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Hydroxyapatite as a bifunctional nanocatalyst for solventless Henry reaction: A demonstration of morphology dependent catalysis

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Supplementary Information

Table S1 Crystallite size of HA nanorods (Catalytically active)

HA samples	**Crystallite Size (nm)** **(002)**
HA_R	44.5
$HA_{R\text{-}Et}$	24.5
$HA_{R\text{-}Ip}$	25.2

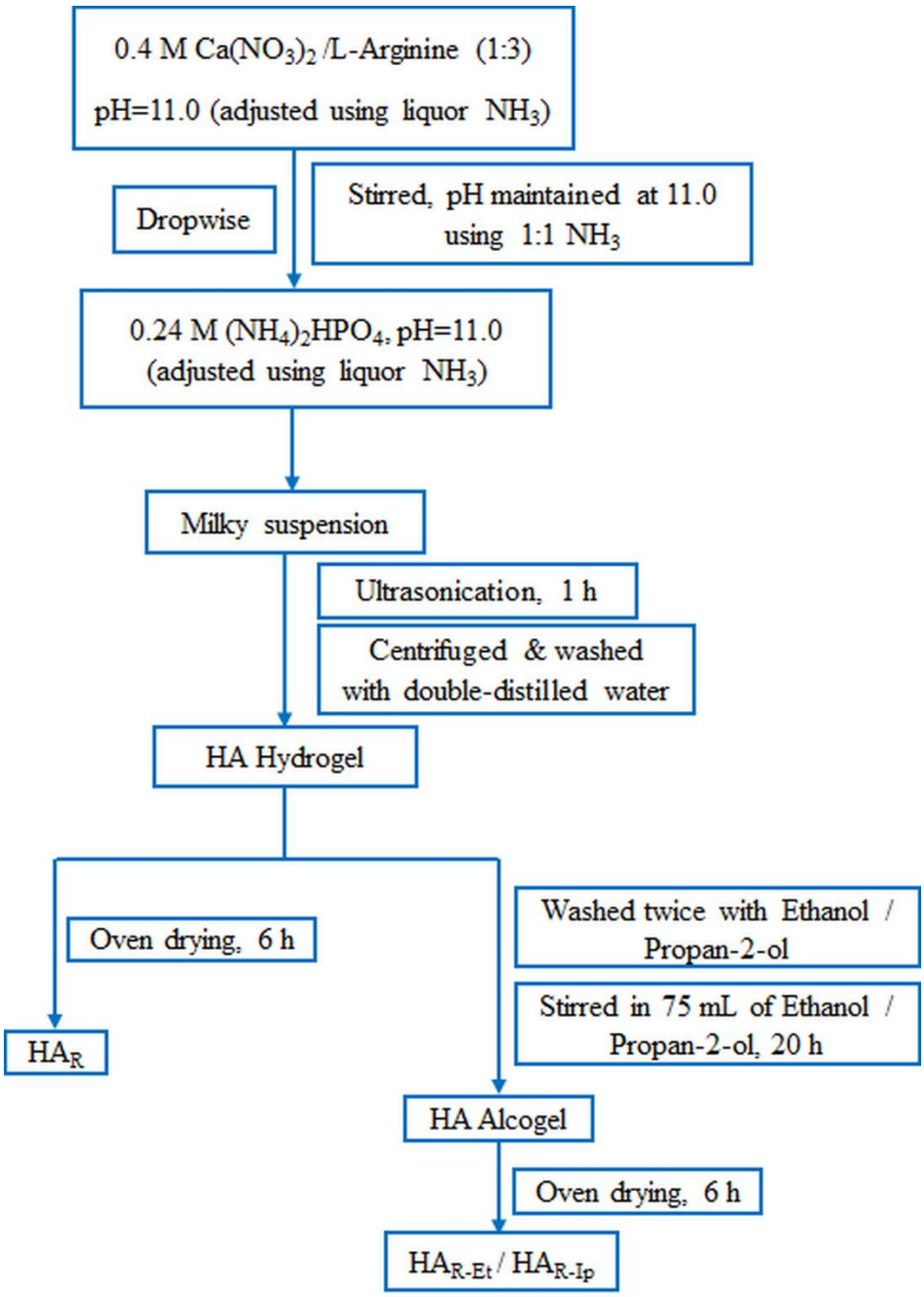


Fig. S1. Flowchart for the synthesis of HA nanorods

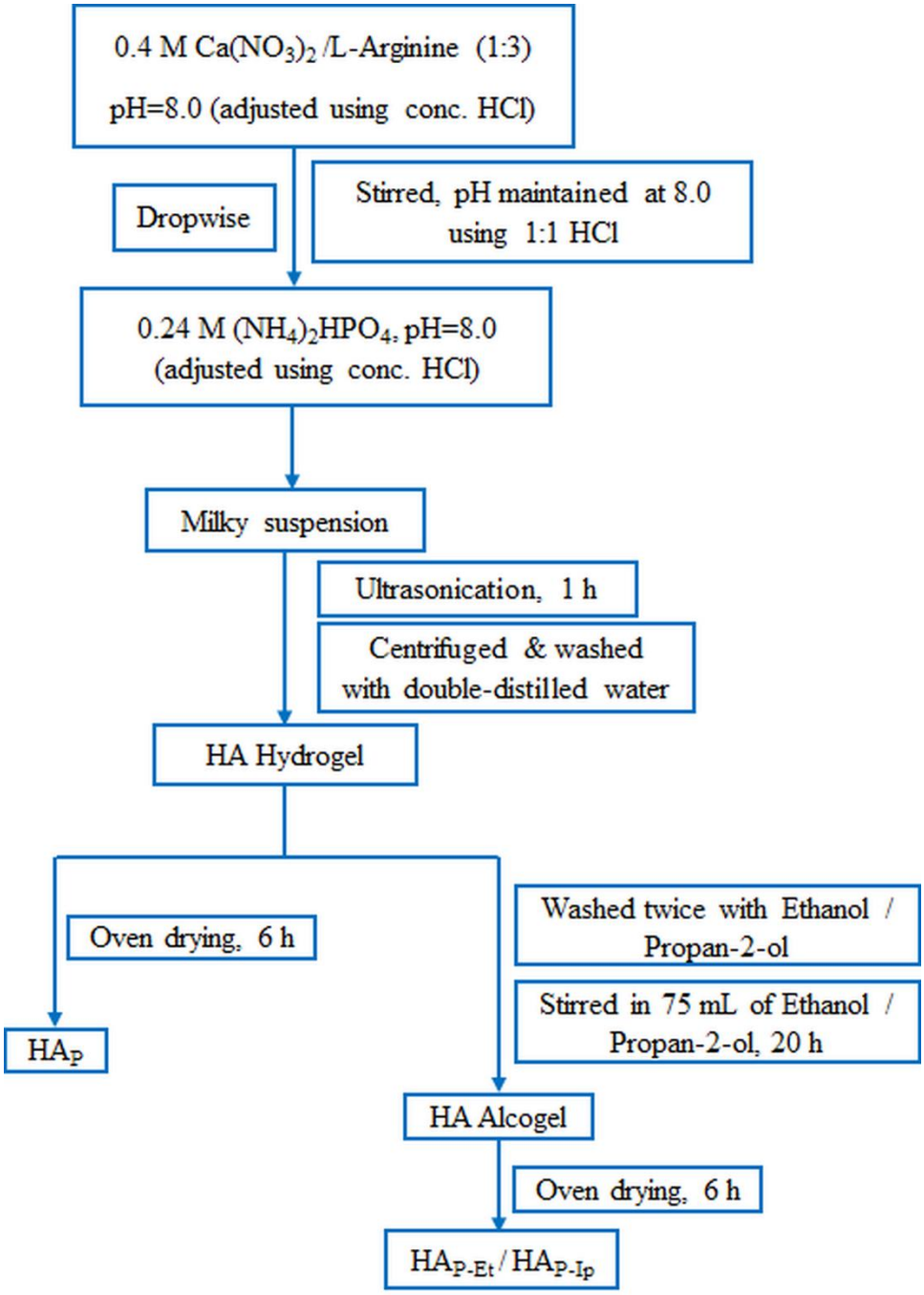


Fig. S2. Flowchart for the synthesis of HA nanoplates

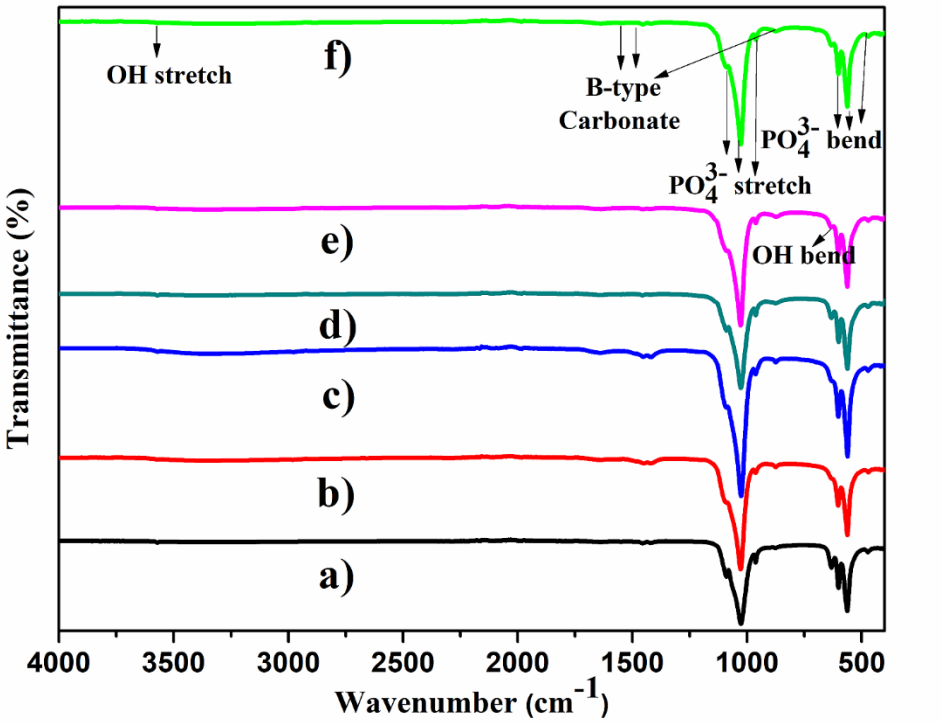


Fig. S3. FTIR spectra of a) HA_R, b) $HA_{R\text{-}Et}$, c) $HA_{R\text{-}Ip}$, d) HA_P, e) $HA_{P\text{-}Et}$, and f) $HA_{P\text{-}Ip}$

