

Supporting Information for Journal of Materials Chemistry A

Multifunctional system based on hybrid nanostructured-rods formation, for *sensoremoval* applications of Pb^{2+} as a model toxic metal.

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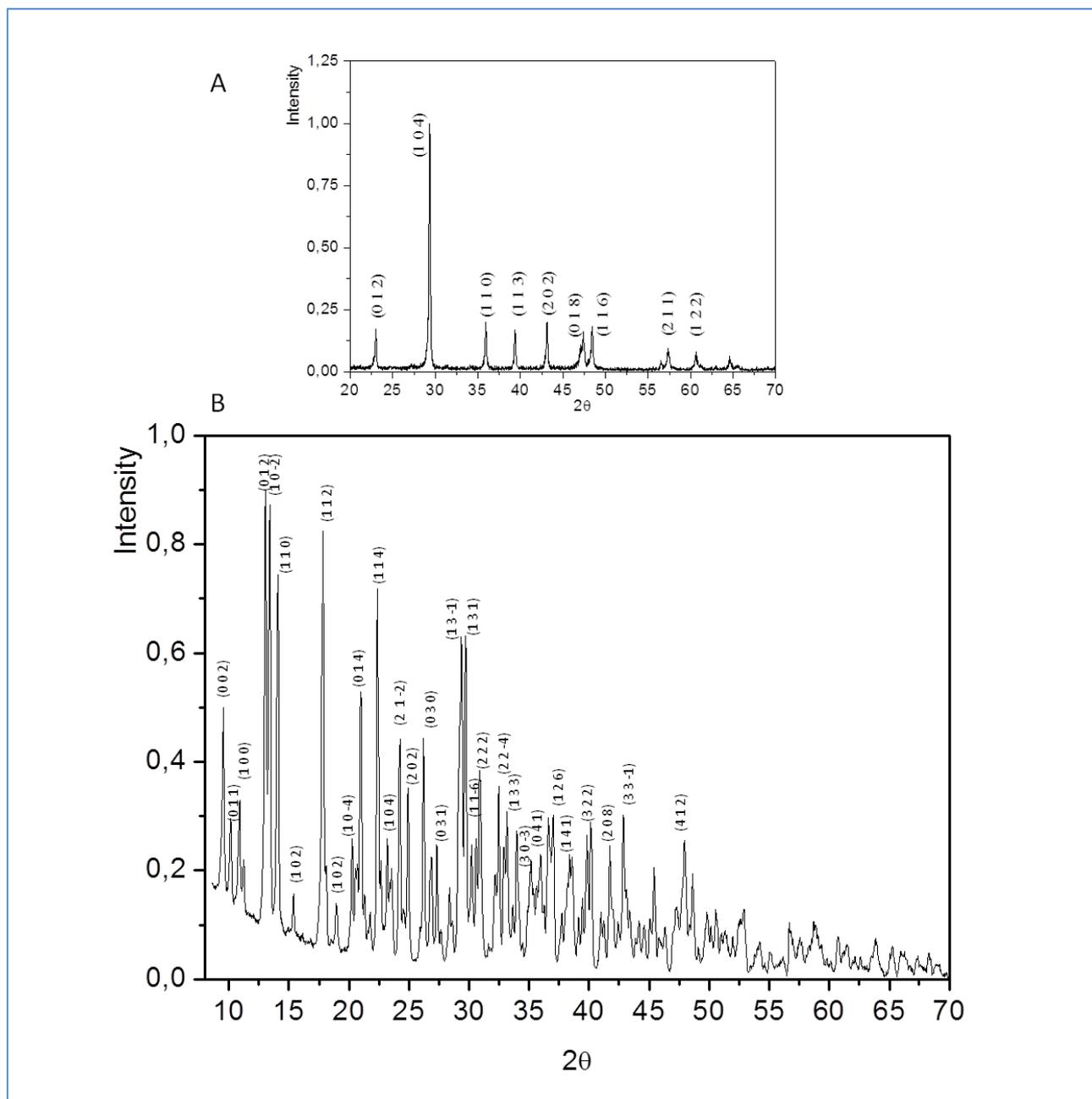
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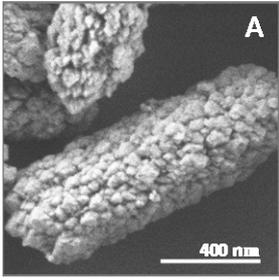
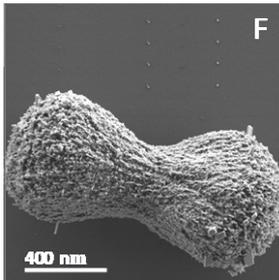
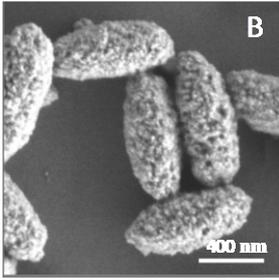
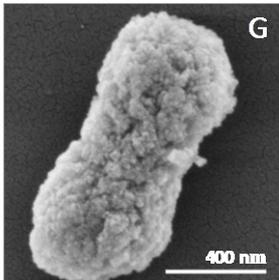
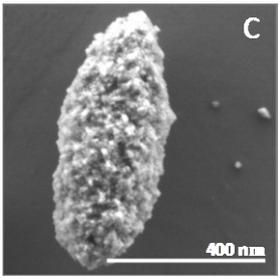
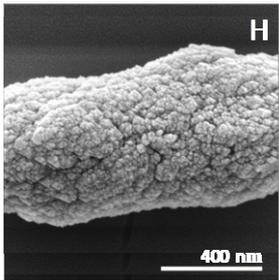
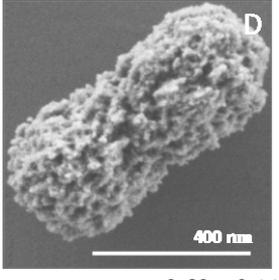
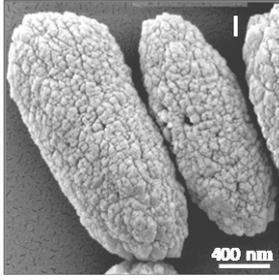
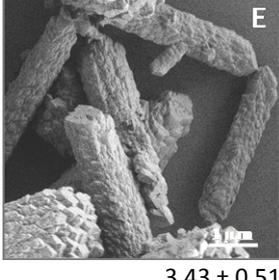
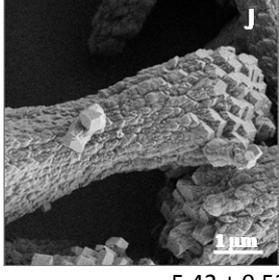
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Figure_S1. XRD patterns of calcite polymorph phase (A) and the Na₂PbEDTA·2H₂O complex (B). The XRD pattern shown in (A) exhibits sharp reflections corresponding to the (0 1 2), (1 0 4), (1 1 0), (1 1 3), (2 0 2), (0 1 8), (1 1 6), (2 1 1) and (1 2 2) crystallographic planes of calcite, the most stable polymorph of CaCO₃. The XRD pattern displayed in (B) exhibits the peaks corresponding with Na₂PbEDTA·2H₂O (P21/c) indexed in CSD.⁴⁷

