

# Nanocrystalline *p*-hydroxyacetanilide (paracetamol) and gold core-shell structure as a model drug deliverable organic-inorganic hybrid nanostructure

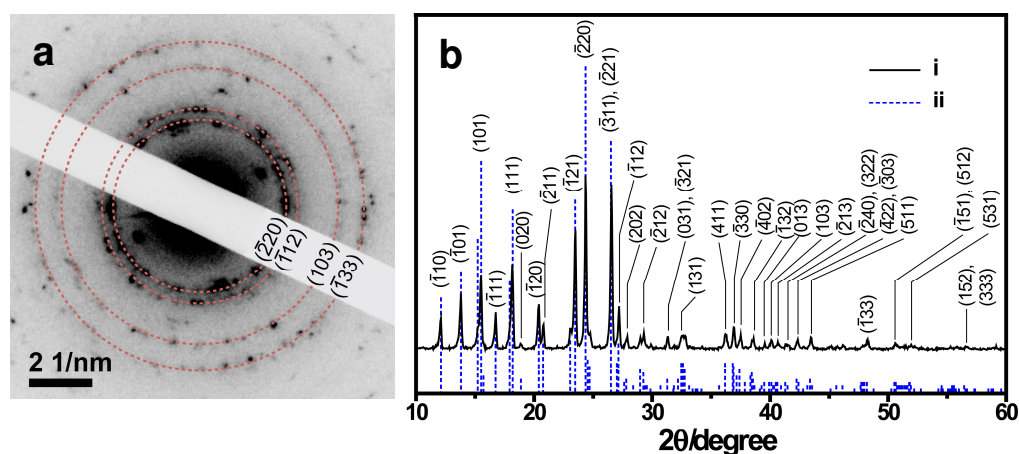
Subhojit Das,<sup>a</sup> Anumita Paul<sup>a</sup> and Arun Chattopadhyay<sup>\*ab</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Guwahati, Assam 781039, India

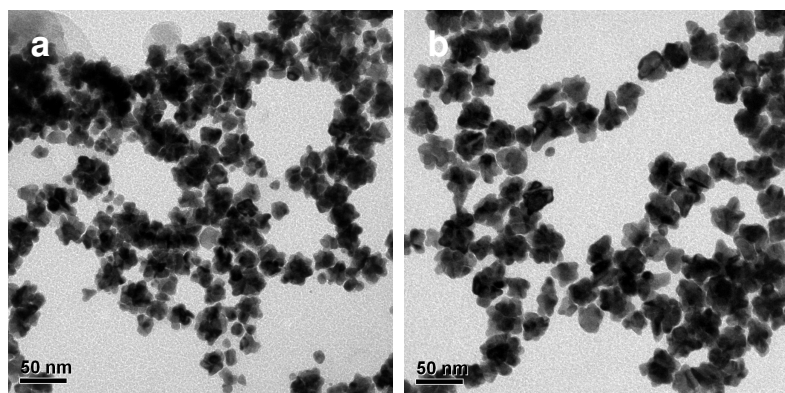
<sup>b</sup>Centre for Nanotechnology, Indian Institute of Technology Guwahati, Assam 781039, India

Email: [arun@iitg.ernet.in](mailto:arun@iitg.ernet.in)

