Electronic Supplementary Information (ESI) for:

In-situ pore-forming alginate hydrogel beads loaded with in-situ

formed nano-silver and their catalytic activity

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1. XRD pattern

Relevant discussion can be found in the manuscript (first paragraph of Results and Discussion).



Figure S1. XRD pattern of CaCO₃/Ca-ALG microspheres

2. Optical photos of porous Ca-ALG beads

Relevant discussion can be found in the manuscript (first paragraph of Results and Discussion).



Figure S2. (a and b) Optical photos of the prepared wet porous Ca-ALG beads and Ag/Ca-ALG. (c) dried Ag/Ca-ALG beads.

3. FT-IR spectra of the three types of gel beads

Figure S3 shows the FT-IR spectra of the prepared Ca-ALG, CaCO₃/Ca-ALG and Ag/Ca-ALG gel beads recorded on a FT-IR instrument (Equinox55, Bruker) using the KBr tablet method. The broad bands near 3435 cm⁻¹ can be assigned to *v*_{-OH}, indicating the intermolecular hydrogen bonds occurred. The peaks at 2930 cm⁻¹ can be assigned to the stretching vibrations of the saturated C-H bonds. The peaks near 1083 and 1029 cm⁻¹ can be assigned to the absorption of C-O-C in the polysaccharide moity. The peaks at 1427 and 1625 cm⁻¹ can be assigned to the symmetric and asymmetric stretching vibrations of -COO⁻, respectively. In addition, a new peak appeared at 1732 cm⁻¹ in spectrum of Ag/Ca-ALG beads can be assigned to the stretching vibrations of C=O originated from the oxidation of secondary hydroxyl groups in alginate during the reduction of Ag⁺ to Ag elementary substance. Namely, alginate can act as a mild reductant.^[1,2] The -COO⁻ and -OH groups are beneficial to the binding and adsorption of Ag⁺ and Ag NPs in the network structure of alginate beads.



Figure S3. FT-IR spectrum of Ca-ALG, CaCO₃/Ca-ALG and Ag/ Ca-ALG beads.

4. SEM images of CaCO₃/Ca-ALG gel beads and the size analysis

Relevant discussion for Figure S4 can be found in the manuscript (second paragraph in Results and Discussion).



Figure S4. SEM images of the surface (a) and cross-section (b) of $CaCO_3/Ca-ALG$ beads. The scale bar is 200 μ m.

Figure S5 show the size analysis of CaCO₃ NPs aggregates on the surface of CaCO₃/Ca-ALG beads and corresponding pores size of the gel beads using the software Image J. It suggested that the average size of CaCO₃ NPs aggregates of all the beads was found to be approximately 10 μ m (Figure S5a). The pore size depends upon the content of pore-forming agent (Figure S5b). The average pore size of the three samples was found to be 61, 70 and 42 μ m, respectively.



Figure S5. Size analysis of CaCO₃ NPs aggregates on the surface of CaCO₃/Ca-ALG beads-1#-3# (a) and their pore size analysis (b) by using the software Image J.

5. UV-vis absorption of AgNO₃ solution



Figure S6. UV-Vis absorption curve (a) and the corresponding standard absorption curve (b) of AgNO₃ solution.

6. Catalytic performance of Ag-loaded Ca-ALG beads



Figure S7. UV-Vis absorption spectra of 4-NP only (red line) and 4-NP mixed with NaBH₄ (black line).

References

- 1. S. Saha, A. Pal, S. Kundu, S. Basu and T. Pal, *Langmuir* 2010, 26, 2885.
- 2. S. Saha, A. Pal, S. Pande, S. Sarkar, S. Panigrahi and T. Pal, J. Phys. Chem. C. 2009, 113, 7553.