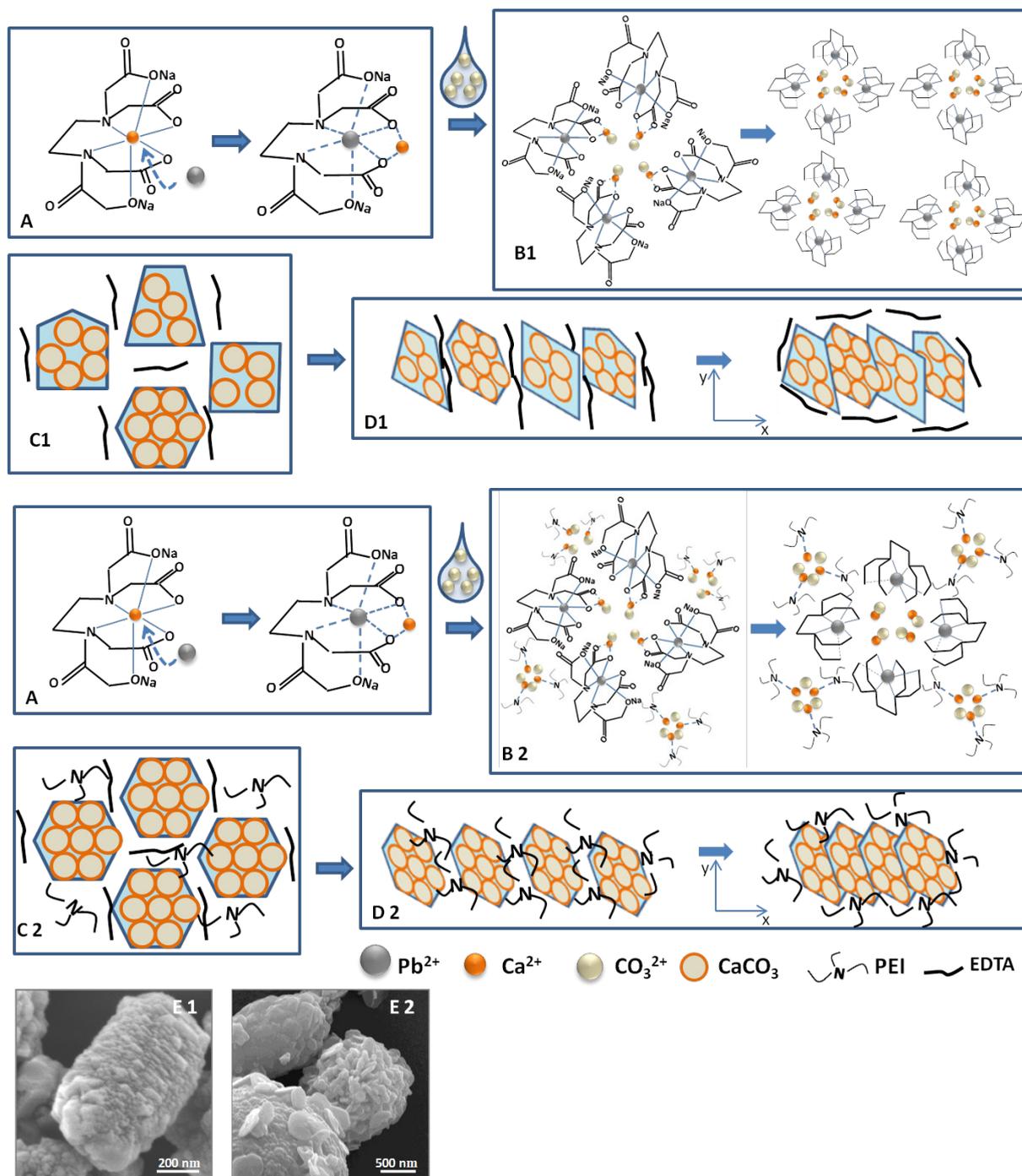
| Reaction conditions and type of assay | SEM view and structure average size [μm] | Reaction conditions and type of assay | SEM view and structure average size [μm] |
|---|--|--|--|
| $\left[\begin{array}{c} 0.33M CaCl_2 + 0.4M Na_3EDTA \\ 5mL H_2O \\ + \left[\begin{array}{c} 0.33M Pb(NO_3)_2 \\ 5mL H_2O \end{array} \right] \\ + \left[\begin{array}{c} 0.33M Na_2CO_3 \\ 5mL H_2O \end{array} \right] \end{array} \right]$ assay 1-v |  <p>1.16 ± 0.41</p> | $\left[\begin{array}{c} 0.33M CaCl_2 + 0.4M Na_3EDTA \\ 2mL H_2O \\ + \left[\begin{array}{c} 0.33M Pb(NO_3)_2 \\ 2mL H_2O \end{array} \right] \\ + \left[\begin{array}{c} 0.33M Na_2CO_3 \\ 2mL H_2O \end{array} \right] \end{array} \right]$ assay 1-z |  <p>1.19 ± 0.42</p> |
| $\left[\begin{array}{c} 0.33M CaCl_2 / PEI + 0.4M Na_3EDTA \\ 5mL H_2O \\ + \left[\begin{array}{c} 0.33M Pb(NO_3)_2 \\ 5mL H_2O \end{array} \right] \\ + \left[\begin{array}{c} 0.33M Na_2CO_3 \\ 5mL H_2O \end{array} \right] \end{array} \right]$ assay 1-w |  <p>0.62 ± 0.06</p> | $\left[\begin{array}{c} 0.3M CaCl_2 / PEI + 0.4M Na_3EDTA \\ 2mL H_2O \\ + \left[\begin{array}{c} 0.33M Pb(NO_3)_2 \\ 2mL H_2O \end{array} \right] \\ + \left[\begin{array}{c} 0.33M Na_2CO_3 \\ 2mL H_2O \end{array} \right] \end{array} \right]$ assay 1-w-z |  <p>1.11 ± 0.25</p> |