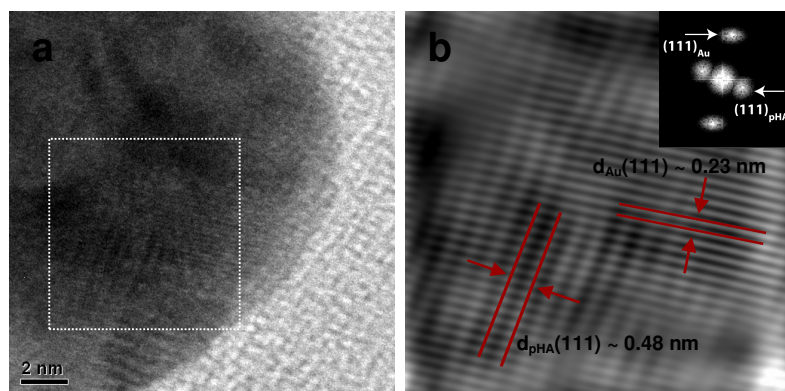
## Electronic Supplementary Information



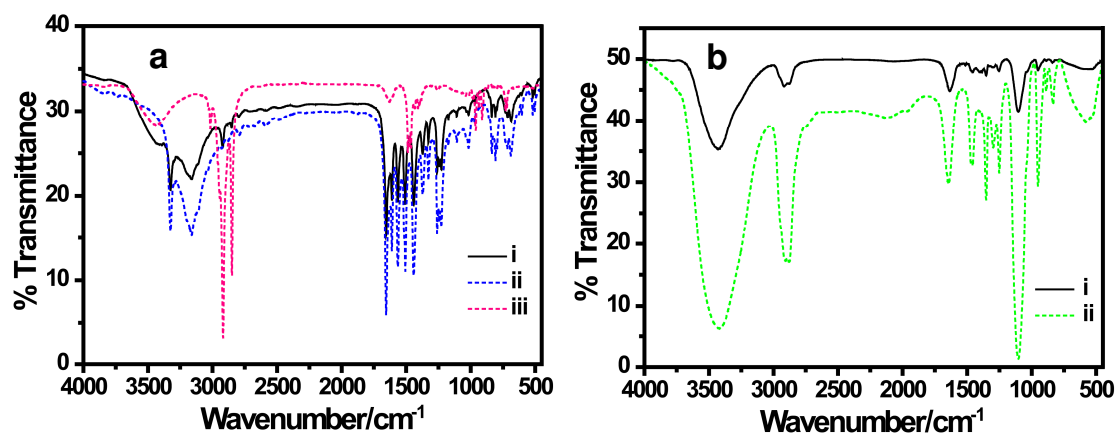
**Fig. S1** (a) SAED patterns of pHA NCs (obtained by focussing electron beam on a region of collection of NCs). (b) (i) Powder XRD patterns of pHA crystals which were obtained as precipitate from the supersaturated solution, and (ii) standard diffraction lines for monoclinic polymorph of pHA (data from JCPDS Card No. 39-1503).



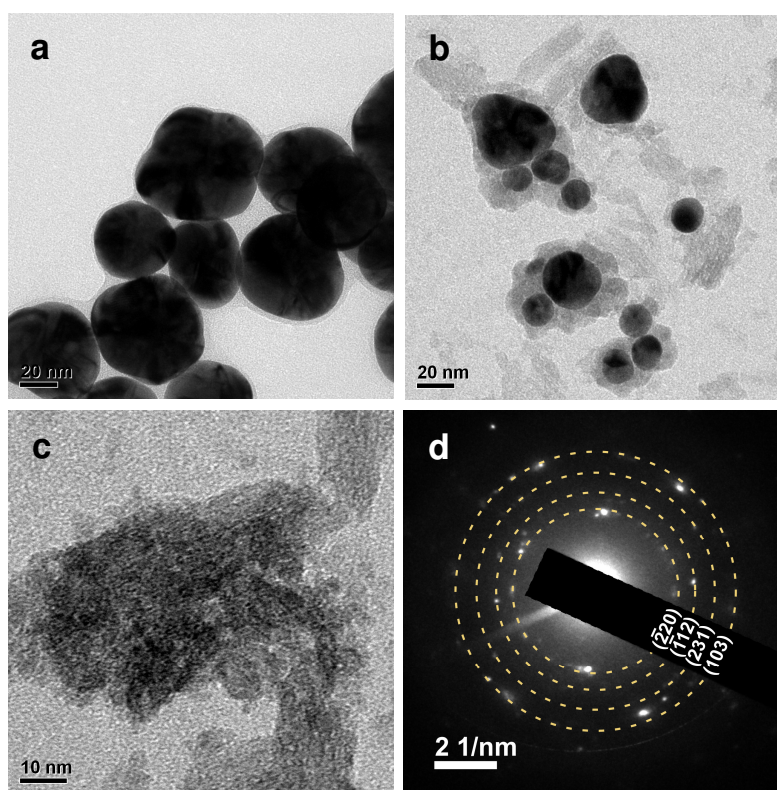
**Fig. S2** TEM images (a and b) of as-prepared star-shaped Au NPs, generated from solution starting with  $4.97 \times 10^{-2}$  and  $7.44 \times 10^{-2}$  mM of  $\text{HAuCl}_4$ , respectively.



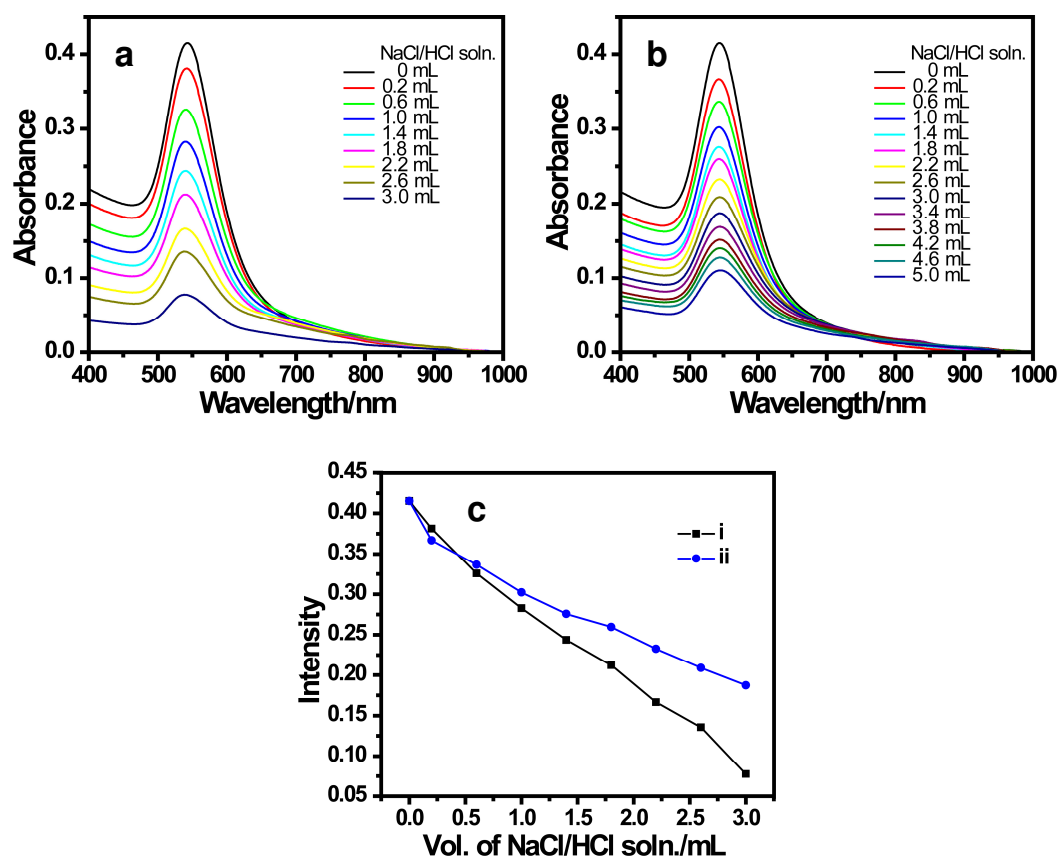
**Fig. S3** (a) HRTEM image of a pHA@Au core-shell particle, and (b) IFFT image of the select region in (a) with the corresponding FFT image in the inset.