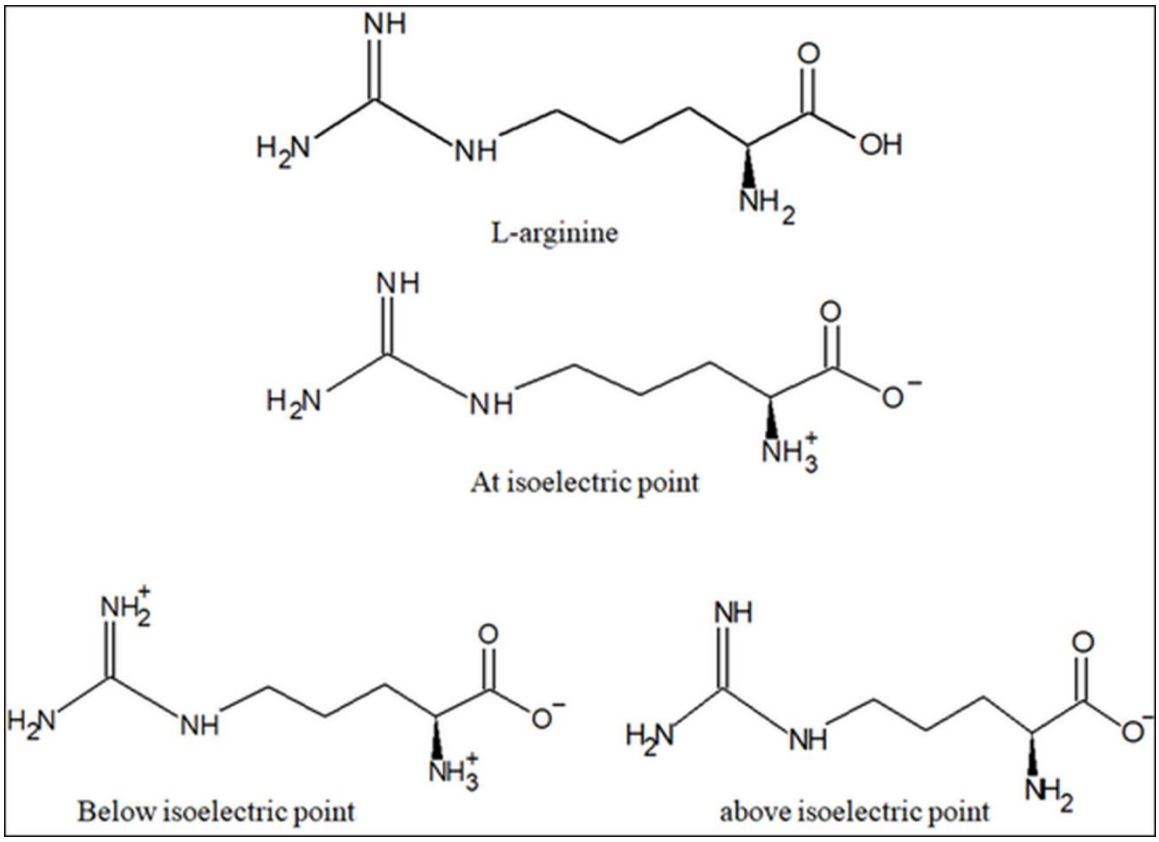


Fig. S4 Structure of L-arginine at various pH conditions