| $\left[\begin{array}{c} 0.33M CaCl_2 + 0.4M Na_3EDTA \\ 5mL H_2O + 2mL ethylacetate \\ + \left[\begin{array}{c} 0.33M Pb(NO_3)_2 \\ 5mL H_2O \end{array} \right] \\ + \left[\begin{array}{c} 0.33M Na_2CO_3 \\ 5mL H_2O \end{array} \right] \end{array} \right]$ assay 1-x |  <p>0.65 ± 0.18</p> | $\left[\begin{array}{c} 0.33M CaCl_2 + 0.4M Na_3EDTA \\ 2.5mL H_2O + 2.5mL ethanol \\ + \left[\begin{array}{c} 0.33M Pb(NO_3)_2 \\ 5mL H_2O \end{array} \right] \\ + \left[\begin{array}{c} 0.33M Na_2CO_3 \\ 5mL H_2O \end{array} \right] \end{array} \right]$ assay 1-x |  <p>1.02 ± 0.31</p> |
| $\left[\begin{array}{c} 0.33M CaCl_2 / PEI + 0.4M Na_3EDTA \\ 5mL H_2O + 2mL ethylacetate \\ + \left[\begin{array}{c} 0.33M Pb(NO_3)_2 \\ 5mL H_2O \end{array} \right] \\ + \left[\begin{array}{c} 0.33M Na_2CO_3 \\ 5mL H_2O \end{array} \right] \end{array} \right]$ assay 1-w-x |  <p>0.63 ± 0.11</p> | $\left[\begin{array}{c} 0.33M Pb(NO_3)_2 \\ 5mL H_2O \end{array} \right] + \left[\begin{array}{c} 0.3M CaCl_2 / gly + 0.4M Na_3EDTA \\ 5mL H_2O \\ + \left[\begin{array}{c} 0.33M Na_2CO_3 \\ 5mL H_2O \end{array} \right] \end{array} \right]$ assay 2-w |  <p>1.80 ± 0.30</p> |
| $\left[\begin{array}{c} 0.33M Ca(NO_3)_2 + 0.4M Na_3EDTA \\ 5mL H_2O \\ + \left[\begin{array}{c} 0.33M Pb(NO_3)_2 \\ 5mL H_2O \end{array} \right] \\ + \left[\begin{array}{c} 0.33M Na_2CO_3 \\ 5mL H_2O \end{array} \right] \end{array} \right]$ assay 1-y |  <p>3.43 ± 0.51</p> | $\left[\begin{array}{c} 0.33M Ca(NO_3)_2 + 0.4M Na_3EDTA \\ 2mL H_2O \\ + \left[\begin{array}{c} 0.33M Pb(NO_3)_2 \\ 2mL H_2O \end{array} \right] \\ + \left[\begin{array}{c} 0.33M Na_2CO_3 \\ 2mL H_2O \end{array} \right] \end{array} \right]$ assay 1-y-z |  <p>5.42 ± 0.52</p> |

