Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary data

Controlled modification of starch in the synthesis of gold nanoparticle with tunable optical properties and its application in heavy metal sensing

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1. UV-VIS absorbance spectra of AuNP:

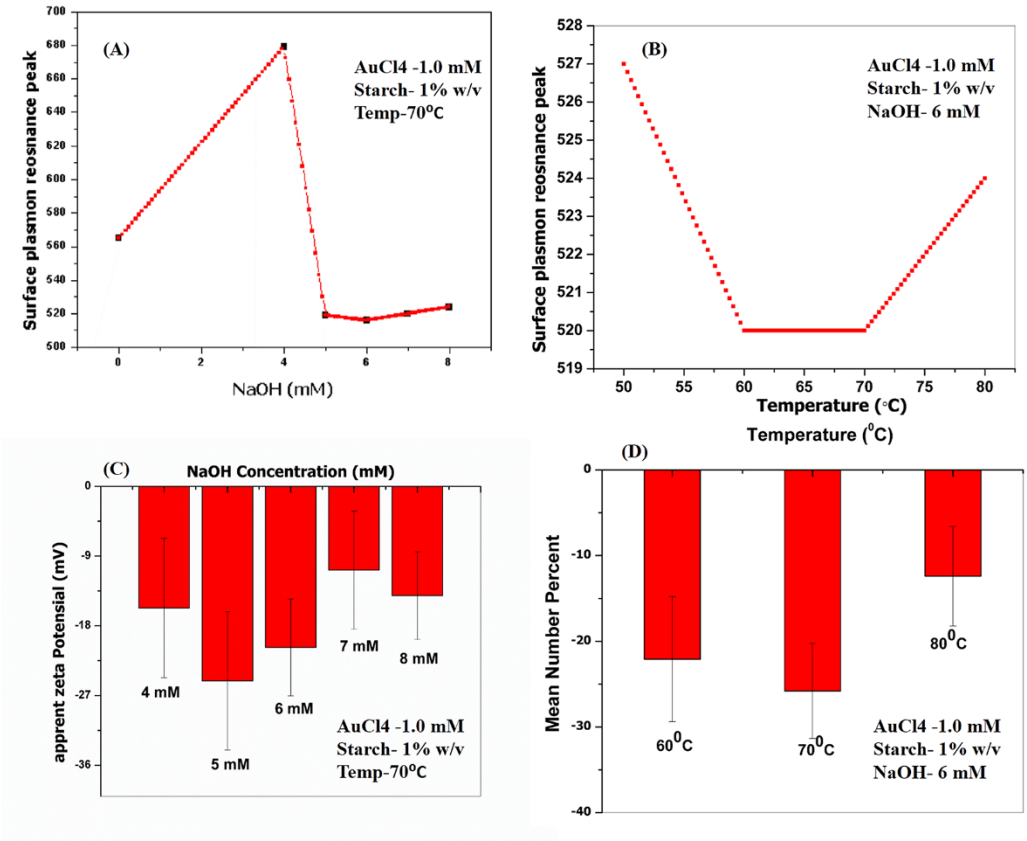

Figure S1. The results showed the SPR peak shift and zeta potential of AuNP; (A) & (C) the effect of NaOH concentrations (4-8 mM) on SPR and zeta potential; (B) & (D) The effect of reaction temperature (60-80°C) on SPR and zeta potential

