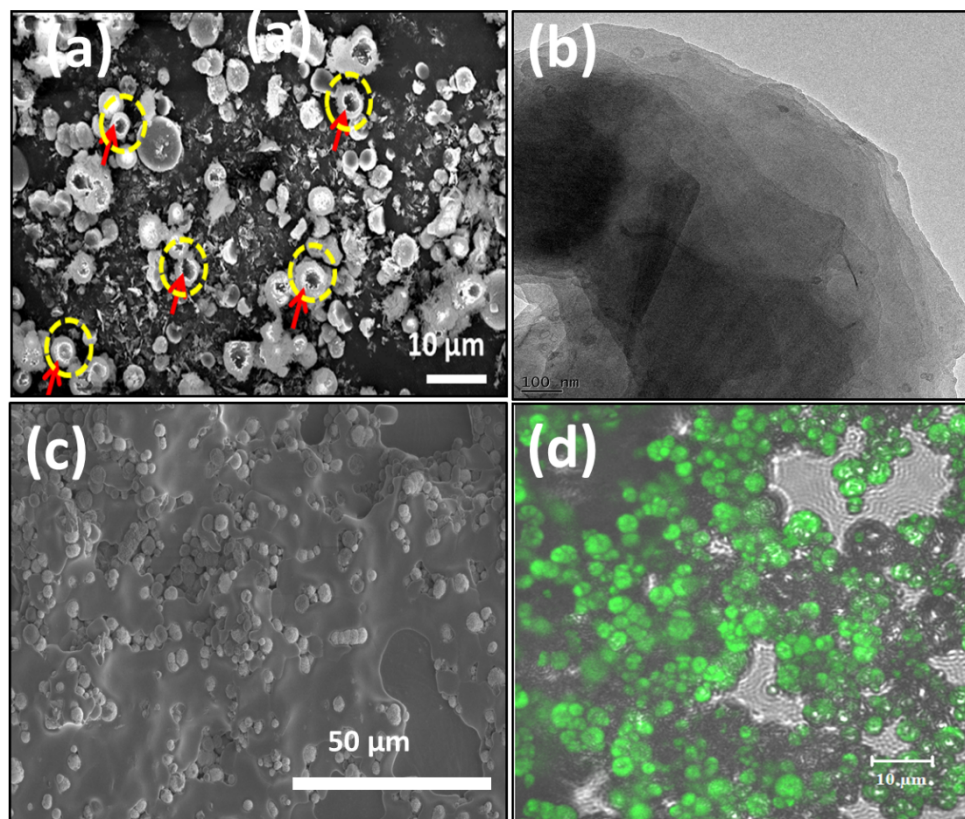


nAg/CaCO <sub>3</sub> (mg/ml)	Width of Inhibition zone (millimeter, mm)		
	<i>E. coli</i>	<i>P. alimentarius</i>	<i>S. equorum</i>
0	0	0	0
0.1	0.7 ± 0.1	1.3 ± 0.1	1.2 ± 0.1