Figure_S2. Effect of different reaction conditions on the calcite morphology. [1], pouring Pb^{2+} and CO_3^{2-} solutions over $CaNa_2EDTA$ solution; [2], pouring $CaNa_2EDTA$ and CO_3^{2-} solutions over Pb^{2+} solution; [v],

without use of CGM; [w], with the use of CGM; [x], using mixed solvents; [y], using $\text{Ca}(\text{NO}_3)_2$ as source of Ca^{2+} cations, [z], decreasing the reagents volume.

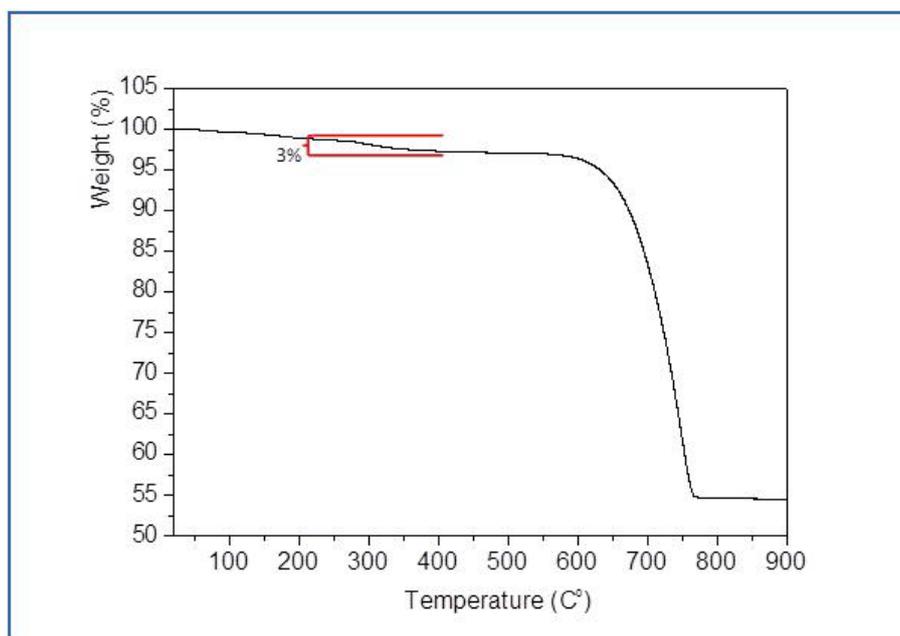
The analysis of the morphology of the product obtained under different changes in the reaction conditions guides to some regularity of behavior for the shape and the surface of the calcite product produced and the applied reaction condition. In first place, rod-like shapes are always obtained using 0.33 M of the basis mixture of Na_2CaEDTA , $\text{Pb}(\text{NO}_3)_2$ and NaNO_3 . In second place the reagents addition order ($\text{Na}_2\text{CaEDTA} + \text{Pb}(\text{NO}_3)_2 + \text{NaNO}_3$ or $\text{Pb}(\text{NO}_3)_2 + \text{Na}_2\text{CaEDTA} + \text{NaNO}_3$) don't affect the product as view in SEM images of the figure 2B and figure_S2-A or figure 2A and figure_S2-B. The addition of PEI in the original Ca^{2+} solution conduces