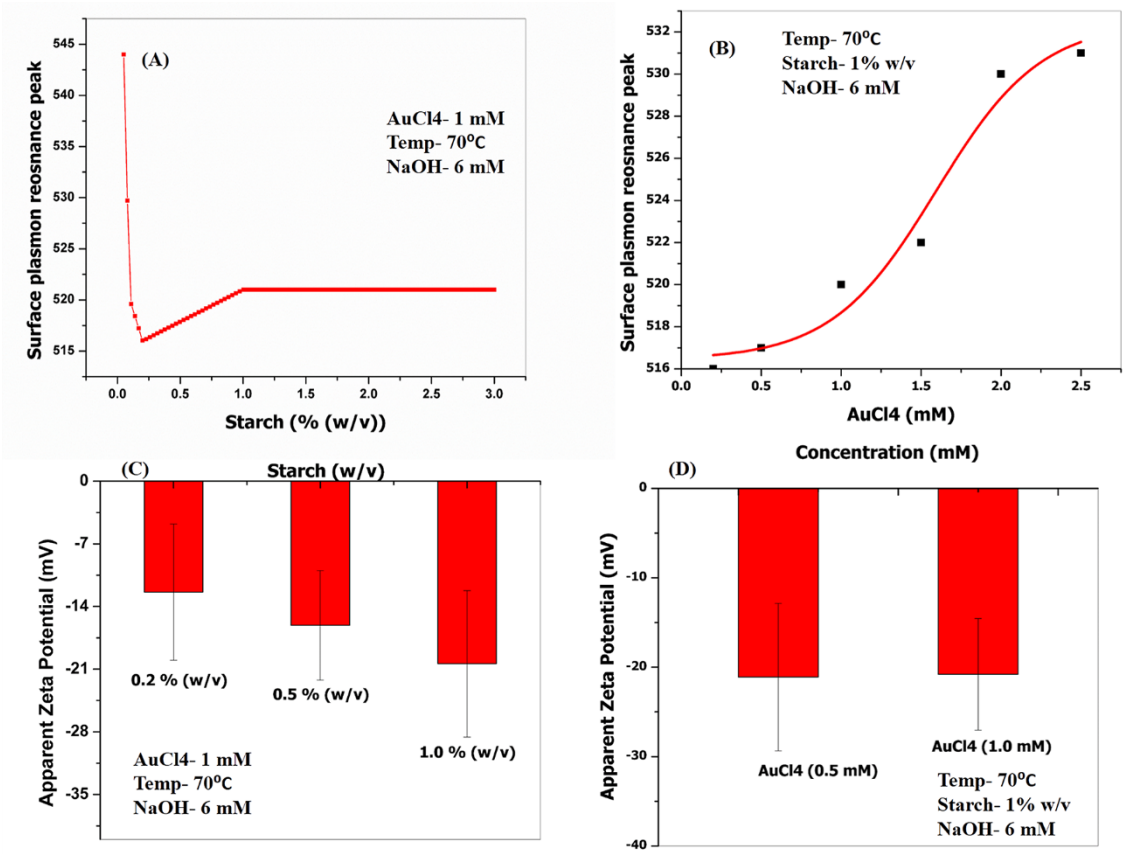

Figure S2. the results showed the SPR peak shift and zeta potential of AuNP; (A) & (C)the effect of various concentration of starch (0.2-1% w/v); (B) & (D) the effect of various concentration of $HAuCl_4$ (0.2-1% w/v).