**Fig. S4** (a) FTIR spectra of (i) pHA/CTAB-stabilized pHA@Au NPs, (ii) pure pHA, and (iii) pure CTAB. (b) FTIR spectra of (i) PEG-stabilized pHA@Au NPs, and (ii) pure PEG.



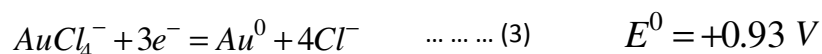
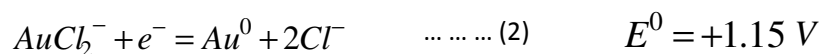
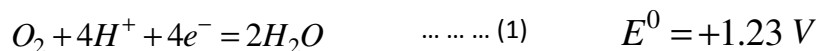
**Fig. S5** TEM images of PEG-functionalized pHA@Au NPs: (a) as-made, and (b) after partial etching of Au shell with NaCl/HCl solution. (c) TEM image and (d) SAED pattern of a flake-like structure in (b); the faint diffraction spots correspond to that of pHA crystals.



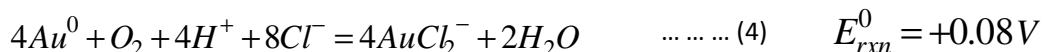
**Fig. S6** UV/Vis spectra of pHA@Au NPs at different concentrations of NaCl/HCl etching solution, (a) with and (b) without bubbling of O<sub>2</sub> gas through the reaction medium. (c) Plot of the peak intensities of absorbance bands, in (a) and (b), against the volume of NaCl/HCl solution added, shown here for 0–3 mL of NaCl/HCl solution; while (i) corresponds to data taken from (a), (ii) is that from (b).

### Plausible mechanism of the dissolution of Au from pHA@Au core-shell NPs

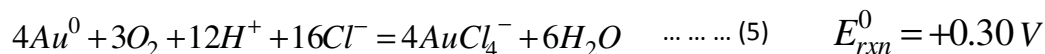
The Au etching reaction, as mentioned in the manuscript, was carried out in the presence of high concentrations of Cl<sup>−</sup> and H<sup>+</sup> ions. The following half-reactions can be written for the oxidation of Au in the presence of oxygen ( $E^0$  values being taken from standard reference):



Combining reactions (1) and (2):



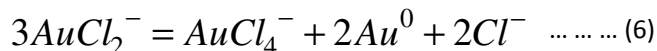
And combining reactions (1) and (3):



The large positive  $E^0$  value of reaction (5) than reaction (4) shows that reaction (5) is more favourable, even though both the reactions are possible. Therefore, the oxidation reaction of Au in the presence of oxygen and higher concentrations of  $Cl^-$  and  $H^+$  ions is spontaneous. Further, the reaction speeds up when carried out in the presence of excess oxygen (by bubbling  $O_2$  gas through the reaction mixture) than in the aerial condition, as evident from Fig. S6 above.

Furthermore, we would like to add here that the species  $AuCl_2^-$  is unstable and on formation undergoes disproportionation reaction<sup>1</sup> to give  $AuCl_4^-$  and  $Au^0$ , as below:

Combining reactions (2) and (3), we have



with redox potential:  $E^0 = E_1^0 - E_2^0 = +0.22 V$

The positive value of  $E^0$  suggests that reaction (8) is feasible, resulting in a decrease in the concentration of  $AuCl_2^-$ .

## Reference

(1) M. J. Nicol, C. Fleming and R. A. Paul, *The Chemistry of the Extraction of Gold*. South African Institute of Mining and Metallurgy, The Extractive Metallurgy of Gold in South Africa. 2, 1987, pp. 831-905.