to microrods with high porous surface and rounded to the ends as shown in figure_S2-B, D and G. While those obtained without CGM (figure_S2-A) or with other CGM as ethanol (figure_S2-H) or glycerol (figure_S2-I) don't present a high porous surface. In the same way the use of water/ethylacetate as mixed solvents produces high porous surface microrods but with sharp ends (figure_S2-C) and when PEI is introduced in this system the ends of this microrods became in rounded ends (figure_S2-D). The substitution of CaCl_2 by $\text{Ca}(\text{NO}_3)_2$ to produce Na_2CaEDTA leads to microrods compound of perfect nanocubes typical of calcite phase. Finally the diminution of the reaction volume from 15 to 7 mL produces the dumbbell-like shape structures (figure_S2-F, G and J). The dumbbell-like shape structure has been reported before by J. Yu *et al.*²⁰ They explain the dumbbell shape in terms of nucleation and growth stimulated at the both ends of the rod-like primary crystals along electric field lines further than the nucleation and growth on the side-surfaces of rod-like primary crystals.

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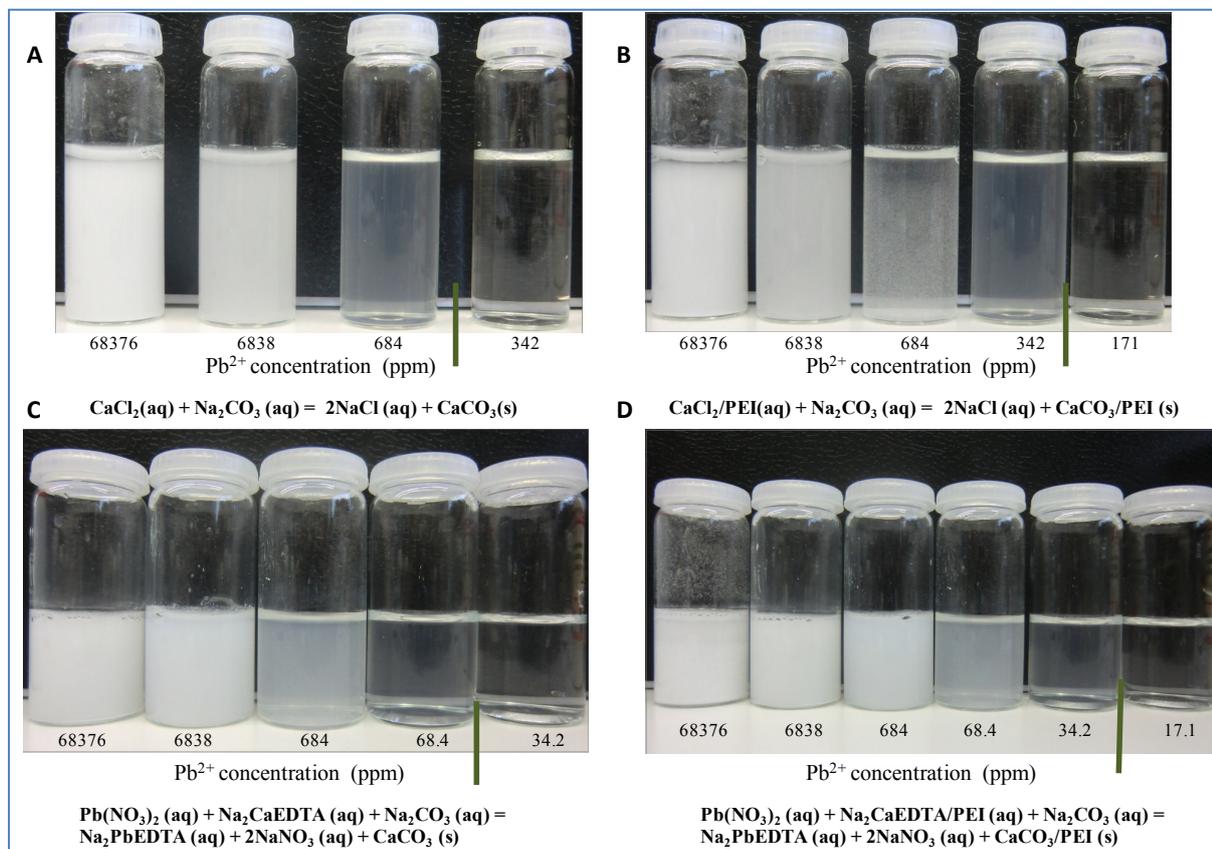