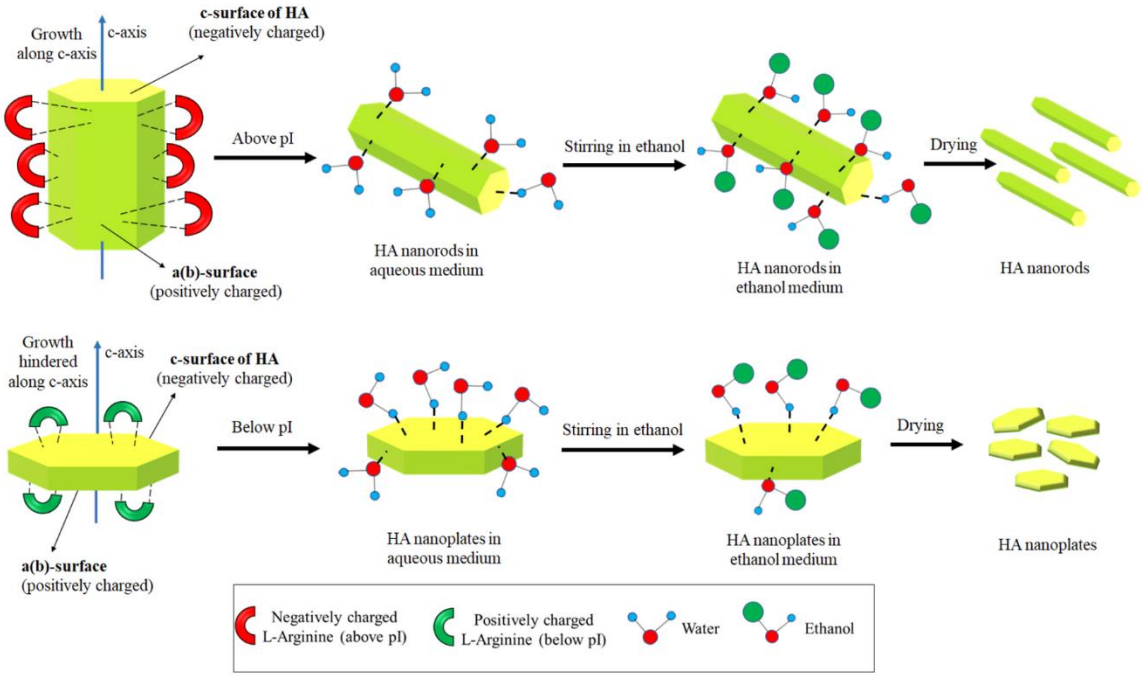


Fig. S5 Formation of HA nanorods and nanoplates using L-Arginine