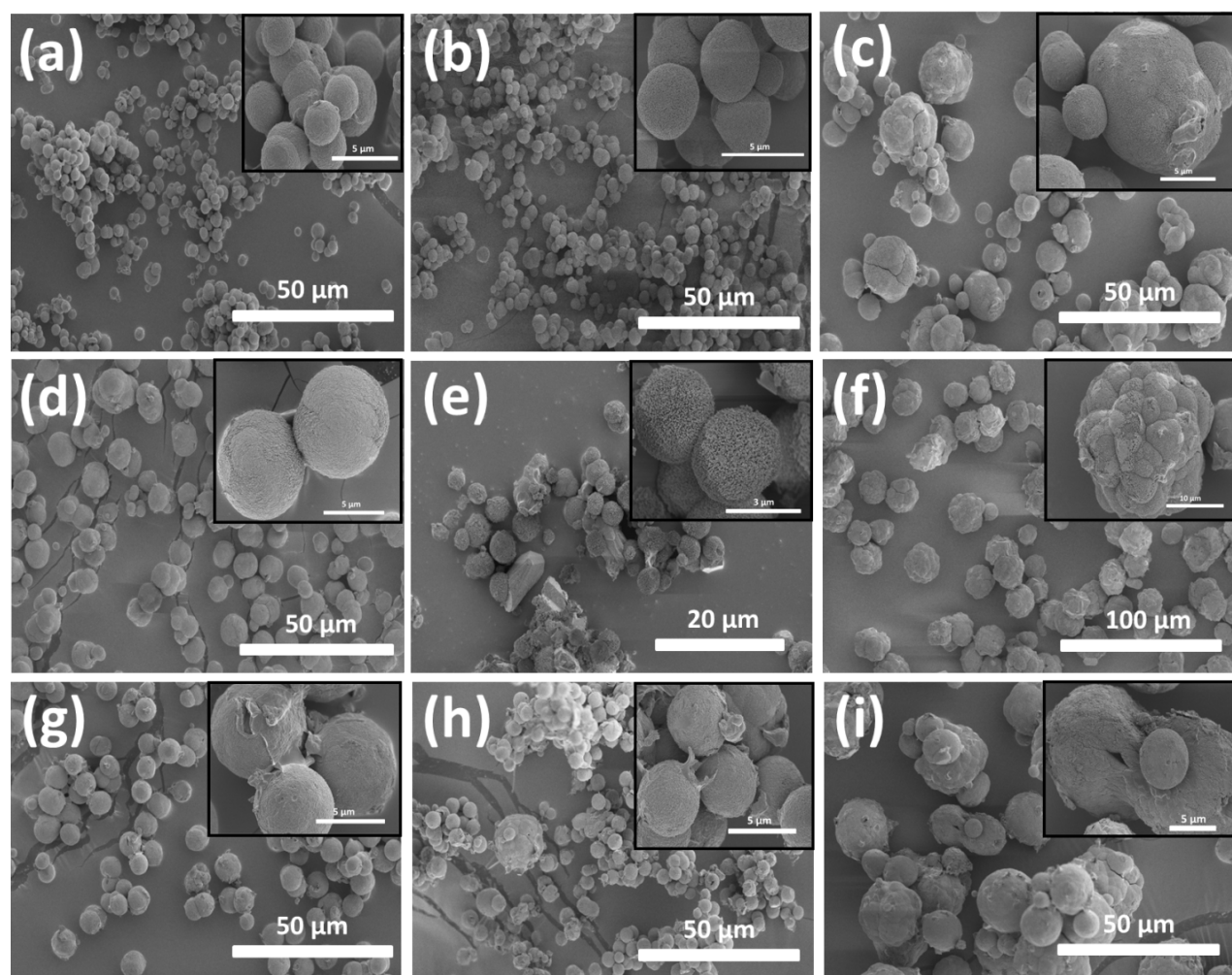
**Fig. S5.** Determination of the effect of nAg/CaCO<sub>3</sub> microsphere additive paints on *E. coli*, *P. alimentarius* and *S. equorum* by agar-diffusion assay method. In each case, 0.1 mg/ml of nAg/CaCO<sub>3</sub> microspheres was added to the commercial water soluble paint of different color and their droplets were added to the agar plate containing different bacterial strain. The zone of inhibition was highlighted with a dashed circle indicating a noticeable antibacterial effect. Here a, c and e represents the untreated commercial paint with bacteria *E. coli*, *P. alimentarius* and *S. equorum* and b, d and f represents the commercial paint emulsion with 0.1 mg/ml of nAg/CaCO<sub>3</sub> microspheres on *E. coli*, *P. alimentarius* and *S. equorum*. It clearly seen that the untreated paint did