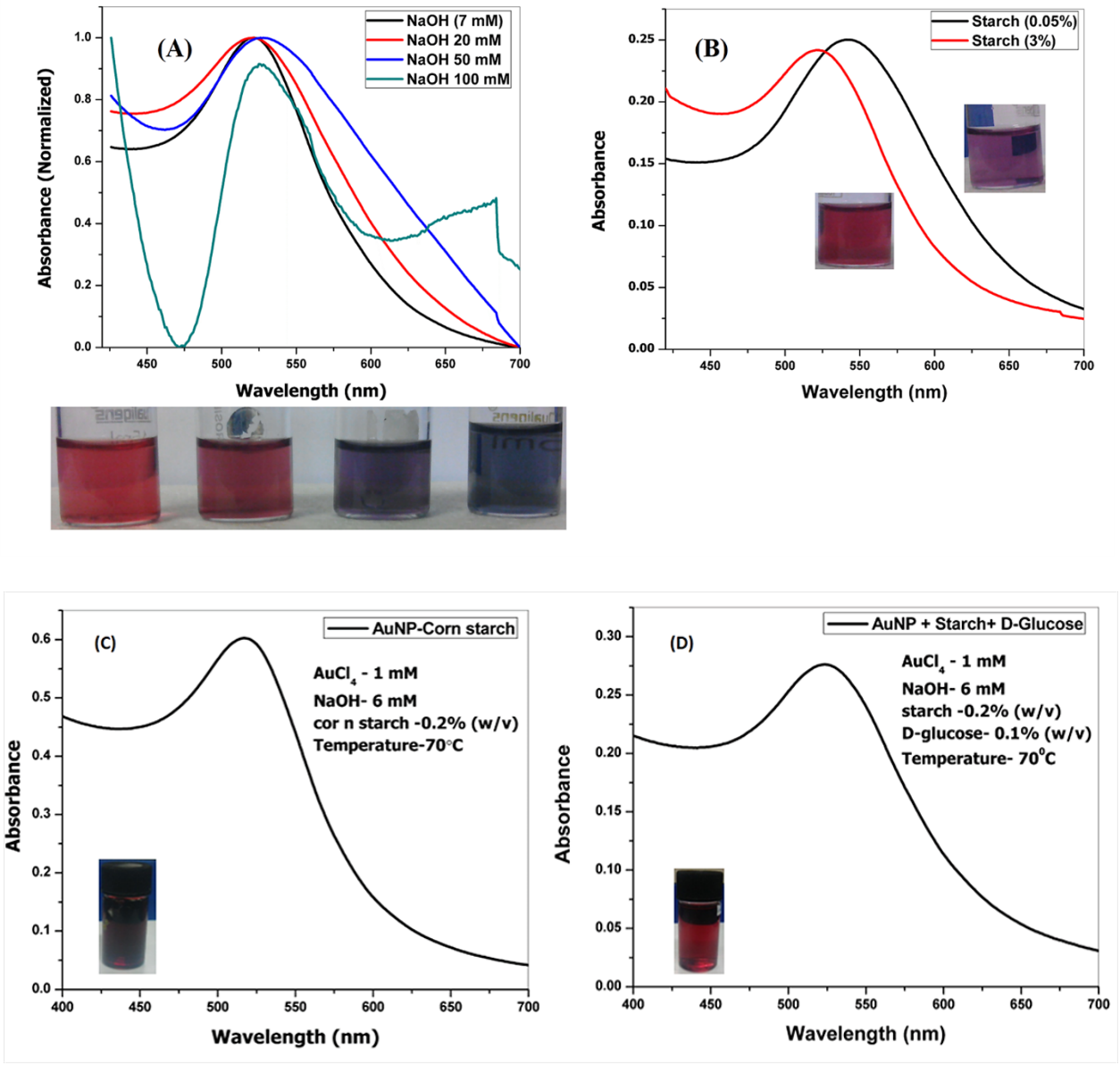

Figure S3. (A) The effect of higher concentration of NaOH (7, 20, 50, 100 mM) on the size and ultimately to the surface plasmon resonance of AuNP. At higher concentration (20-100 mM) SPR become broad and showed red shift in comparison to 7mMNaOH and color change from ruby red to deep violet and blue showed the size variation. (B) at lower concentration of starch (0.05%) when NaOH concentration was 6 mM produce bright violet color, it showed formation of larger nanoparticles, while at 3% starch deep ruby red color. SPR analysis showed red shift for AuNP with 0.05% starch. AuNP synthesized using corn starch with (C) NaOH and (D) D-glucose and NaOH.

2. FTIR analysis Starch:

To analyze the effect of various factors such as microwave heating, normal heating on the hot plate, treatment of different concentrations of NaOH with heating on the hot plate was analyzed to understand the role of various factors in starch modification (Fig. S4 A-F).