via alcogel method

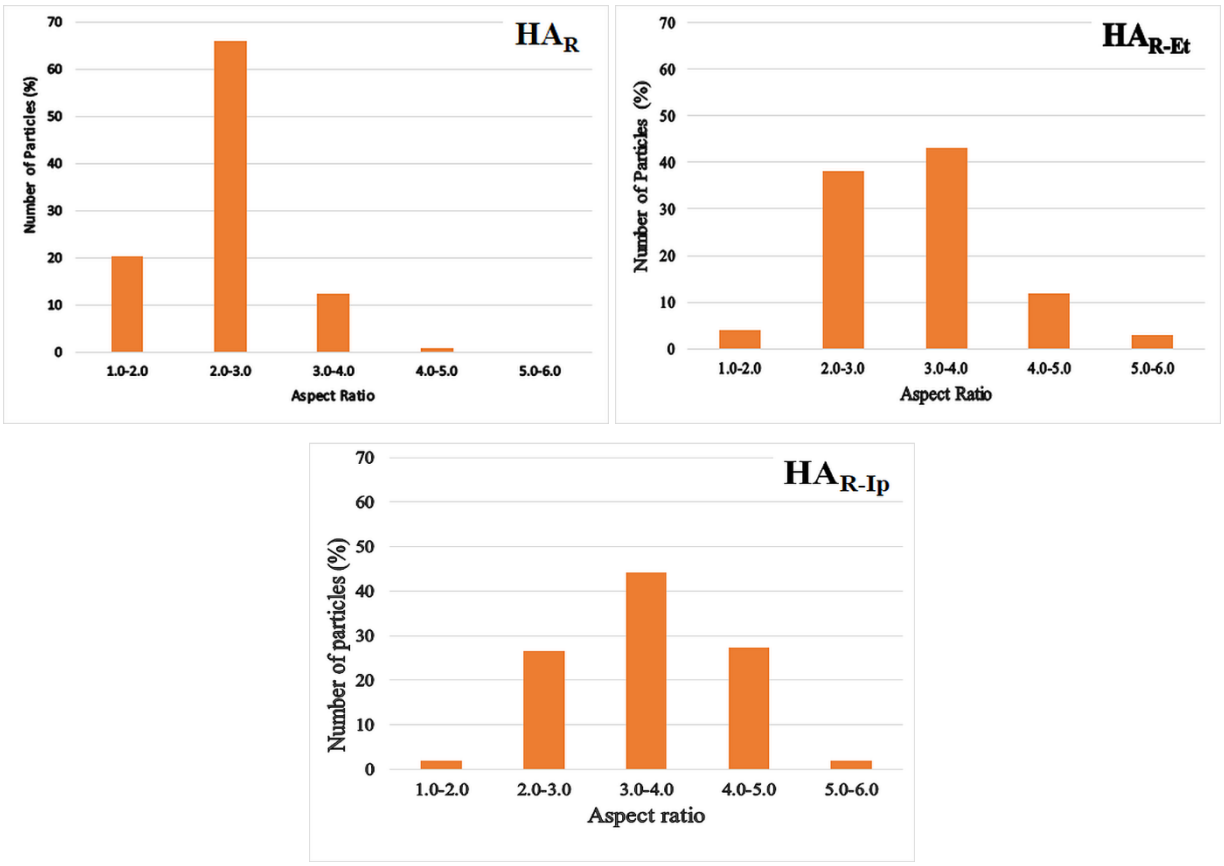
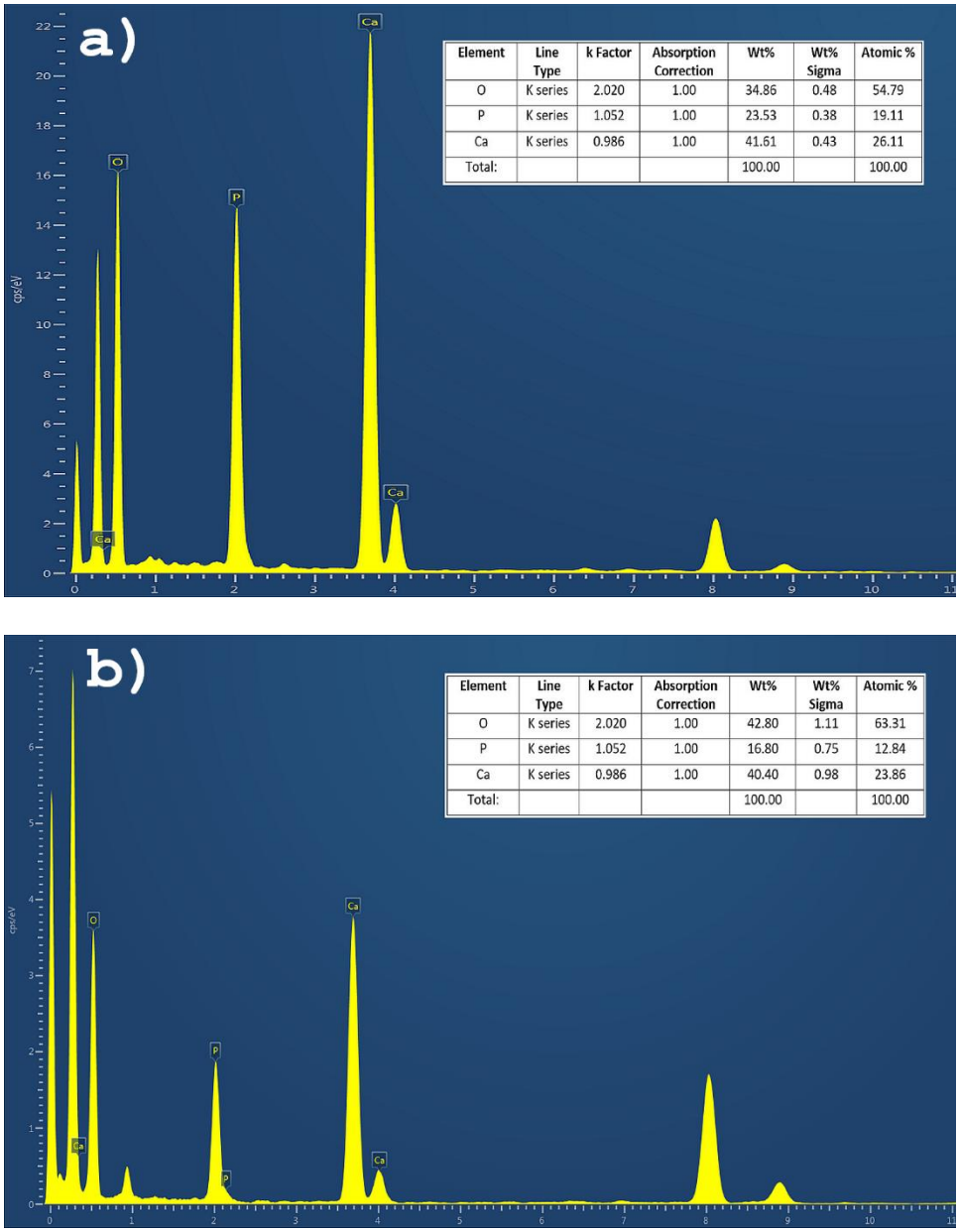