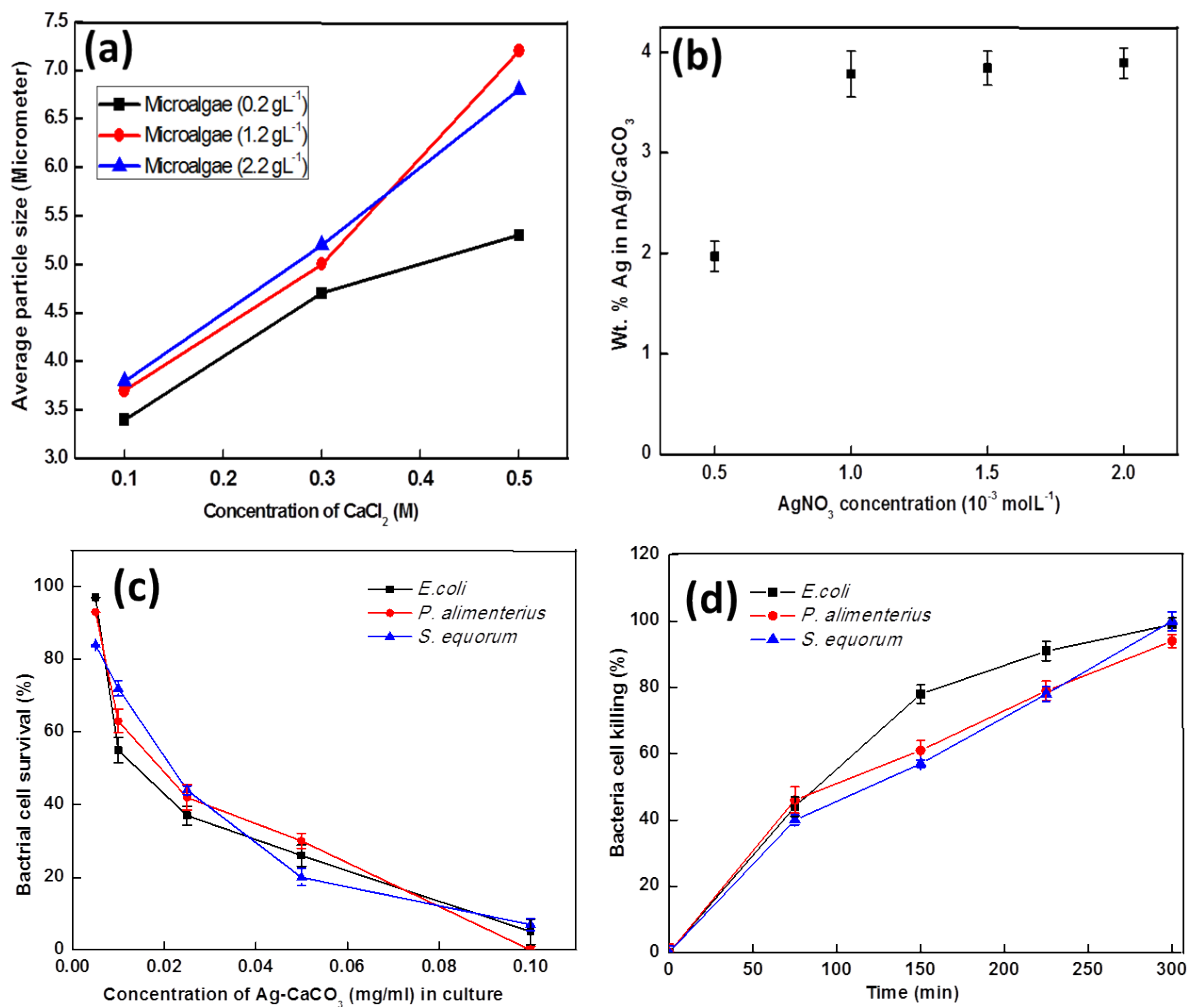
not show any inhibition zone, whereas the treated paint showed distinguished inhibition zone after 24 h incubation at 35 °C. The table below represents the width of the inhibition zone in mm.



**Fig.S6. (a) SEM image of  $\text{CaCO}_3$  microspheres where electron beam etched their outer surface. It can be clearly seen that the particles appeared as hollow with an inner lighter layer indicated with red arrow (which might arise from the associated microalgae cells) and an outer dark core (caused likely by thick  $\text{CaCO}_3$  coverings). (b) FE-TEM image of  $\text{CaCO}_3$  microsphere showing the outer brighter layer and inner darker layer due to  $\text{CaCO}_3$  and microalgae, respectively. (c) Low magnified image of  $\text{CaCO}_3$  prepared using microalgae. It showed that most of the  $\text{CaCO}_3$  exists as microsphere. (d) Confocal microscopic image of  $\text{CaCO}_3$  showing that most of them exists as microsphere.**



**Fig. S7. SEM images of the obtained  $\text{CaCO}_3$  crystals with different reactant concentrations. (a) [Microalgae]:  $0.2\text{g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.1\text{ M}$ ; (b) [Microalgae]:  $0.2\text{g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.3\text{ M}$ ; (c) [Microalgae]:  $0.2\text{g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.5\text{ M}$ ; (d) [Microalgae]:  $1.2\text{g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.1\text{ M}$ ; (e) [Microalgae]:  $1.2\text{g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.3\text{ M}$ ; (f) [Microalgae]:  $1.2\text{g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.5\text{ M}$ ; (g) [Microalgae]:  $2.2\text{g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.1\text{ M}$ ; (h) [Microalgae]:  $2.2\text{g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.3\text{ M}$ ; (i) [Microalgae]:  $2.2\text{g L}^{-1}$ ,  $[\text{Ca}^{2+}] = 0.5\text{ M}$ . The crystallization conditions remain the same as mentioned in the experimental section.**



**Fig.S8 (a) Average particle size variation with different CaCl<sub>2</sub> concentration. (b) Ag loading in CaCO<sub>3</sub> microspheres at different AgNO<sub>3</sub> concentration. (c) Survival percentage of *E. coli*, *P. alimenterius* and *S. equorum* after treatment with different concentrations (0–0.1%) of nAg/CaCO<sub>3</sub> along with 0.1 mg dry white paint added to the medium and (b) Killing percentage of *E. coli*, *P. alimenterius* and *S. equorum* by 0.1% nAg/CaCO<sub>3</sub> along with 0.1 mg dry white paint added to the medium.**