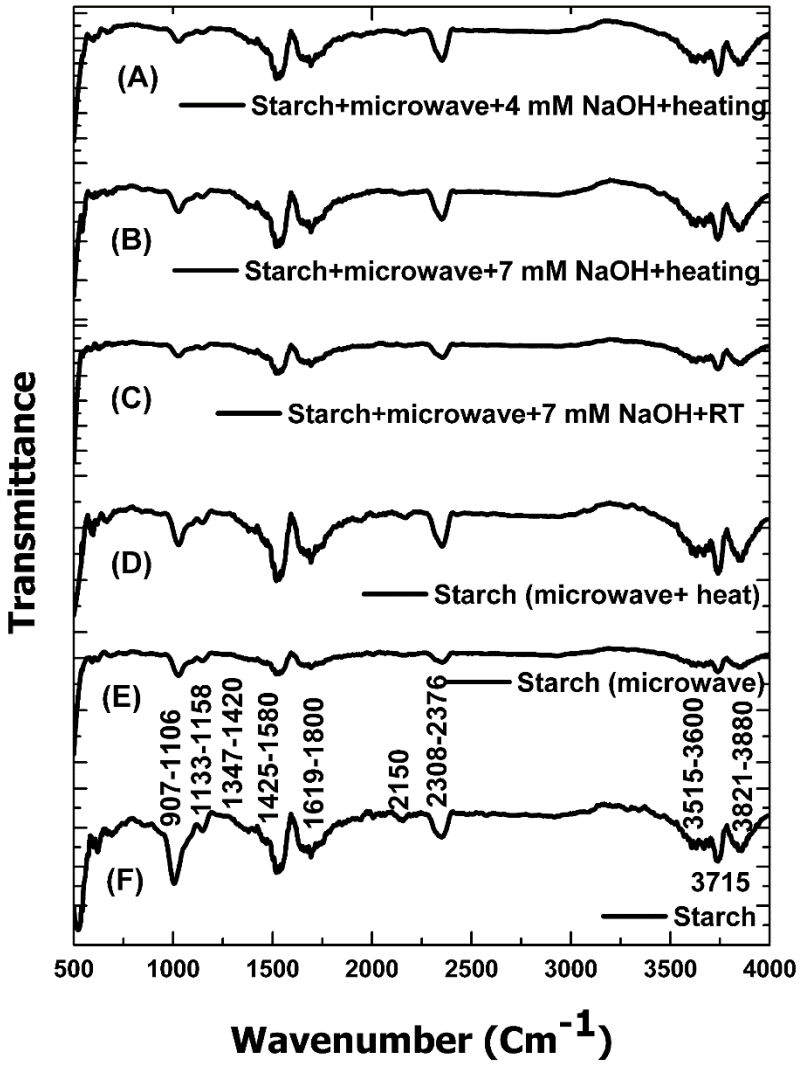

Figure S4. FTIR analysis of starch solution after microwave heating in the presence of NaOH, and heating at 70^0C and at room temperature.

3. Semi-quantitative Benedict test for reducing sugar:

The 1% starch sample was dissolved in water by heating in microwave for 1 min. After cooling to room temperature, the sample was divided into three parts and added 2, 4 and 7 mM NaOH solution and heated for 20 min. After cooling to room temperature, equal volume of benedict solution was added and incubates in boiling water for 5 min and observes the color variation. The color variation of samples indicates the presence of reducing sugar in solution. Such variation was compared with respect to known concentrations (0.5, 1, 2, 3, 4 % w/v) of reducing sugar (D-glucose) (Fig.S5 showed only 0.5 and 4% images).

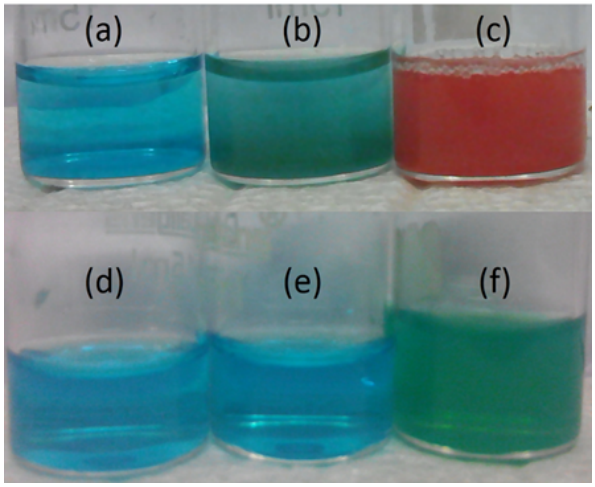

Figure S5. Benedict test for starch. (a) Benedict solution, (b) 0.5% D-Glucose with Benedict solution (c) 3% D-glucose with benedict solution. Different concentration of NaOH mixed with 1% starch solution and heated for 20 min (d) 2 mM NaOH, (e) 4 mM NaOH, (f) 7 mM NaOH. The comparison of starch solution with known quantity of reducing sugar showed that 7 mM NaOH produced approximately 0.1-0.5% reducing species, which act as reducing sugar in AuNP synthesis.

4. Reaction mechanism of AuNP synthesis:

Ji et al. (2007) and Zhang et al. (2008) reported that reaction of NaOH with auric chloride produced intermediate gold hydroxide that caused conversion of yellow color to transparent and the order of hydroxide was increased from 1.0 to 4.0 with increasing the NaOH concentration.

Moreover, higher order of Au(OH)x was responsible for the different redox potential and reduction rate of gold[1, 2].

$$[AuCl_4]^- + H_2O \rightleftharpoons AuCl_3(H_2O) + Cl^- \quad (1)$$

$$AuCl_3(H_2O) \rightleftharpoons [AuCl_3(OH)]^- + H^+ \quad (2)$$

$$[AuCl_3(OH)]^- + H_2O \rightleftharpoons AuCl_2(H_2O)(OH) + Cl^- \quad (3)$$

$$AuCl_2(H_2O)(OH) \rightleftharpoons [AuCl_2(OH)_2]^- + H^+ \quad (4)$$

$$[AuCl_2(OH)_2]^- + H_2O \rightleftharpoons [AuCl(OH)_3]^- + H^+ + Cl^- \quad (5)$$

$$[AuCl(OH)_3]^- + H_2O \rightleftharpoons [Au(OH)_4]- + H^+ + Cl^- \quad (6)$$

5. Retrogradation of starch:

Figure S6. Retro-gradation of starch was performed by freezing and thawing. The bottom of the bottle showed retrograded starch (light pink color) with AuNP while dark ruby red color showed AuNP suspension.