Fig. S6 Percentage of rod-like particles



Element	Line Type	k Factor	Absorption Correction	Wt%	Wt% Sigma	Atomic %
O	K series	2.020	1.00	34.86	0.48	54.79
P	K series	1.052	1.00	23.53	0.38	19.11
Ca	K series	0.986	1.00	41.61	0.43	26.11
Total:				100.00		100.00

Element	Line Type	k Factor	Absorption Correction	Wt%	Wt% Sigma	Atomic %
O	K series	2.020	1.00	42.80	1.11	63.31
P	K series	1.052	1.00	16.80	0.75	12.84
Ca	K series	0.986	1.00	40.40	0.98	23.86
Total:				100.00		100.00

Fig. S7 EDXA profile of a) HA_P-Et and b) HA_R-Ip

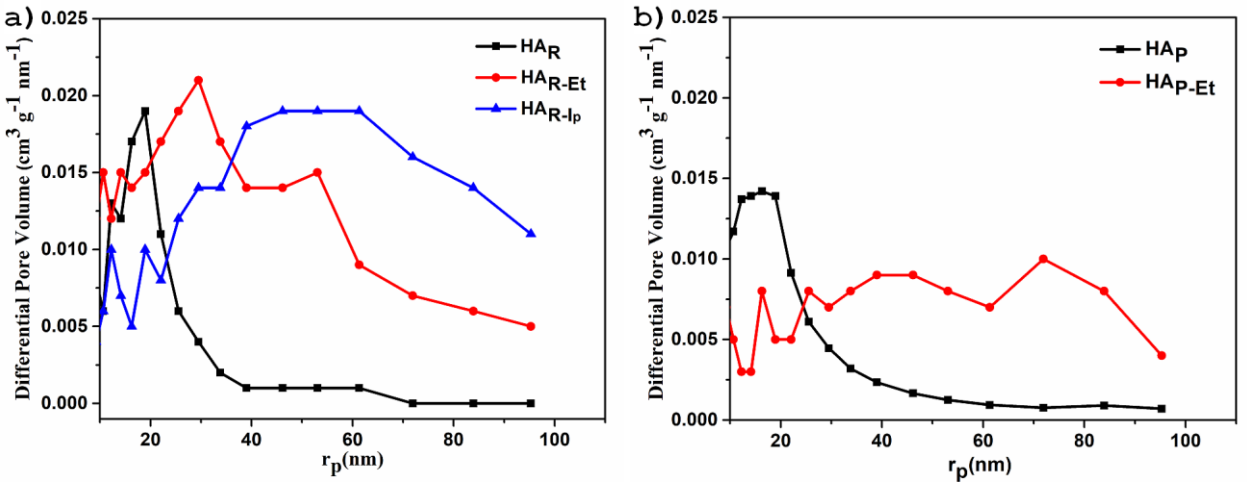


Fig. S8 Pore size distribution of the HA nanoparticles

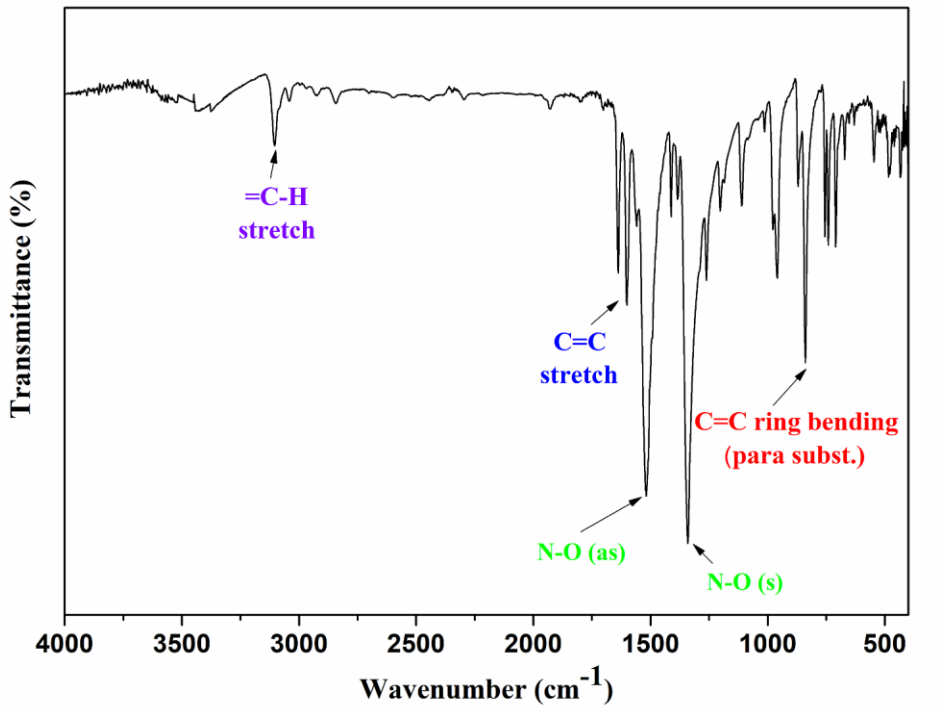


Fig. S9 FTIR spectrum of (E)-1-Nitro-4-(-2-nitrovinyl) benzene

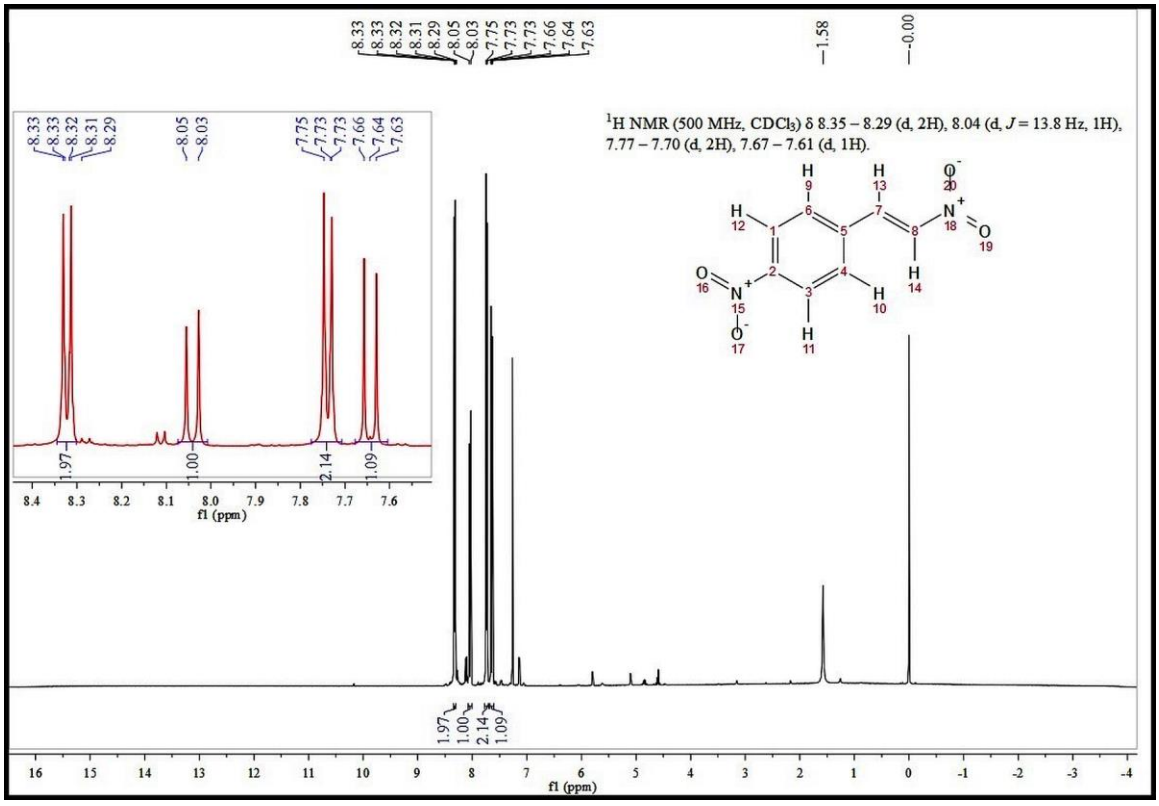


Fig. S10 ^{1}H-NMR spectrum of (E)-1-Nitro-4-(-2-nitrovinyl) benzene

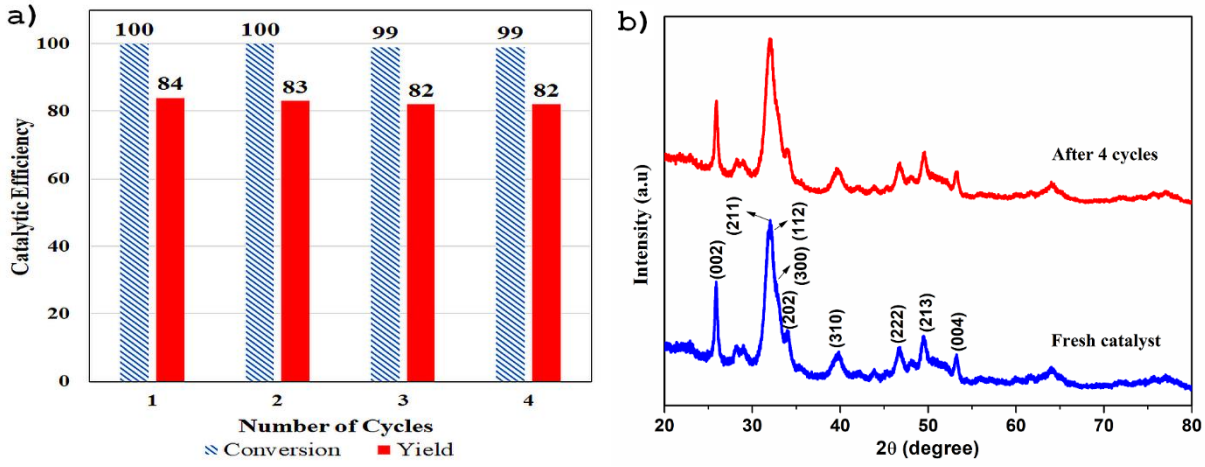
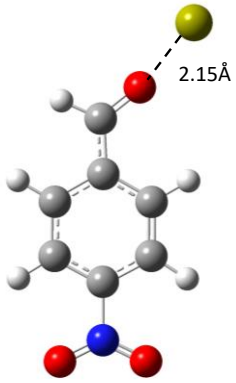
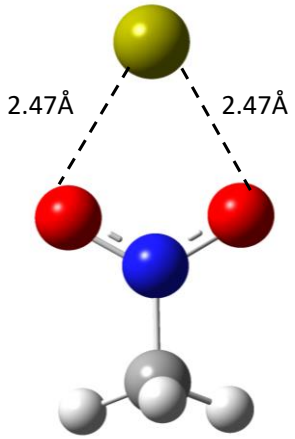