Figure_S3. Schematic representation of the NRs formation mechanism without use of CGM (1) and using PEI as CGM (2). (A) Formation of the possible intermediate complex Ca-Na₂EDTA-Pb as Ca²⁺ self-reagent-delivery. (B1) Arising of the first local CaCO₃ nucleation centers by calcium supersaturation and nearly CaCO₃ nanoparticles stabilized by Na₂PbEDTA; (B2) Formation of additional primary CaCO₃ nanoparticles by calcium supersaturation due to its interaction with nitrogen amino in PEI polymer. (C1) Growth of heterogeneous plate-like crystals by aggregation of the nearly CaCO₃ nanoparticles in preferential y-axis and its temporal Na₂PbEDTA stabilization. (C2) Growth of homogeneous hexagonal plate-like crystals by aggregation of the nearly CaCO₃ nanoparticles in preferential y-axis and its PEI stabilization by polymer retention onto particle surface. (D) Spontaneous self-assembly of the heterogeneous (D1) or hexagonal (D2) plate crystals mediated by organic

stabilizer that acts as link of the plate building block into preferential *x*-axis. E1 and E2 SEM images that suggest the microrods composition by self assemble of heterogeneous and hexagonal nanoplates, respectively.

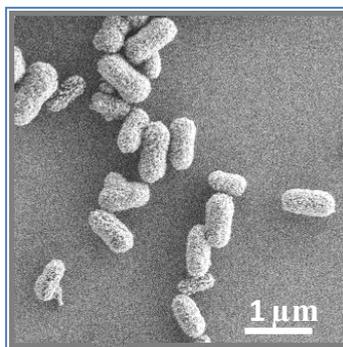


Figure_S4. TGA curve obtained for CaCO₃-PEI powder.



Figure_S5. Photos corresponding to the turbidity assays produced by CaCO₃ precipitation when decrease the reagents concentration. (A) Turbidity produced by CaCO₃ precipitation using CaCl₂ and Na₂CO₃ to synthesize

the CaCO_3 . (B) Turbidity produced by CaCO_3 precipitation using CaCl_2/PEI and Na_2CO_3 to synthesize the CaCO_3 . (C) Turbidity produced by CaCO_3 precipitation using $\text{Pb}(\text{NO}_3)_2$, Na_2CaEDTA and Na_2CO_3 to synthesize the CaCO_3 . (D) Turbidity produced by CaCO_3 precipitation using $\text{Pb}(\text{NO}_3)_2$, $\text{Na}_2\text{CaEDTA}/\text{PEI}$ and Na_2CO_3 to synthesize the CaCO_3 .



Figure_S6: SEM image taken to calcite powder after 48 h of removal treatment to initial Na_2PbEDTA solution (342 ppm) at pH 4.