6. Heavy Metal sensing:

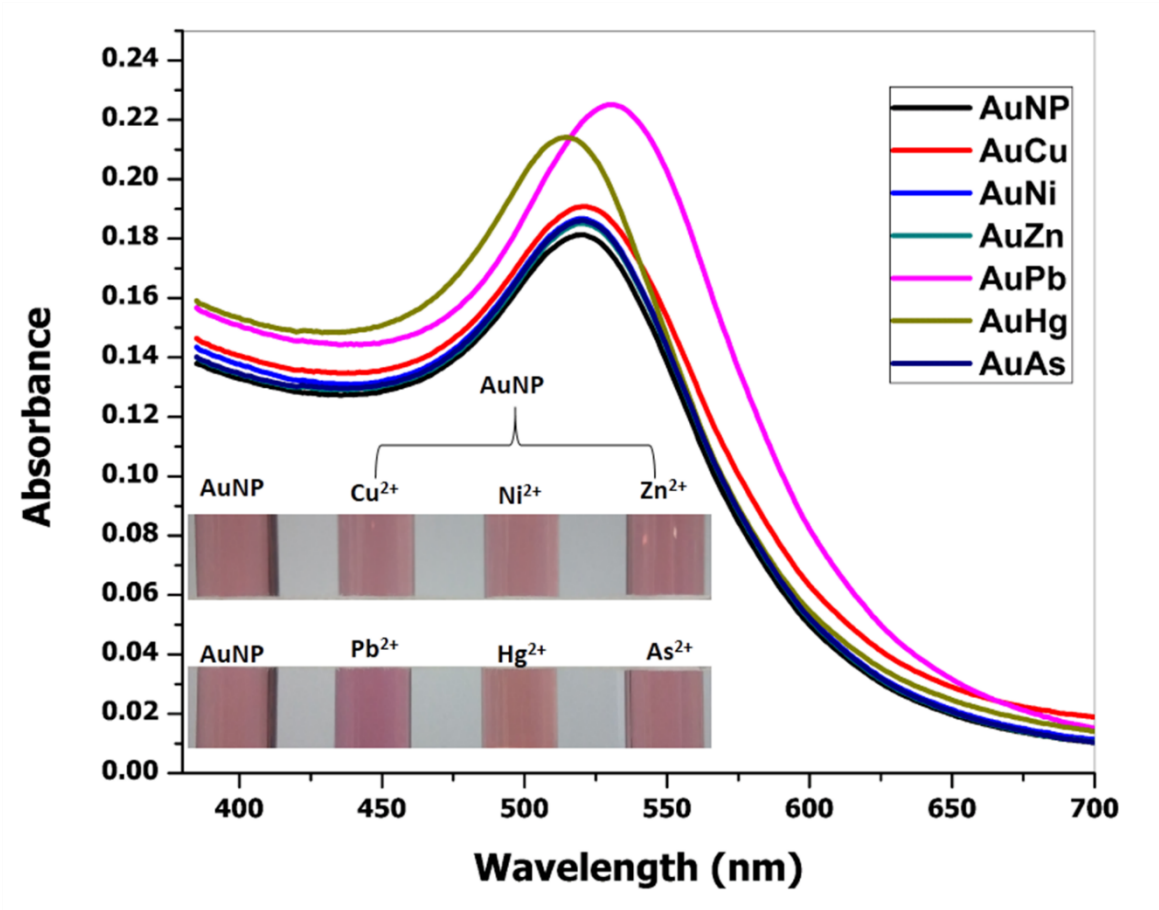

Figure S7. Heavy metal sensing by AuNP showed that Hg, Pb, Cu showed significant SPR shift but only Cu and Pb showed significant change in AuNP color that can be easily detectable by naked eye.

References:

1. H. Zhang, J.-J. Xu and H.-Y. Chen, *The Journal of Physical Chemistry C*, 2008, 112, 13886-13892.
2. X. Ji, X. Song, J. Li, Y. Bai, W. Yang and X. Peng, *Journal of the American Chemical Society*, 2007, 129, 13939-13948.