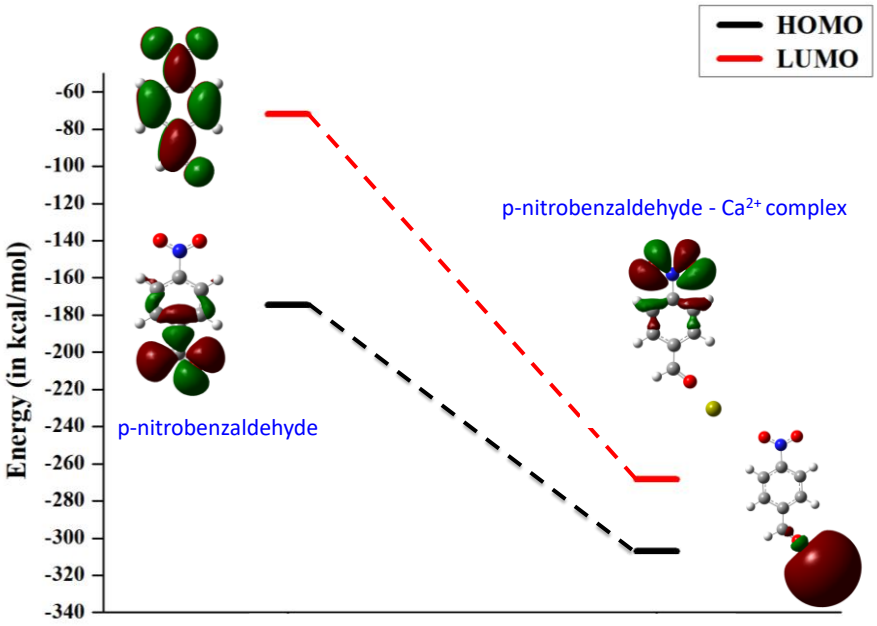
Fig. S11 (a) Recyclability test, (b) XRD patterns of $HA_{R\text{-}Ip}$ before and after the recycling tests



S12 (a) Optimized geometry of p-nitrobenzaldehyde-Ca^{2+}



S12 (b) Optimized geometry of nitromethane -Ca^{2+}



S12 (c) The FMOs of the p-nitrobenzaldehyde and p-nitrobenzaldehyde – Ca^{2+} complex

Note on S12: The optimized geometries of the complexes (p-nitrobenzaldehyde-Ca^{2+} & nitromethane- Ca^{2+}) are given in figure S12 (a) and S12 (b). From the figure we can understand the calcium ion interacts with the ligands with a bond distance of 2.15Å in the case of p-nitrobenzaldehyde and 2.47Å in the case of nitromethane respectively. The interaction energy for p-nitrobenzaldehyde-Ca^{2+} & nitromethane-Ca^{2+} are -79.99 kcalmol^{-1} and -75.08 kcalmol^{-1} respectively. This means that the formation of both the complexes is feasible. The HOMO-LUMO images of p-nitrobenzaldehyde and its complex with Ca^{2+} along with their energy values are given in figure S12 (c). From the graph, it can be understood that on formation of complex with calcium the LUMO energy is lowered from -71.90 kcalmol^{-1} to -268.25 kcalmol^{-1}. The figure suggests that the LUMO of p-nitrobenzaldehyde is spread throughout the molecule whereas in the complex with Ca^{2+} it is localized around NO_2 group. The HOMO of the complex is mainly localized on C=O group and calcium ion.

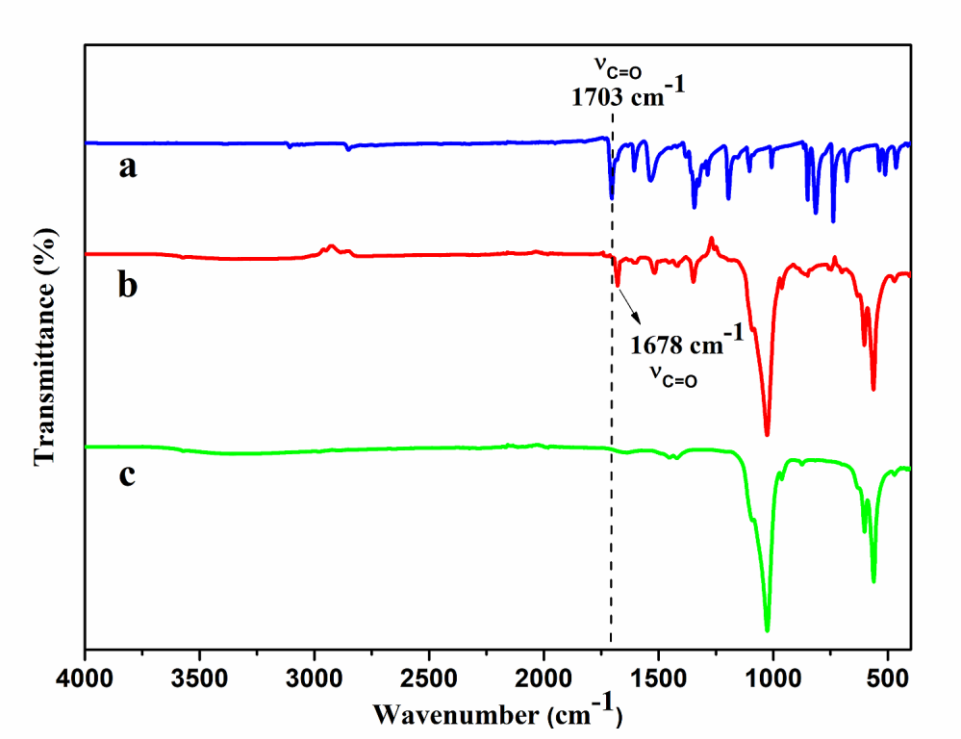


Fig. S13 FTIR spectra of (a) 4-nitrobenzaldehyde, (b) 4-nitrobenzaldehyde adsorbed on $HA_{R\text{-}Ip}$ and (c) pure $HA_{R\text{-}Ip}$